XLIX Congress of the Physical Chemistry Division of the Società Chimica Italiana

Physical Chemistry: a fresh glimpse into the microscopic world

UNIVERSITÀ DI TORINO

chimica

Torino 4-7 September 2023

Società Chimica Italiana
Divisione di Chimica Fisica

Local Organizing Committee

P. Ugliengo – *Chair*
A. Damin
F. Bonino
S. Casassa
A. M. Ferrari
L. Maschio
G. Ricchiardi
V. Crocellà
S. Bordiga
B. Civalleri
E. Groppo
L. Mino
D. Scarano
M. Corno
G. Berlier
E. Borfecchia
A. Erba
G. Magnacca
S. Morandi
M. Signorile

Scientific Committee

M. Meneghetti - *Chair*
S. Brutti
M. Ferretti
G. Marletta
L. Petraccone
A. Polo
F. Ridi
M. L. Saladino
P. Ugliengo
F. Zerbetto

https://www.cdcf49.unito.it

Collane@unito.it
Università degli Studi di Torino

ISBN: 9788875902704

Publication date: 25-08-2023

WELCOME IN TURIN

Welcome to the **49th National Congress of Physical Chemistry** (XLIX CNCF, Turin 2023), promoted by the **Physical Chemistry Division of the Società Chimica Italiana**.

The Conference, organized by the Physical Chemists of the University of Turin, is be hosted by the Department of Molecular Biotechnology and Health Sciences.

The aim of the conference is to show how the physical-chemical approach, based on a multi-scale view of matter, offers fundamental contributions, through experimental, theoretical and computer modeling methodologies, in fields ranging from astrochemistry, biochemistry, catalysis, soft-matter to materials science (to name but a few).

The scientific program is divided into six thematic sessions, introduced by plenary lectures by researchers who will demonstrate the synergy between experimental and theoretical methods in understanding the fundamental mechanisms of chemistry

Activities open to the public, dedicated to topics of general interest, will be offered during the conference.

Social events will make your stay more enjoyable with additional opportunities for an informal exchange of ideas.

PATRONAGE & SPONSORS

Patronage

UNIVERSITÀ
DI TORINO

chimica

INSTM

Società
Chimica
Italiana
Divisione di Chimica Fisica

Sponsors

aethia
open computing solutions

ALFATEST
strumentazione scientifica

Assing

Automation
Advanced Lab Solutions

BRUKER

chimet®
REFINING AND FINE CHEMICALS

DISA
MILANO

E4
COMPUTER
ENGINEERING

Hellma®

HIDEN
ANALYTICAL

HIDEN
ISOCHEMA

Mercer-instruments

mi
micromeritics®

GENERAL INFORMATION

Venue

University of Turin UniTO
Dept. of Molecular Biotechnology and Health Sciences
Via Nizza 52, 10126 Torino

Wifi

Participants can access the wi-fi infrastructure by using the personal Eduroam account.
Please check the service has been activated on your devices.

SOCIAL PROGRAMME

Welcome Party

Monday 4 September, 2023 – h 18:30
University of Turin UniTO
Dept. of Molecular Biotechnology and Health Sciences
Via Nizza 52, 10126 Torino

Public Engagement

Tuesday 5 September, 2023 – h 18:00
Clima ed energia: quali scelte per il futuro?
Cavallerizza Reale
Via Giuseppe Verdi 9, 10124 Torino

Social Dinner

Wednesday 6 September, 2023 – h 20;00
Esperia Restaurant
Corso Moncalieri 2, 10131 Torino
(Only with reservation)

Techinical Secretariat

EVENTually MEETINGS & EVENTS

EVENTually Meetings & Events
info@eventuallyevents.it
www.eventuallyevents.it
phone + 39 327 3752740

In occasione del XLIX Congresso Nazionale della Divisione di Chimica Fisica della SCI

Clima ed energia: quali scelte per il futuro?

Gli effetti della crisi climatica sono già sotto i nostri occhi. Per mitigare quelli futuri e provare a rallentarla, un passaggio fondamentale riguarda il modo in cui produciamo energia. Dobbiamo quanto prima azzerare le emissioni: le fonti rinnovabili sono la principale risposta. Il nucleare continuerà ad avere un ruolo, ma le scelte non potranno che essere diversificate in base alle peculiarità delle diverse regioni del mondo. Che cosa dobbiamo aspettarci? Su quali tecnologie è meglio investire? La ricerca fornirà nuove soluzioni in grado di cambiare gli scenari?

Martedì 5 Settembre 2023

Aula Magna Cavallerizza Reale
Via Giuseppe Verdi, 9 - Torino

Con **Nicola Armaroli**, chimico e Dirigente di Ricerca Consiglio Nazionale delle Ricerche CNR Bologna, **Elisa Palazzi**, climatologa, dipartimento di Fisica dell'Università di Torino e **Daniele Tomatis**, R&D manager di newcleo Futurable Energy, esperti rispettivamente di energie rinnovabili, cambiamento climatico e nucleare di 4ª generazione.
Modera **Alberto Agliotti**, divulgatore scientifico.

www.settimanedellascienza.it

Organizzato da

chimica

UNIVERSITÀ DI TORINO

Società Chimica Italiana
Divisione di Chimica Fisica

Nell'ambito di

CDCF 2023

In collaborazione con

Centro Scienza onlus

PROGRAMME AT A GLANCE

DARWIN Room

LEONARDO Room

ARISTOTELE Room

Room DARWIN

Time	Monday 04
8:30	Registration
9:30	**Welcome**
Chair	*Civalleri*
10:30	Tkatchenko T4
11:15	Alessio (T4)
11:30	Caruso (T4)
11:45	Grobas Illobre (T4)
12:00	Maltoni (T1)
12:15	Silmani (T1)
12:30	Armetta (T1)
13:00	Light lunch
Chair	*Polo*
14:30	Auditore (T1)
14:45	Baricic (T1)
15:00	Tielens (K-T4)
15:30	Calvino (T1)
15:45	Coffee break & poster
16:30	**Flash communication**
18:30	Welcome Party

Time	Tuesday 05
Chair	*Bordiga*
9:00	Dini T3
9:45	Litti (T1)
10:00	Locardi (T1)
10:15	Martini (T1)
10:30	Coffee break & poster
Chair	*Ridi*
11:30	Melani (T1)
11:45	Miranda Murillo (T1)
12:00	Pavan (K-T1)
12:30	Mudassir (T1)
12:45	**Negro (T1)**
13:00	Light lunch
Chair	*Tielens*
14:30	Diebold T1
15:15	Rizzuto (T4)
15:30	Nicoli (T4)
15:45	Invernizzi (T4)
16:00	Pavone (T4)
16:15	Coffee break & poster
18:00	Public engagement

Time	Wednesday 06
Chair	*Selli*
9:00	Nova T5
9:45	Bocus (T5)
10:00	Bonacchi (T5)
10:15	Campisi (T5)
10:30	Coffee break & poster
Chair	*Brutti*
11:45	Delle Piane (T5)
12:00	Damin (K-T5)
12:30	Agostini (T3)
12:45	Bartoli (T3)
13:00	Light lunch
Chair	*Petraccone*
14:30	Elia (T3)
14:45	Grigioni (T3)
15:00	Labarile (T3)
15:15	Lionello (T3)
15:30	**Sponsors**
16:30	Coffee break & poster
17:00	**Assemblea divisione**
20:00	Social dinner

Time	Thursday 07
Chair	*Pavan*
9:00	Mennucci T2
9:45	Alberti (T2)
10:00	Baglioni (T2)
10:15	Campanile (T2)
10:30	Coffee break & poster
Chair	*Berlier*
11:30	Campione (T2)
11:45	Casale (T2)
12:00	Lambert (K-T2)
12:30	D'Aria (T2)
12:45	Artini (T6)
13:00	Light lunch
Chair	*Zerbetto*
14:30	Graziano (K-T6)
15:00	Baratta (T6)
15:15	Barbon (T6)
15:30	Coffee break & poster
16:15	Balucani T6
17:00	Casu (T6)
17:15	S. Ferrero (T6)
17:30	Closing remarks

DARWIN

Room LEONARDO

Time	Monday 04
Chair	*Greco*
11:30	Zoccante (T4)
12:00	Tabacchi (T4)
12:30	Duce (T1)
12:45	Gallo (T1)
13:00	Light lunch
Chair	*Coluccia*
14:15	Garroni (T1)
14:30	Peddis (K-T1)
15:00	Grandolfo (T1)
15:15	Lettieri (T1)
15:45	Coffee break & poster
16:30	**Flash communication**
18:30	Welcome Party

Time	Tuesday 05
Chair	*Giovannini*
9:45	Scardaci (T1)
10:00	Abdolrahimi (T1)
10:15	Spampinato (T1)
10:30	Coffee break & poster
11:30	Toffoletti (T1)
11:45	Vandenhaute (T1)
12:00	Polo (T3)
12:15	Pierini (T3)
12:30	Narzi (K-T2)
13:00	Light lunch
Chair	*Condorelli*
15:15	Perrone (T3)
15:30	Romagnoli (T3)
15:45	Sassone (T3)
16:15	Coffee break & poster
18:00	Public engagement

Time	Wednesday 06
Chair	*Avanzini*
9:45	Papatola (T5)
10:00	Pareras Niell (T5)
10:15	Giannetti (T2)
10:30	Coffee break & poster
Chair	*Graziano*
12:00	Salvestrini (T5)
12:15	Zeppilli (T5)
12:30	Parnigotto (T5)
12:45	Gianotti (T5)
13:00	Light lunch
14:30	Cioni (T5)
14:45	Dosa (T5)
15:00	Bodo (K-T3)
16:30	Coffee break & poster
20:00	Social dinner

Time	Thursday 07
Chair	*Bisio*
9:45	**R. Ferrero (T2)**
10:00	Pioppi (T2)
10:15	Rizzi (T2)
10:30	Coffee break & poster
11:30	Avanzini (K-T6)
12:00	Martínez-Bachs (T6)
12:15	Maris (T6)
12:30	Mannucci (T6)
12:45	Melandri (T6)
13:00	Light lunch
Chair	*Maschio*
14:30	Miglio (T6)
14:45	Perrero (T6)
15:00	Mino (K-T3)
15:30	Coffee break & poster
17:00	Tavani (T6)
17:15	Vanuzzo (T6)

Room ARISTOTELE

Time	Monday 04
Chair	*Mino*
11:45	Pedone (T4)
12:00	Giovannini (K-T4)
12:30	Corsaro (T1)
12:45	**Ribaldone (T4)**
13:00	Light lunch
Chair	*Lambert*
14:30	D'Agostini (T1)
14:45	Dai (T1)
15:00	Della Latta (T1)
15:15	Di Gregorio (T1)
15:45	Coffee break & poster
16:30	**Flash communication**
18:30	Welcome Party

Time	Tuesday 05
Chair	*Peddis*
9.45	Pelosi (T1)
10:00	Piscino (T1)
10:15	Pratolongo (T1)
10:30	Coffee break & poster
11:30	Punis (T1)
11:45	Salemi (T1)
12:00	Livolsi (T3)
12:15	Malannata (T3)
12:30	Marazzi (T3)
12:45	Mulas (T3)
13:00	Light lunch
Chair	*Gianotti*
15:15	Muñoz García (T3)
15:30	Bisio (K-T1)
16:00	Murgia (T3)
16:15	Coffee break & poster
18:00	Public engagement

Time	Wednesday 06
Chair	*Gentili*
9:45	Etzi (T5)
10:00	De Leo (T2)
10:15	Piacenza (T2)
10:30	Coffee break & poster
11:30	Condorelli (K-T5)
12:00	Ghibaudo (T5)
12:15	Gatto (T2)
12:30	Honorio Franco (T2)
12:45	**Lazzarini (T5)**
13:00	Light lunch
Chair	*Damin*
14:30	Malferrari (T2)
14:45	Mangiacapre (T2)
15:00	Massardo (T2)
15:15	Mastrogiacomo (T2)
16:30	Coffee break & poster
20:00	Social dinner

Time	Thursday 07
Chair	*Erba*
9:45	Maurelli (T2)
10:00	Gentili (K-T2)
10:30	Coffee break & poster
11:30	Tortorella (T2)
11:45	Tuccitto (T2)
12:00	Varsalona (T2)
12:15	Ruffino (T2)
12:30	Selli (K-T5)
13:00	Light lunch
Chair	*Scarano*
14:30	Gomez Maya (T2)
14:45	Venanzi (T2)
15:00	Kakkar (T6)
15:15	Vaghi (T4)
15:30	Coffee break & poster
17:00	Maccarino (T6)
17:15	Mancini (T6)

PROGRAMME

DARWIN

LEONARDO

ARISTOTELE

Room DARWIN

Time	Monday 04	Title
09:30	Welcome	
10:30	**Tkatchenko T4**	Fully Quantum (Bio)Molecular Simulations: Dream or Reality?
11:15	**Alessio (T4)**	Quantum Chemical Study of Nickelocene: From Magnetic Molecules to Materials
11:30	**Caruso (T4)**	Tracking High-Dimensional Fluctuations in Complex Molecular Systems via Time-Variations of Local Environments
11:45	**Grobas Illobre (T4)**	Fluorescence Enhancement of Chromophores near Plasmonic Nanoparticles: Atomistic vs. Continuum Models
12:00	**Maltoni (T1)**	From Ferrite Nanostructures to Sintered Bulk Permanent Magnets
12:15	**Slimani (T1)**	Morpho-Structural and Magnetic Properties of CoFe2O4/SiO2 Nanocomposites: The Effet of the Molecular Coating
12:30	**Armetta (T1)**	Multi phosphor system for multimodal luminescence
13:00	Light lunch	
14:30	**Auditore (T1)**	Interaction of giant argon cluster ions with polymer surfaces: the effect of cluster size
14:45	**Baricic (T1)**	Polyol Synthesis Tuning of Morphology and Néel Temperature in CoO nanoparticles
15:00	**Tielens (K-T4)**	Computational chemistry as the missing piece in the characterization puzzle of biological mineralization
15:30	**Calvino (T1)**	Distinctive properties of Patch Halloysite Nanotubes: NMR study of water confinement and rheological behavior
15:45	Coffee break & poster	
16:30	Flash communication	

SOCIAL PROGRAMME

18:30	Welcome Party

Tuesday 05, September DARWIN

Room DARWIN

Time	Tuesday 05	Title
9:00	**Dini T3**	Hybrid systems for the conversion of light into electrical energy
9:45	**Litti (T1)**	Magnetic-Plasmonic Fe3O4@Au Nanorods for Surface-Enhanced Raman Scattering Analysis of Antibiotics in Water
10:00	**Locardi (T1)**	The enigmatic case of emissive hybrid manganese metal halides
10:15	**Martini (T1)**	Local dynamics in triptycene-based porous polymers by multi-nuclear and multi-technique solid-state NMR
10:30	**Coffee break & poster**	
11:30	**Melani (T1)**	Structure and reactivity of bismuth vanadate-water interfaces
11:45	**Miranda Murillo (T1)**	Exchange coupled CoFe2O4/CoO/CoFe nanocomposites synthetized by colloidal chemistry
12:00	**Pavan (K-T1)**	Into the dynamics of complex molecular systems
12:30	**Mudassir (T1)**	Preparation and characterization of PET (Polyethylene terephthalate) nanoparticles by using Hexafluoro Isopropanol: Chloroform (1:1)
12:45	**Negro (T1)**	New insight into structure, optical and vibrational properties of g-C3N4 as building block for innovative architectures
13:00	**Light lunch**	
14:30	**Diebold T1**	Seeing is believing: A direct view of surface chemistry
15:15	**Rizzuto (T4)**	Molecular Modelling of a per-fluorinated CeIV-based metal-organic framework for CO2 capture
15:30	**Nicoli (T4)**	Fully Atomistic QM/Classical Models for Surface Enhanced Raman Scattering
15:45	**Invernizzi (T4)**	Electronic Properties of Neurotransmitters in a Hybrid System with Zeolite L
16:00	**Pavone (T4)**	Challenges in modelling Singlet Oxygen release from Li-air battery cathode: periodic DFT versus embedded cluster CASPT2
16:15	**Coffee break & poster**	
SOCIAL PROGRAMME		
18:00	Public engagement	

Room DARWIN

Time	Wednesday 06	Title
9:00	**Nova T5**	Modelling reaction mechanisms of multicomponent catalytic systems
9:45	**Bocus (T5)**	Machine Learning Potentials for Accurate Simulations of Zeolite-Catalyzed Reactions
10:00	**Bonacchi (T5)**	Atomically Precise Metal Nanoclusters: Insights into their Photoluminescence Properties and Catalytic Activities
10:15	**Campisi (T5)**	A multi-technique study of acido-basicity of apatitic surfaces and their evolution with temperature
10:30	Coffee break & poster	
11:45	**Delle Piane (T5)**	Capturing probabilities and complexity in reactive systems: from host-guest systems to heterogenous catalysis on metals
12:00	**Damin (K-T5)**	Cu+ bi-pyridine based homoleptic complexes for hydrocarbons oxygenation reactions
12:30	**Agostini (T3)**	Electron Paramagnetic Resonance resolves different triplet states in organic mixed-valence molecular systems
12:45	**Bartoli (T3)**	Unraveling the Effect of Carbon Nanotube Oxidation on Solid-State Decomposition of Ammonia Borane/Carbon Nanotube Composites
13:00	Light lunch	
14:30	**Elia (T3)**	Addressing key challenges in the development "beyond Li-ion" chemistries
14:45	**Grigioni (T3)**	High-rate CO2 and CO electroreduction to formate and acetate
15:00	**Labarile (T3)**	Photosynthetic bacteria in coffee-based photoelectrochemical system
15:15	**Lionello (T3)**	Supramolecular Semiconductivity through Emerging Ionic Gates in Ion–Nanoparticle Superlattices
15:30	Sponsors	
16:30	Coffee break & poster	
17:00	Assemblea divisione	
SOCIAL PROGRAMME		
20:00	Social dinner	

Thursday 07, September DARWIN

Room DARWIN

Time	Thursday 07	Title
9:00	**Mennucci T2**	Light-driven processes in biology through the lenses of physical chemistry
9:45	**Alberti (T2)**	Synthesis and characterization of hybrid magnetic/polymeric nanocomposites
10:00	**Baglioni (T2)**	PVA-Based Cryogels Loaded with Nanostructured Fluids for the Cleaning of Art: a SAXS-USAXS Study
10:15	**Campanile (T2)**	The anticancer peptide LL-III selectively recognizes the human telomere and cMyc G-quadruplexes: new frontiers in the development of effective peptide-based drugs
10:30	Coffee break & poster	
11:30	**Campione (T2)**	Polymeric electroactive P3HT-MWCNT composites for bioelectronic applications
11:45	**Casale (T2)**	Effect of external magnetic fields on the contact angle of magneto-responsive fluids
12:00	**Lambert (K-T2)**	Steps towards Life - How inorganic surfaces may have been involved in the complexification of biomolecules
12:30	**D'Aria (T2)**	G-quadruplex/ligand interaction in anticancer therapy: a physico-chemical study
12:45	**Artini (T6)**	The double activation energy to ionic conduction in doped ceria: a journey through impedance and Raman spectroscopy
13:00	Light lunch	
14:30	**Graziano (K-T6)**	Cytosine epigenetic modifications and conformational changes in G-quadruplex DNA: an ultraviolet resonance Raman spectroscopy study
15:00	**Baratta (T6)**	Removal of Non-Steroidal Anti-Inflammatory Drugs from Drinking Water Sources by GO-SWCNT Buckypapers
15:15	**Barbon (T6)**	The nitroxide/ammonium cation redox couple as mediator for water oxidation
15:30	Coffee break & poster	
16:15	**Balucani T6**	Unveiling the secrets of bimolecular reactions at the microscopic level
17:00	**Casu (T6)**	Investigating Eutectic Mixtures formed with Choline Chloride and ortho, meta and para Hydroxyphenol
17:15	**S. Ferrero (T6)**	A QM/MM strategy for the study of interstellar surface diffusion
17:30	Closing remarks	

Room LEONARDO

Time	Thursday 07	Title
11:30	**Zoccante (T4)**	Thermodynamics of Self Assembled Monolayers formation: a computational investigation
12:00	**Tabacchi (T4)**	Energy Transfer Mechanism in Magnetic Nanoparticle Hyperthermia
12:30	**Duce (T1)**	Thermal analysis and calorimetry to fingerprint the oxidative behaviour of oils in paint films
12:45	**Gallo (T1)**	Silica-cyclodextrin hybrid materials
13:00	Light lunch	
14:15	**Garroni (T1)**	Sustainable processing routes to development of new Eco-friendly Piezoceramics
14:30	**Peddis (K-T1)**	Sustainable Design of New Permanent magnets
15:00	**Grandolfo (T1)**	Ag nanoparticles decorated reduced graphene oxide based hybrid nanocomposites for textile coatings with superior antibacterial characteristics
15:15	**Lettieri (T1)**	From dairy product waste to plastic: preparation and characterization of new fully biobased composite materials
15:45	Coffee break & poster	
16:30	Flash communication	

SOCIAL PROGRAMME

18:30	Welcome Party

Tuesday 05, September LEONARDO

Room LEONARDO

Time	Tuesday 05	Title
9:45	**Scardaci (T1)**	Tuning Wettability of Graphene Oxide by Laser Induced Reduction in Liquids
10:00	**Abdolrahimi (T1)**	XAS investaigations and Magnetic response of magnetic Zeolite Synthesis from Polluted Mt. Etna Volcanic ash
10:15	**Spampinato (T1)**	Correlated Intrinsic Electrical and Chemical Properties of Epitaxial WS2 via Combined C-AFM and ToF-SIMS Characterization
10:30	Coffee break & poster	
11:30	**Toffoletti (T1)**	Design, preparation and optical characterization of plexcitonic nanohybrids based on gold nanorods and J-aggregate of organic dyes
11:45	**Vandenhaute (T1)**	Rare event sampling in nano-structured materials beyond standard DFT
12:00	**Polo (T3)**	Multiple effects induced by molybdenum doping in highly performing BiVO4 photoanodes: surface vs bulk properties
12:15	**Pierini (T3)**	Screening of electrolytes for novel batteries through polarizable molecular dynamics
12:30	**Narzi (K-T2)**	The electron–proton bottleneck of photosynthetic oxygen evolution
13:00	Light lunch	
15:15	**Perrone (T3)**	Exploring the chemical physical properties of Phase Transition - MOlecular Solar Thermal materials under a computational lens
15:30	**Romagnoli (T3)**	Thermodynamic study of chalcogenide perovskites and its precursors for photovoltaic applications
15:45	**Sassone (T3)**	Synergic effect of Carbon Nanotubes on Zeolitic Organic Framework catalyst for CO2 electroreduction
16:15	Coffee break & poster	

SOCIAL PROGRAMME

18:00	Public Engagement

Room LEONARDO

Time	Wednesday 06	Title
9:45	**Papatola (T5)**	Immobilization of enzymes on magnetic nanoparticles for polymer synthesis
10:00	**Pareras Niell (T5)**	True astrocatalysis, iron catalysed formation of interstellar complex organic molecules.
10:15	**Giannetti (T2)**	Design and characterization of oligopeptides capable of interacting with the programmed death ligand 1 receptor for future theragnostic applications
10:30	Coffee break & poster	
12:00	**Salvestrini (T5)**	Combination of MnO2 and persulfate as oxidants for degradation of water pollutants at low temperatures
12:15	**Zeppilli (T5)**	Reactivity of zinc fingers in oxidizing environments: insight from molecular models through activation strain analysis
12:30	**Parnigotto (T5)**	The influence of the surface area and the thiophenic groups concentration on the Pt NPs, a synergic effect for the increment of the Catalytic activity vs. the Oxygen Reduction
12:45	**Gianotti (T5)**	Multi-site organic-inorganic porous hybrid catalysts
13:00	Light lunch	
14:30	**Cioni (T5)**	Sampling the real-time atomic dynamics of metal nanoparticles via combination of experiments, simulations and machine learning
14:45	**Dosa (T5)**	In-situ IR spectroscopy studies on Layered Double Hydroxides as possible electrocatalysts for CO2 reduction reaction to CO
15:00	**Bodo (K-T3)**	OpMetBat project
16:30	Coffee break & poster	

SOCIAL PROGRAMME

20:00	Social Dinner

Thursday 07, September LEONARDO

Room LEONARDO

Time	Thursday 07	Title
9:45	R. Ferrero (T2)	Cyclodextrins: how to face an open challenge with state-of-the-art computational methods
10:00	**Pioppi (T2)**	Vibrational Spectroscopy for the Detection and Identification of Myocardial Chemical Alterations in Heart-Failure with Preserved Ejection Fraction
10:15	**Rizzi (T2)**	Dendritic mesoporous silica core@shell nanostructures with dahlia-like morphology as pH-responsive delivery systems of 5-Fluorouracil for colorectal cancer treatment
10:30	Coffee break & poster	
11:30	**Avanzini (K-T6)**	Circuit Theory for Chemical Reaction Networks
12:00	**Martínez-Bachs (T6)**	Dissipation of the Nascent Reaction Energy of Formamide Formation Route on Interstellar Water Ice Surfaces
12:15	**Maris (T6)**	Insights on the NO bond
12:30	**Mannucci (T6)**	Understanding Deep Eutectic Solvents Formation through L-Menthol Mixtures with Butylated Hydroxytoluene Derivatives
12:45	**Melandri (T6)**	Sigma- and pi-hole activation upon perfluorination of aryl halides: direct evidence from gas phase rotational spectroscopy
13:00	Light lunch	
14:30	**Miglio (T6)**	Swellable Organically Modified Silicas for the removal of PFAS from aqueous solutions
14:45	**Perrero (T6)**	The Interaction of Sulphur-Bearing Species With Olivine Clusters: A New Perspective on Sulphur Depletion In The Interstellar Medium
15:00	**Mino (K-T3)**	Combining shape-controlled TiO2 nanoparticles with MoxC co-catalysts for efficient noble-metal free photocatalytic hydrogen evolution
15:30	Coffee break & poster	
17:00	**Tavani (T6)**	X-ray absorption spectroscopy allows the detection of general Bromine oscillatory behaviour in the Belousov-Zhabotinskii reaction
17:15	**Vanuzzo (T6)**	Crossed Molecular beam studies of elementary reactions relevant in combustion and astrochemistry: O(3P) + small aromatics

Room ARISTOTELE

Time	Monday 04	Title
11:45	**Pedone (T4)**	Molecular Dynamics Simulations of the Ceria-Silica Chemical Mechanical Polishing Process
12:00	**Giovannini (K-T4)**	Multiscale Multilevel Methods for Complex Systems
12:30	**Corsaro (T1)**	Carbon-Polymer Dots as Optical Sensors for Sensing of Airborne Thiols
12:45	**Ribaldone (T4)**	Hybrid Born-Oppenheimer Molecular Dynamics for Condensed Matter Simulations Made Possible: NVE and NVT Trajectories and Post-Processing Properties
13:00	Light lunch	
14:30	**D'Agostini (T1)**	3D-printed geopolymer-hydrotalcite porous scaffolds for CO2 capture at elevated temperatures
14:45	**Dai (T1)**	Solvatochromic Emission from the “Dark” Double-Exciton state of a Polyhalogenated Thiele Hydrocarbon: a joint quantum-chemical and experimental investigation
15:00	**Della Latta (T1)**	Effect of dopant concentration in ITO nanoparticles: a Solid-State NMR study
15:15	**Di Gregorio (T1)**	Exploring Persistent Luminescence in Halide Double Perovskites
15:45	Coffee break & poster	
16:30	**Flash communication**	

SOCIAL PROGRAMME

18:30	Welcome Party

Tuesday 05, September ARISTOTELE

Room ARISTOTELE

Time	Tuesday 05	Title
9:45	**Pelosi (T1)**	Insights into the microwave-assisted preparation and physicochemical characterization of type-II Deep Eutectic Solvents
10:00	**Piscino (T1)**	Improving the thermoelectric performance of Fe/Ni-based skutterudite by multi-filling
10:15	**Pratolongo (T1)**	Halides perovskites nanocrystals synthesized in green solvents
10:30	Coffee break & poster	
11:30	**Punis (T1)**	Copper-binder complexes characterization in verdigris pigment by CW-EPR and ESEEM spectroscopies
11:45	**Salemi (T1)**	Plasmonic nanoparticles as the scattering medium in colloidal random dye lasers
12:00	**Livolsi (T3)**	Solar energy conversion via photothermocatalytic hydrogen production
12:15	**Malannata (T3)**	Photo-electrocatalytic approach for simultaneous hydrogen production and pollutant abatement
12:30	**Marazzi (T3)**	Design challenges for efficient molecular solar-thermal systems
12:45	**Mulas (T3)**	Structural investigation and kinetic features of CO2 conversion processes induced by photochemical and mechanochemical activation
13:00	Light lunch	
15:15	**Muñoz García (T3)**	First principles assessment of the electronic and charge transfer properties at functional interfaces for emerging photovoltaics
15:30	**Bisio (K-T1)**	Functionalized silica-based monoliths for the removal of metal ions from aqueous phase
16:00	**Murgia (T3)**	Metastable NaCB11H12 polymorph prepared by mechanical milling as new superionic conductor for post-Li solid-state batteries
16:15	Coffee break & poster	

SOCIAL PROGRAMME

18:00	Public engagement

Room ARISTOTELE

Time	Wednesday 06	Title
9:45	**Etzi (T5)**	Influence of the architecture of the gas diffusion layer on the performances of Cu-based electrodes for the CO2 electroreduction in flow cells
10:00	**De Leo (T2)**	Polydopamine-coated liposomes: preparation, characterization, and evaluation of their behavior in biological fluids
10:15	**Piacenza (T2)**	Green selenium nanoparticles in an innovative confined environment: synthesis, characterization, and size prediction
10:30	Coffee break & poster	
11:30	**Condorelli (K-T5)**	Silver Nanoflower as single platform for in situ photocatalitic reactions
12:00	**Ghibaudo (T5)**	Application of chemometric approaches to a photocatalytic pilot plant for environmental issues and study of the material recovery
12:15	**Gatto (T2)**	Photocurrent Generation in Supramolecular Bio-Inspired Nanoarchitectures on Gold Surface
12:30	**Honorio Franco (T2)**	Photosynthetic Bacteria Biohybrid Systems for Self-Powered Pollutants Detection
12:45	**Lazzarini (T5)**	Monitoring CO-induced surface phenomena in supported metal catalysts by IR spectroscopy
13:00	Light lunch	
14:30	**Malferrari (T2)**	Characterization of a 3D Bioprinted Tumor Model by Scanning Electrochemical Microscopy
14:45	**Mangiacapre (T2)**	Water-based Deep Eutectic Solvents: a new generation of green solvents
15:00	**Massardo (T2)**	First detection of µ-plastics in human urines and kidneys using µ-Raman spectroscopy
15:15	**Mastrogiacomo (T2)**	Synthesis, characterization, in vitro and in vivo studies on antibody decorated liposomes encapsulating MCC950 for the treatment of fatty liver disease
16:30	Coffee break & poster	

SOCIAL PROGRAMME

20:00	Social dinner

Thursday 07, September ARISTOTELE

Room ARISTOTELE

Time	Thursday 07	Title
9:45	**Maurelli (T2)**	Pluronic micelles for curcumin extraction: characterization and potential applications in the biomedical field
10:00	**Gentili (K-T2)**	Tracing a New Path in the Field of AI and Robotics: Mimicking Human Intelligence through Soft Matter
10:30	**Coffee break & poster**	
11:30	**Tortorella (T2)**	Surviving high salt? Investigating the response of bacterial model membranes to the high salinity of the deep subsurface of Mars
11:45	**Tuccitto (T2)**	Interfacial instability at liquid-liquid interphase enables high performance synthetic molecular communication
12:00	**Varsalona (T2)**	Polymerization of dopamine via anoxygenic photosynthetic bacteria: bio-optoelectronics for sustainable energy production
12:15	**Ruffino (T2)**	The effects of the interplay of substrate surface free energy and nano-geometry on the assembly of semi-crystalline polymer thin films
12:30	**Selli (K-T5)**	Photo(electro)catalytic and time resolved spectroscopy characterization of metal oxide semiconductor materials for solar energy conversion
13:00	**Light lunch**	
14:30	**Gomez Maya (T2)**	Modeling Complex Spectroscopies of Systems in Complex Environments
14:45	**Venanzi (T2)**	Ultrasound-assisted formation of therapeutic peptide microcapsules
15:00	**Kakkar (T6)**	Computational Insights into CO2 Formation on Interstellar Water Ice
15:15	**Vaghi (T4)**	Bromine transfer to a Cu complex to activate an ARGET ATRP reaction
15:30	**Coffee break & poster**	
17:00	**Maccarino (T6)**	Organo-modified silicas for the removal of dye molecules from water media
17:15	**Mancini (T6)**	A theoretical characterization of bimolecular reactions leading to the formation of interstellar phosphorus- and silicon-bearing molecules

INVITED LECTURES

Seeing is believing: A direct view of surface chemistry

Ulrike Diebold[1]
[1]Institute of Applied Physics, TU Wien, Wiedner Hauptstrasse 8-10/134, 1040 Vienna, Austria

Chemical reactions at surfaces are central to a wide range of applications and at the heart of heterogeneous catalysis. With surface science methods, a deeper understanding of the active site and of the reaction mechanisms is possible. In particular scanning probe techniques, in conjunction with area-averaging techniques and first-principles calculations, affords deep insights. In the talk, I will give a few selected examples including the measurement of atomic-scale properties [1], and of 'single-atom' catalysts [2] investigated with appropriate model systems.

[1] M. Wagner et al. Nature 592 (2021) 722
[2] J. Hulva et al. Science 371 (2021) 375

Light-driven processes in biology through the lenses of physical chemistry

Benedetta Mennucci
Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via G. Moruzzi 13, 56126 Pisa, Italy
benedetta.mennucci@unipi.it

Many fundamental processes in biology are activated by light and they are based on light-responsive proteins which exploit embedded chromophore(s) capable of absorbing photons of a specific wavelength. To investigate these processes and eventually be able to manipulate them, a high-precision temporal and spatial characterization is needed but the many time and length scales involved make it extremely challenging. A possible strategy is to integrate the outputs of sophisticated spectroscopic methods with an accurate molecular modeling. In this talk, I'll discuss how this integration works and present its application to different photosensitive proteins.

Hybrid systems for the conversion of light into electrical energy

Danilo Dini
Dept. of Chemistry, University of Rome "La Sapienza", p.le Aldo Moro 5, 00185 Rome (Italy)
e-mail address: *danilo.dini@uniroma1.it*

The conversion of light into electrical energy is the function that photovoltaic (PV) devices (either junctions or electrochemical cells) accomplish by means of the separation and the displacement of the charges photogenerated in a light-absorbing material provided that this is interfaced with electron/hole acceptors that either conduct electricity or constitute charge carriers per se, and an electric field is present through the interfaces under irradiation. Among photoactive systems (i) the combination nanostructured inorganic semiconductors with molecular dye-sensitizers [1] and (ii) the halogen-based perovskites containing polyatomic monovalent cations [2] represent the hybrid systems which stand at the basis of last generation PV technologies: the dye-sensitizer solar cell (DSC) and perovskite solar cell (PSC). The comprehension of the mechanisms of charge generation/transfer operating in the photoactive systems of DSCs and PSCs is fundamental for the identification of the primary causes controlling the photoconversion performances in the respective devices, and allows the successive development of new materials, their combinations, and novel configurations for the further improvement of device performance. Depending on the type of photoconversion device different approaches can be adopted for the improvement of the corresponding performances. In the context of DSCs research at the University La Sapienza these have involved the preparative chemistry of multi-component nanostructured semiconductors, the design and synthesis of dye-sensitizers with functional blocks, and the definition and assembly of tandem devices.[3] In the ambit of PSC the research activity has been mainly directed to the development of cells with inverted configuration [4] for specific applications that exploit the special spectral properties of the photoactive perovskite.[5]

[1] A. Hagfeldt et al. Chem. Rev. 110 (2010) 6595
[2] A. Kojima et al. J. Am. Chem. Soc. 131 (2009) 6050
[3] M. Bonomo et al. Sust. Energy Fuels 5 (2021) 4736
[4] D. Di Girolamo et al. Adv. Energy Mater. (2019) 1901642
[5] V. Carpenella et al. J. Phys. Chem. C, in press

Fully Quantum (Bio)Molecular Simulations: Dream or Reality?

Alexandre Tkatchenko[1]
[1]Department of Physics and Materials Science, University of Luxembourg, L-1511 Luxembourg City, Luxembourg
Presenter's e-mail address: alexandre.tkatchenko@uni.lu

The convergence between accurate quantum-mechanical (QM) models (and codes) with efficient machine learning (ML) methods seem to promise a paradigm shift in molecular simulations. Many challenging applications are now being tackled by increasingly powerful QM/ML methodologies. These include modelling covalent materials, molecules, molecular crystals, surfaces, and even whole proteins in explicit water (https://arxiv.org/abs/2205.08306). In this talk, I attempt to provide a reality check on these recent advances and on the developments required to enable fully quantum dynamics of complex functional (bio)molecular systems. Multiple challenges are highlighted that should keep theorists in business for the foreseeable future:

(1) Ensuring the accuracy of high-level QM methods (https://doi.org/10.1038/s41467-021-24119-3),

(2) Describing intricate QM long-range interactions (https://doi.org/10.1126/sciadv.aax0024; https://doi.org/10.1126/science.aae0509; https://doi.org/10.1103/PhysRevLett.128.106101),

(3) Treating quantum electrodynamic effects that become relevant for complex molecules (https://doi.org/10.1021/acs.jpclett.1c04222;https://doi.org/10.1103/PhysRevResearch.4.013011).

(4) Developing increasingly accurate, efficient, scalable, and transferable ML architectures for molecules and materials (https://doi.org/10.1038/s41467-022-31093-x; https://arxiv.org/abs/2209.14865; https://arxiv.org/abs/2209.03985).

(5) Accounting for the quantum nature of the nuclei and the influence of external environments (https://doi.org/10.1038/s41467-020-20212-1; https://doi.org/10.1038/s41467-022-28461-y).

I argue that only a conjunction of all these developments will enable the long-held dream of fully quantum (bio)molecular simulations.

Modelling reaction mechanisms of multicomponent catalytic systems

Ainara Nova[1,2]
[1]Hylleraas Centre for Quantum Molecular Sciences and Centre for Material Science and Nanotechnology, Department of Chemistry, University of Oslo, 1033 Blindern, Oslo, 0315, Norway
ainaran@kjemi.uio.no

On the way to achieving more challenging transformations, such as the selective activation of inert bonds, catalysts have increased in complexity. To combine activity and selectivity, many of these systems contain several active components, which should be well-defined and cooperate. This property, well known in nature, is relatively novel in homogeneous and heterogeneous catalysis and their study involves methodological challenges.

In this presentation, I will go through a couple of examples from our group where multicomponent catalysts used in CO_2 reduction were studied. In system **A** (Figure),[1] Ab Initio Molecular Dynamics simulations were crucial for understanding the flexibility of the catalyst and the cooperation between the two active sites. The study of system **B** (Figure) required multiple computational models to understand the catalyst activation phase,[2] the interaction of the catalyst with the products,[3] and the CO_2 hydrogenation pathway.[4] In both systems, **A** and **B**, resolving the complexity of the underlying reaction mechanisms required the synergic use of experiments and computations.

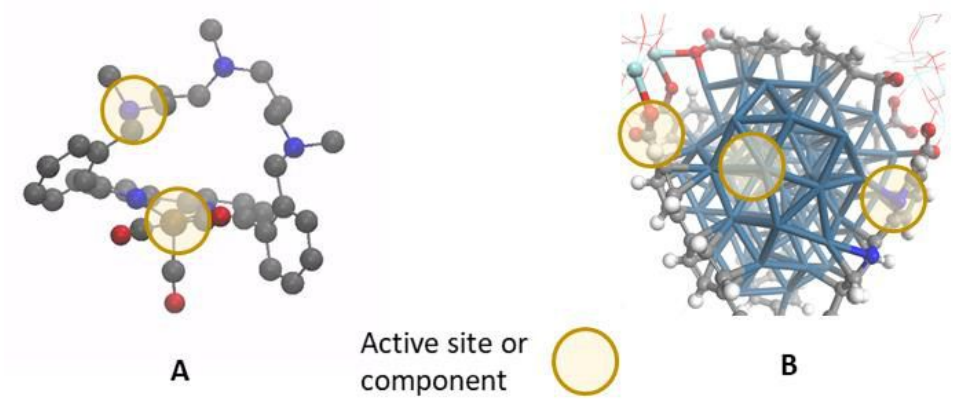


Figure: Multicomponent catalytic systems

[1] W. Hong, et al. *ACS Catal.* 13, (2023), 3109.
[2] E. S. Gutterød, et al., *J. Am. Chem. Soc.* 142, (2020), 999.
[3] E. S. Gutterød, et al. *J. Am. Chem. Soc.* 142, (2020), 17105.
[4] H. Pulumati et al. Manuscript in preparation

Unveiling the secrets of bimolecular reactions at the microscopic level

Nadia Balucani
Dipartimento di Chimica, Biologia e Biotecnologie – Università degli Studi di Perugia
Via Elce di Sotto, 8 – 06123 Perugia, Italy
nadia.balucani@unipg.it

One of the fundamental goals of chemical physics is to understand how chemical reactions occur at the microscopic level. This is the realm of reaction dynamics, a research field that has complemented the more classical approach of chemical kinetics. The idea that a chemical reaction can be described in terms of the dynamics of motion of single atoms along a potential energy surface (PES) goes back London [1] and Eyring et al [2], but almost a quarter of a century elapsed before the first microscopic-level experimental data became available. Among the experimental techniques which can be used to obtain those data, the crossed molecular beam (CMB) technique with mass spectrometric detection, developed by the Nobel Laureates Y. T. Lee and D. R. Herschbach [3], has proved to be the most versatile in facing the study of a variety of reactive systems. For many years, this approach has been used to address fundamental aspects on the reaction micro-mechanisms by investigating several benchmark systems. Only more recently, improvements in the production of beams of transient species and in vacuum technology have allowed us to study elementary reactions of practical interest, such as those of relevance in astrochemistry, atmospheric chemistry and combustion chemistry [4,5].

In this talk, I will present recent results obtained in our laboratory on the reactions involving either atomic oxygen in its ground electronic state, $O(^3P)$, or atomic nitrogen in its first electronically excited state, $N(^2D)$, with unsaturated and aromatic hydrocarbons. The investigated systems are of relevance in combustion chemistry, in the chemistry of the interstellar medium or in the chemistry of the upper atmosphere of Titan, the giant moon of Saturn with potential implications in prebiotic chemistry. In all cases, the interpretation of the experimental results has been assisted by dedicated *ab initio* calculations of the underlying PES and statistical estimates of the production branching fractions (see, for instance, [6-9]).

[1] F. London. Z. Elektrochem 35 (1929) 552.
[2] H. Eyring and M. Polanyi. Z. Phys. Chem. Abt. B 12 (1931) 279.
[3] D. R. Herschbach. Chem. Scr. 27 (1987) 327; Y. T. Lee. Chem. Scr. 27 (1987) 215.
[4] P. Casavecchia et al. Phys. Chem. Chem. Phys. 11 (2009) 46.
[5] P. Casavecchia et al. Int. Rev. Phys. Chem. 34 (2015) 161.
[6] C. Cavallotti et al. J. Phys. Chem. Lett. 11 (2020) 9621; G. Vanuzzo et al. J. Phys. Chem. A 125 (2021) 8434.
[7] P. Recio et al. Nature Chemistry 14 (2022) 1405.
[8] G. Vanuzzo et al. ACS Earth and Space Chemistry 6 (2022) 2305.
[9] N. Balucani et al. Faraday Discussions (2023) in press; doi: 10.1039/D3FD00057E

KEYNOTES

T1. PHYSICAL CHEMISTRY OF MATERIALS

Functionalized silica-based monoliths for the removal of metal ions from aqueous phase

Stefano Marchesi[1], Gioele Ancora[1], Fabio Carniato[1], Leonardo Marchese[1] and Chiara Bisio[1,2]
[1] Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale, Viale Teresa Michel 11, 15121 Alessandria (AL)
[2] CNR-SCITEC Istituto di Scienze e Tecnologie Chimiche "Giulio Natta", Via C. Golgi 19, 20133 Milano (MI), Italy
chiara.bisio@uniupo.it

Transition and rare-earth metals represent essential raw materials for the scientific and technological advancement of human society and they are employed in a wide range of applications. Nevertheless, their consumption is often associated with a high waste production. In this context, the recycling and recovery of these precious metal elements from end-of-life products or metal-contaminated aqueous environments is of considerable importance from a circular economy perspective.[1,2] In our study, we focused the attention on the application of synthetic mesoporous silica in monolithic form, obtained by a sol-gel method and functionalized with specific chelating groups (DTPA, diethylenetriaminepentaacetic acid) (Fig. 1) for the recovery of metal ions from aqueous matrices. The solid was characterized in detail from a physico-chemical point-of-view with a multi-technique approach. DTPA-modified silica monoliths were tested in the recovery of paramagnetic Gd^{3+}, Cu^{2+} and Co^{2+} ions from slightly acidic aqueous solutions (at pH 5) at $[M^{n+}] = 10$ mM, using the Fast Field Cycling (FCC) ^{1}H-NMR relaxometry to evaluate their uptake performance in real time and in simple experimental conditions (298 K, 10 MHz and in static conditions). These experiments do not need destructive and/or expensive pre-treatment procedures on multiple analysis samples.[3] It was shown that silica monoliths were able to remove a large fraction of metal ions from the metal solutions thanks to the chelating effect of DPTA molecules: up to >60% of the initial Cu^{2+} ion concentration was effectively recovered, followed by Co^{2+} (50%) and Gd^{3+} (40%) (Fig. 1). In terms of mg of captured metal ions per gram of solid sorbent, instead, the order is $Gd^{3+} > Cu^{2+} > Co^{2+}$ (Fig. 1). Detailed information on the kinetics of the capture process were also extrapolated from NMR data as well, providing more hints on the metal uptake mechanisms. Finally, the regeneration of the solid sorbent was also evaluated for potential future application.

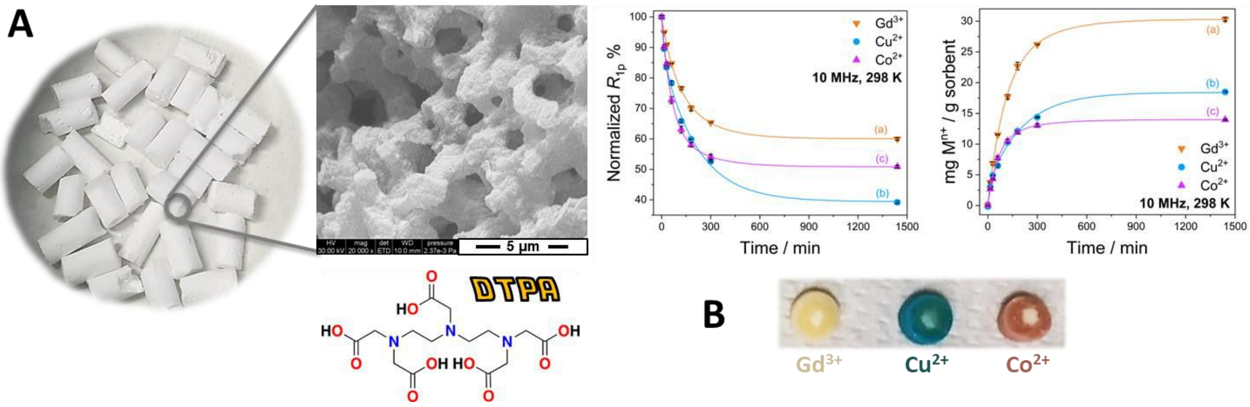


Fig. 1. **A)** SEM micrograph of DPTA-doped mesoporous silica monoliths; **B)** Normalized R_1 (%) vs Time and related mg of M^{n+} ions captured per gram of solid sorbent vs Time graphs derived from the FFC ^{1}H-NMR relaxometric experiments; the monoliths at the end of the capture processes are also shown in frame B.

[1] U.S. Geological Survey (2022). Mineral Commodity Summaries 2022. U.S. Geological Survey, Reston, Virginia, 134-135.
[2] V. Balaram. Geoscience Frontiers 10(4) (2019) 1285-1303, ISSN 1674-9871.
[3] S. Marchesi et al. Dalton Trans. 51(11) (2022) 4502-4509.

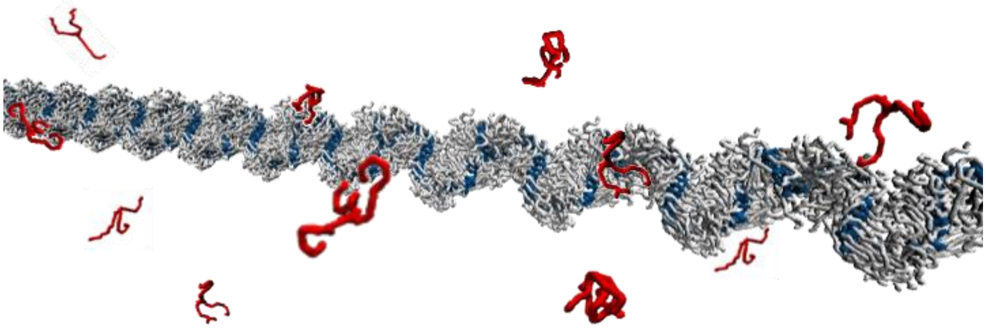
Into the dynamics of complex molecular systems

Giovanni M. Pavan[1,2]
[1]*Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy*
[2]*Department of Innovative Technologies, University of Applied Sciences and Arts of Southern Switzerland, Polo Universitario Lugano, Campus Est, Via la Santa 1, 6962 Lugano-Viganello, Switzerland*
Presenter's email address: giovanni.pavan@polito.it

Nature uses self-assembly for building complex (supra)molecular systems with fascinating properties. In these systems, the constitutive units self-organize via reversible interactions, generating higher scale assembled structures/entities that are in continuous dynamic communication with each other and with the external environment. Such innate dynamics imparts to these systems unique properties such as, e.g., the ability to dynamically adapt or reconfigure in response to specific stimuli, to convert energy into autonomous behaviors, or to control chemical reactivity within them. Learning the key principles to rationally design artificial molecular systems with similar programmable behaviors[1] would be a breakthrough in many fields. But the microscopic details of their dynamic behavior and the key factors controlling them remain often difficult to ascertain.

Multiscale molecular models,[2] advanced computer simulations[3] and machine learning[4] may offer a fundamental support to reaching such an ambitious goal.

In this presentation, I will show some examples of how the rich, multilayered dynamics that characterize complex molecular systems may have a profound impact on collective ensemble properties emerging within them.[5,6,7] I will discuss recent efforts conducted in our group to unravel the intricate communication networks present within innately dynamic self-organizing molecular systems[8] and abstract data-driven descriptors that we developed for tracking local structural and dynamical fluctuations emerging within them.[9,10] The results that we are obtaining have general character and are bringing us new knowledge, challenging in a broad sense classical paradigms in chemistry and materials science.[11,12]



[1] T. Aida, E. W. Meijer, and A. I. Stupp, Science, 335, 813 (2012)
[2] A. L. de Marco, D. Bochicchio, A. Gardin, G. Doni, and G. M. Pavan, ACS Nano, 15, 14229 (2021)
[3] D. Bochicchio, M. Salvalaglio, and G. M. Pavan, Nature Commun., 8, 147 (2017)
[4] A. Gardin, C. Perego, G. Doni, and G. M. Pavan, Commun. Chem., 5, 82 (2022)
[5] C. Lionello, C. Perego, A. Gardin, R. Klajn, and G. M. Pavan, ACS Nano, 17, 275 (2023)
[6] M. Delle Piane, L. Pesce, M. Cioni, and G. M. Pavan, Chem. Sci., 13, 11232 (2022)
[7] C. Lionello, A. Gardin, A. Cardellini, D. Bochicchio, M. Shivrayan, A. Fernandez, S. Thayumanavan, and G. M. Pavan, ACS Nano, 15, 16149 (2021)
[8] M. Crippa, C. Perego, A. L. de Marco, and G. M. Pavan, Nature Commun., 13, 2162 (2022)
[9] C. Caruso, A. Cardellini, M. Crippa, D. Rapetti, and G. M. Pavan, J. Chem. Phys., 158, 214302 (2023)
[10] Crippa, A Cardellini, C. Caruso, and G. M. Pavan, Proc. Natl. Acad. Sci. U. S. A., 120, e2300565120 (2023)
[11] M. Cioni, D. Polino, D. Rapetti, L. Pesce, M. Delle Piane, and G. M. Pavan, J. Chem Phys. 158, 124701 (2023)
[12] D. Rapetti, M. Delle Piane, M. Cioni, R. Ferrando, and G. M. Pavan, Commun. Chem., 6, 143 (2023)

Abstract ID. T1K02

Sustainable Design of New Permanent magnets

P. Maltoni[1], G. Varvaro[2], G.Barucca[3], F. Locardi[5], M.Ferretti[5], R.Mathieu[1] and D. Peddis[2,5]
[1] Department of Materials Science and Engineering, Uppsala University, Box 35, SE-751 03 Uppsala, Sweden[2]Author's
[2]Institute of Structure of Matter, CNR, nM2-Lab, Via Salaria km 29.300, Monterotondo Scalo 00015, Roma, Italy
[2]Department SIMAU, University Politecnica delle Marche, Via Brecce Bianche, Ancona, Italy
[3] Department of Chemistry and Industrial Chemistry & INSTM , University of Genova, nM2-Lab, 16146 Genova,
Davide.peddis@unige.it

The increasing efforts towards a greener and more sustainable future has significantly enhanced the demand for permanent magnets based on rare-earth elements (RE-PM), which are key components of environmentally friendly energy technologies, such as hybrid and electric vehicles and wind turbines [1]. To respond to this growing demand and to cope with the Chinese monopoly [2] of the production and treatment of RE elements, an intense computational and experimental activity has been recently carried out to develop effective solutions that allow reducing the demand and use of REEs. In this framework, Nanostructured magnetic materials laboratory (www.nm2lab.com) is proposing specific strategies to implement a sustainable design of new permanent magnets such us a) the recycling/reuse of End-of-Life (EoL) magnets; b) the optimization of existing materials; c) the development of new hard magnetic phases. These communications will focus on the optimization of exiting materials discussing the design of hard/soft exchange coupled nanocomposite (NCs). It will be presented an in-depth structural, morphological and magnetic characterization of ferrite-based nanostructures obtained through a bottom-up sol−gel approach. The combination of the high coercivity of a hard phase $SrFe_{12}O_{19}$ (SFO) and the high saturation magnetization of a soft phase, $CoFe_2O_4$ (CFO), allowing to develop exchange-coupled bi-magnetic NCs. A symbiotic effect is observed in a SFO/CFO nanocomposite, as the unique oriented growth of SFO prevents grain growth of the CFO, thus restricting the crystallite size of both. Through X-ray powder diffraction (XRPD), transmission electron microscopy (TEM), and magnetic measurements we clarify the relationship between the distribution and size of hard/soft particles, the optimization of interfaces and the obtained uniform magnetic response. This study allowed us to establish the potentiality of hard/soft SFO/CFO nanostructures in current permanent magnet technology.

[1] P. Maltoni, T. Sarkar, G. Barucca, G. Varvaro, D. Peddis, e R. Mathieu, «, Journal of Magnetism and Magnetic Materials, vol. 535, p. 168095, ott. 2021, doi: 10.1016/j.jmmm.2021.168095.

[2] P. Maltoni et al., «Towards bi-magnetic nanocomposites as permanent magnets through the optimization of the synthesis and magnetic properties of SrFe 12 O 19 nanocrystallites», J. Phys. D: Appl. Phys., vol. 54, fasc. 12, p. 124004, mar. 2021, doi: 10.1088/1361-6463/abd20d.

[3] P. Maltoni et al., «Tuning the Magnetic Properties of Hard–Soft SrFe12O19/CoFe2O4 Nanostructures via Composition/Interphase Coupling», J. Phys. Chem. C, vol. 125, fasc. 10, pp. 5927–5936, mar. 2021, doi: 10.1021/acs.jpcc.1c00355.

ORALS

T1. PHYSICAL CHEMISTRY OF MATERIALS

XAS investigations and Magnetic response of Magnetic Zeolite Synthesis from Polluted Mt. Etna Volcanic ash

Maryam Abdolrahimi[1,2], Claudia Belviso[4], Carlo Meneghini[3], Davide Peddis[1,2]
[1]Department of Chemistry and Industrial Chemistry & INSTM, University of Genova, nM2-Lab, 16146 Genova, Italy
[2]Institute of Structure of Matter, nM2-Lab, Via Salaria km 29.300, Monterotondo Scalo 00015, Roma, Italy
[3]Department of Science, University of Roma Tre, Rome, 00146, Italy
[4]Istituto di Metodologie per l'Analisi Ambientale_CNR, 85050 Tito Scalo, Italy

Magnetic zeolites are a category of nanostructured materials that find applications in various fields such as water treatment, catalysis, selective magnetic filtration, and more. Natural volcanic ashes (VA), owing to the presence of iron oxides/hydroxides in their chemical composition, serve as suitable precursors for the cost-effective synthesis of magnetic zeolites on a large scale. However, natural materials are often characterized by an intrinsic variability of composition and Physical-chemical properties. In this framework it is crucial to achieve an accurate description of their local atomic structure, coordination chemistry, and electronic state of the active elements, particularly Fe, which provides the magnetic behaviour. This knowledge is necessary to understand the macroscopic properties of the materials and to design optimal synthesis routes for magnetic zeolites. In this regard, X-ray absorption fine structure (XAFS) spectroscopy is a highly suitable technique thanks to its element-selective local probe specificity.

In this study, the magnetic characterization and Fe-K edged XAFS analysis have been combined to relate the average Fe coordination chemistry and valence state, to the magnetic properties of zeolites hydrothermally synthesised from natural volcanic ash collected from Mt. Etna in pure (VA-H) or sea (VA-HM) water [1]. The zeolite formation has been confirmed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The magnetic properties of the natural volcanic ash and zeolites were probed by the field and temperature dependence (ZFC-FC) of the magnetization at 5K and 300K. The Fe-K edge XAFS were analysed in the near edge (XANES) and extended (EXAFS) regions.

The magnetic characterization demonstrated that the formation of zeolite directly affected the magnetic properties of the volcanic ash decreasing the saturation magnetization. Interestingly, the first derivative of M_{FC}- M_{ZFC} of pristine (VA) and zeolite (VA-H) samples point out a sharp pick at ~55K in the spectra of VA (Fig.1a) suggesting an antiferromagnetic-paramagnetic transition [2] that can be likely associated to olivine phases (fayalite or forsterite) detected in X-ray diffraction patterns and having similar TN= 55K. The pre-edge spectra (Fe-XANES) demonstrated the local structure of iron in VA samples changing after hydrothermal treatments (Fig. 2b). Quantitative analysis showed the Fe oxidation $Fe^{2+} \rightarrow Fe^{3+}$, associated to a change in Fe-O coordination. This behaviour comes in agreement with the expected changes in evolution of olivine with thermal treatments.

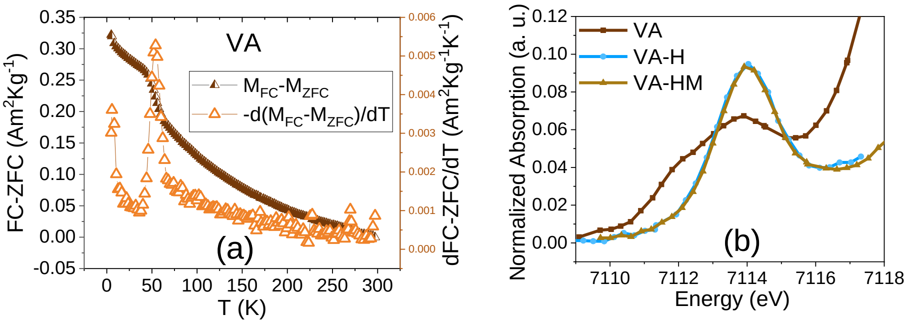


Figure 1. (a). (M_{FC}-M_{ZFC}) and the derivative of (M_{FC}-M_{ZFC}) curves of the volcanic ash and (b). The pre-edge region of the experimental Fe K-edge XAS spectra of the samples.

[1] C. Belviso et al. Molecules. 23 (2018) 2122.
[2] A Ardu et al. Interuniversitario & Unit, (2016).

Multi phosphor system for multimodal luminescence

Alessando Lo Bianco[1], Francesco Armetta[1], Vitalii Boiko[2], Dariusz Hreniak[2], Maria Luisa Saladino[1]
[1] *STEBICEF Department, University of Palermo, Viale delle Scienze Bld.17, I-90128 Palermo,Italy*
[2] *Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Ul Okólna 2, Wrocław, Poland*
francesco.armetta01@unipa.it

Luminescent materials have found a wide range of applications in all walks of daily life, including advanced optical displays, solid state lighting, X-ray intensification, scintillation and many more. Recently, the lanthanide based luminescent nanostructures have been recognized worldwide for their better chemical and optical properties originating from their unique electronic structures as well as to their wide range of applications [1]. Ln-based light conversions, i.e., downshifting and up-conversion, and Persistent phosphors have been adopted in commercial anti-counterfeiting [2-4]. In this field, multimodal luminescence has become an important tool for ensuring the authenticity of a product. This is because the combination of different luminescent processes can create a unique and complex pattern that is difficult to replicate, making it easier to detect and prevent counterfeit products. On this view, the preparation of systems with a couple of phosphors where one material emits and excites a second one is becoming a common strategy.

Here, the development of a dual-control system, able to generate a different signal compared to the radiation used to excite it, is reported. The phosphors designed for the preparation of the system are: a persistent phosphor emitting in the red region, with maximum peaks at 615 and 626 nm and a persistence of about 3 hours, $Y_2O_2S:Eu^{3+},Ti^{2+},Mg^{4+}$, and the cuprorivaite ($CaCuSi_4O_{10}$), known as Egyptian Blue, emitting in the infrared region if exited in the red region. When irradiated with a 365 nm lamp, the system emits both in the red region of the visible spectrum and in the infrared ones. When irradiated with a 640 nm lamp, only the emission in the infrared region is observed (Figure 1). The study was carried out in order to understand the energy transfer mechanism between the phosphors and to obtain a system with the highest efficiency trough the investigation of the optical properties (emission and excitation spectra, luminescence decays, thermoluminescence techniques). Finally, the best system was dispersed in different media, both organic polymers and inorganic matrix, to test the feasibility as anti-counterfeiting inks or markers.

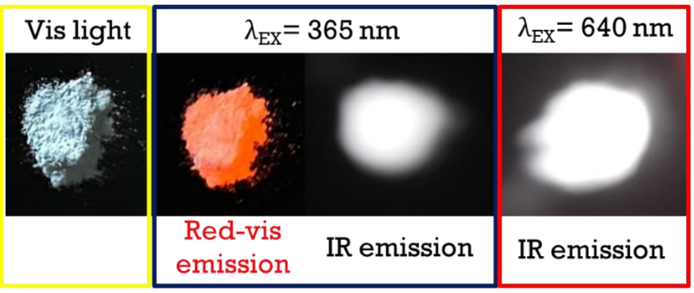


Figure 1. Emission of solid-state mixtures of the powders y under UV (365 nm) and red (640 nm) light.

[1] F. Armetta et al. Scientific Reports, 9 (1) (2019) art. no. 3368.
[2] H. Suo et al. Materials Today Physics 21 (2021) 100520
[3] H. Huang Small (2020) 2000708
[4] F. Armetta et al. Materials Letters (2023) 133653.

Interaction of giant argon cluster ions with polymer surfaces: the effect of cluster size

Alessandro Auditore, Valentina Spampinato, Enrica Maria Malannata, Giuseppe Ragusano, Nunzio Tuccitto, Antonino Licciardello
Dipartimento di Scienze Chimiche, Università degli Studi di Catania, v. A. Doria 6, 95125 Catania (Italy)
alessandro.auditore@unict.it

The availability of small sized sources capable of generating large gas cluster ion beams (GCIB) opened new scenarios in the study of organic solids and polymer materials by means of secondary ion mass spectrometry, largely overcoming the limitations caused by the damage produced by the beam-sample interaction, which involves the loss of molecular as well as spatial information. Actually, it turns out from several literature data that the use of GCIBs makes it possible, at least in principle, the acquisition of 3D chemical images from organic, biologic and polymeric systems. However, in many instances, such as hybrid organic/inorganic systems or highly crosslinked polymers, the experimental results are relatively poor and do not fit with the previsions obtained from MD simulations that, on the contrary, make good previsions in the case of many model systems. In this respect it is necessary to obtain additional experimental information for increasing the understanding of the mechanisms involved in the cluster-surface interaction. In this contribution we show some results, obtained by Time-of-Flight Secondary Ion Mass Spectrometry, on the effect of the bombardment with large argon clusters (Ar_n^+, $500<n<5000$) of polymers with various structures/cross-linking degree, with focus on the effect of cluster size on the measured compositional depth profiles. These results will be compared with the previsions of a recently introduced MD-based transport and reaction model for the simulation of the sputter erosion of molecular targets [1].

[1] N. Tuccitto, D. Maciazek, Z. Postawa, and A. Licciardello, *J. Phys. Chem. C,* 2019, 123, 20188−20194

Polyol Synthesis Tuning of Morphology and Néel Temperature in CoO nanoparticles

M. Baričić[1,5], J. M. Nuñez[2,3], M. Aguirre[3], D. Hrabovsky[4], M. Seydou[1], C. Meneghini[5], D. Peddis[6], S. Ammar-Merah[1]
[1]ITODYS, UMR-CNRS 7086, Université Paris Cité, 15 Rue Jean Anotoine de Baif, 75205, Paris, France
[2]Instituto De Nanociencia y Nanotecnología, CNEA, CONICET, S. C. Bariloche 8400, Rio Negro, Argentina
[3]Laboratorio de Microscopías Avanzadas, Universidad de Zaragoza, C/ Pedro Cerbuna 12, 50009, Zaragoza, Spain
[4]IMPMC, UMR-CNRS 7590, Sorbonne Université, 6 Place Jussieu, 75005 Paris, France
[5]Dipartimento di Scienze, Università degli Studi Roma Tre, Via della Vasca Navale 84, 00146 Roma, Italy
[6]DCCI, Università degli Studi di Genova, Via Dodecaneso, 31, 16146 Genova, Italy
miran.baricic@u-paris.fr

Cobalt (II) oxide (CoO) is a vastly studied material for its catalytic, electrochemical, and magnetic properties[1]–[3]. Several colloidal chemistry methods are routinely employed to synthesize nanostructured phases with size and morphology control; among them, the one-pot polyol method stands out among the others for using green solvents and being easily scalable[4].

CoO polyol synthesis is typically performed in DEG and at a fixed hydrolysis ratio ($h = [H_2O]/[Co^{2+}] = 46$), where it forms ~ 100 nm aggregates made of ~ 5 nm primary nanoparticles (NPs) with partial crystal alignment[5], [6]. However, careful temperature control (180° C) is required to ensure CoO formation, since lower temperatures form just a layered hydroxide (LH) intermediate, while higher ones bring to the formation of carbides in massive quantities[4], thus preventing any temperature control on the result; also the hydrolysis ratio has to be sufficiently high, otherwise the reaction is not triggered by temperature.

In our study, we systematically investigated the influence of temperature, hydrolysis ratio and polyol solvent length (di-, tri-, tetra- and polyethylene glycol), controlling the result with XRD, HR-TEM and EELS techniques. As a result, we found that proper solvent choice allows to get rid of the traditional synthesis limitations and extend its feasibility to much higher temperatures (250°C and possibly up to the solvent boiling point) and lower h (down to 7), which both proved to be effective tools to tune the aggregates sizes (20-150 nm), shapes (spherical and octahedral) and XRD crystal domain lengths (5 to 35 nm).

Furthermore, good synthetic conditions were found to avoid the formation of ferromagnetic LH phases, resolving several ambiguities present in literature about CoO low temperature magnetic behaviour. Finally, the Néel temperature (T_N) of CoO was also recognized in the zero-field cooled (ZFC) curves, and a regular variation with XRD crystal domain lengths was observed, allowing us to tune T_N over a range of 80 K, making this chemical approach interesting for magnetic applications[7].

[1] L. Liao *et al.*, *Nat. Nanotechnol.*, **2014** , *9*, 69–73,
[2] K. Park en A. M. Kolpak, *J. Catal.*, **2018** , *365*, 115–124,
[3] P. M. Sarte, S. D. Wilson, J. P. Attfield, en C. Stock, *J. Phys. Condens. Matter*, **2020** .
[4] F. Fiévet *et al.*, *Chem. Soc. Rev.*, **2018** , *47*, 5187–5233,
[5] T. Gaudisson *et al.*, *CrystEngComm*, **2021** , *23*, 1756–1764,
[6] L. Poul, *et al.*, *Solid State Sci.*, **2001** , *3*, 31–42,
[7] N. Flores-Martinez *et al.*, *Part. Part. Syst. Charact.*, **2018** , *35*, 1–8,

Distinctive properties of Patch Halloysite Nanotubes: NMR study of water confinement and rheological behavior

Calvino M.M.[1], Topgaard D.[2], Cavallaro G. [1], Lazzara G. [1], Milioto S. [1]
[1]Dipartimento di Fisica e Chimica "Emilio Segrè", Università degli Studi di Palermo, Viale delle Scienze, pad. 17, 90128, Palermo, Italy
[2]Division of Physical Chemistry, Chemistry Department, Lund University, P.O. Box 124, Lund, 22100, Sweden.
martinamaria.calvino@unipa.it

Nanoclays, as halloysite nanotubes (HNTs) and kaolinite, have attracted significant attention due to their physico-chemical properties and widespread applications as natural materials in different fields. Among the different forms of halloysite, Patch halloysite exhibits distinct properties compared to conventional halloysite and kaolinite. In this study, we focused our research on kaolinite, as platy clay, and two types of halloysite nanotubes, as tubular clays, with different morphological, physical, and dispersibility properties: one with short and thick tubes (50−3000 nm length) and the Patch with longer and thinner tubes (200−30 000 nm length). On one side, we propose an investigation of the water confinement in these systems exploiting NMR techniques and focusing on the self-diffusion and transverse relaxation time (T2) of water. Various hydration levels were tested in the experiments, revealing the existence of distinct water populations within the analyzed systems. In this way, we highlighted that the morphology, of the nanoclays play an essential role in the aforementioned properties of water. On the other side, the rheological behavior of Patch was also investigated, proving that it gives rise to the formation of gels already at low concentrations that are not evidenced in other samples of halloysite. Specifically, flow ramp tests indicate that Patch is a non-Newtonian fluid and, depending on the concentration, we can also observe yield stress demonstrating the resistance of the sample structure to deformation or break.

Results indicate that the unique structure of Patch, compared to the other clays, influences both the rheological behavior and water diffusion and relaxation. These findings have implications for the development of new materials and applications of these clays in different fields.

Carbon-Polymer Dots as Optical Sensors for Sensing of Airborne Thiols

Paolo Corsaro[1], Nunzio Tuccitto[1], Stefania Vitale[2], Paolo Samorì[2]
[1] University of Catania, Italy
[2]Institute of Supramolecular Science and Engineering, University of Stransbourg
Presenter's e-mail address: Paolo.corsaro@phd.unict.it

We conducted a study to develop nanomaterials able to detect anthropogenic pollutants in the troposphere. We have focused on the detection of odorous compounds, thiols, which are commonly found in the air nearby oil and gas plants. We employed Carbon-Polymer Dots (CPDs) based on polyethylenimine as a detection medium. These CPDs are carbon-based nanoparticles that have a carbon core (likely aromatic) wrapped by an amine rich polymer shell. These exhibit fluorescent optical properties which allow them to be used as optical sensors. We are going to present the synthesis and complete characterization of CPDs. We demonstrated that the CPDs fluorescence can be quenched by Cu (II) solutions.

By adding to the solution sulphide compounds the fluorescence turns back ON because of the precipitation of the formed copper sulphides salt. We are going to report that the detection method is useful for both any high concentrations situation, typically present close to the pollution source, and even for lower concentrations experienced by a receptor placed far away from the source.

To detect airborne thiols, we transferred the analytes to the solution by bubbling the contaminated air sample. To achieve a proper transferring a basic pH of the receiving solution is need. We are going to report that the amine rich polymer shell of the synthetized CPDs allows the maintaining of Cu (II) in solution avoiding the hydroxide precipitation. So, allowing the Cu(II)-CPDs to be employed in the detection of airborne thiols. This method can then be used for environmental impact assessments, risk analyses, and emergency planning, ensuring the safety and well-being of workers and surrounding communities.

Solvatochromic Emission from the “Dark” Double-Exciton state of a Polyhalogenated Thiele Hydrocarbon: a joint quantum-chemical and experimental investigation

Yasi Dai[1], Angela Punzi[2], Carlo N. Dibenedetto[2,3], Ernesto Mesto[4], Emanuela Schingaro[4], Marinella Striccoli[3], Tobias Ullrich[5], Dirk M. Guldi[5], Fabrizia Negri[1], Gianluca M. Farinola[2], Davide Blasi[2]
[1]*Dipartimento di Chimica ‘Giacomo Ciamician’, Università di Bologna & INSTM, UdR Bologna, Via F. Selmi 2, 40126, Bologna, Italy*
[2]*Dipartimento di Chimica, Università degli Studi di Bari “Aldo Moro”, Via Orabona 4, 70125, Bari, Italy*
[3]*CNR-Istituto per i Processi chimico Fisici (CNR-IPCF), SS Bari, Via E. Orabona 4, 70125 – Bari, Italy*
[4]*Dipartimento di Scienze della Terra e Geoambientale, Università degli Studi di Bari “Aldo Moro”, Via E. Orabona 4, 70125, Bari, Italy*
[5]*Department of Chemistry and Pharmacy and Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander-University Erlangen-Nuremberg, 91058 Erlangen, Germany*
Presenter’s e-mail address: *yasi.dai2@unibo.it*

Recently there has been a considerable interest in the exploration of organic neutral radicals for various applications including optoelectronics [1]. Radical-based OLEDs can reach values of internal quantum efficiency of 100%[2], but two major unsolved problems affect these devices: a severe roll-off and a device lifetime of few minutes [1,3]. An alternative to free radicals, potentially capable to overcome these problems, is represented by luminescent diradicaloids. Here we present a computational investigation on the luminescence properties of the first example of an inert and photostable non-perchlorinated Thiele hydrocarbon (TTH) recently synthesized [4]. This molecule exhibits an intense solvatochromic emission with a large Stokes shift of ca. 0.66 eV. Diradicals have attracted considerable attention due to their potential applications in optoelectronic devices [5] and in singlet fission process [6]. A distinctive character of these molecules is to exhibit a dark low-lying double-exciton (**DE**) state dominated by the doubly excited H,H→L,L configuration [7]. The luminescence properties of TTH have been interpreted with quantum-chemical (QC) calculations demonstrating the key role of its moderate diradical character in determining the unconventional fluorescence properties. QC calculations have been carried out at DFT, TDDFT and with multi-reference multi-configurational approaches such as DFT/MRCI and CASSCF + NEVPT2. Specifically, the calculations suggest that a mixing of the bright state responsible for the absorption spectrum with the low-lying **DE** state, assisted by the twisting around one of the two (strongly elongated) exocyclic CC bonds of TTH, drives the formation of the emitting species which (because of state mixing) acquires a charge-separated character, accounting for the observed solvatochromism. Such charge separation occurs therefore with a mechanism similar to sudden polarization [8]. Interestingly, *fs* and *ns* transient absorption spectroscopy unambiguously show the involvement of two excited states and strongly support the twisting-induced mixing in the deactivation pathways of TTH, in excellent agreement with computational results. We believe that understanding the luminescence mechanism in TTH will contribute to design *p*QDM derivatives and related conjugated diradicaloids with increased luminescence efficiency.

[1] J. M. Hudson, et al. J. Appl. Phys. 129 (2021) 180901
[2] H. Guo, et al., Nat. Mater. 18 (2019) 977
[3] X. Ai, et al., Nature 563 (2018) 536
[4] A. Punzi, et al., *Submitted*
[5] (a) Y. Huang, et al., Polym. J. 50 (2018) 603; (b) X. Hu, et al., J. Mater. Chem. C 6 (2018) 11232.
[6] S. Lukman, et al., J. Am. Chem. Soc. 139, (2017) 18376
[7] (a) F. Negri, et al., in *Diradicaloids* (ed. J. Wu) (2022),145 (Jenny Stanford Publishing); (b) S. Canola et al., Phys. Chem. Chem. Phys. 20, (2018) 24227.
[8] M. Filatov, et al., J. Chem. Theory Comput. 17 (2021) 5123.

3D-printed geopolymer-hydrotalcite porous scaffolds for CO_2 capture at elevated temperatures

Marco D'Agostini[1], Margherita Cavallo[2], Natale Gabriele Porcaro[2], Francesca Bonino[2], Valentina Crocellà[2], Paolo Colombo[1,3], Giorgia Franchin[1]
[1]*Department of Industrial Engineering, University of Padova, Padova, Italy*
[2]*Department of Chemistry, NIS and INSTM Centres, University of Torino, Torino, Italy*
[3]*The Pennsylvania State University, Department of Materials Science and Engineering, University Park, PA USA*
Presenter's email address: marcolorenzo.dagostini@phd.unipd.it

Anthropogenic CO_2 emissions are primarily responsible for the greenhouse effect and their prompt limitation is essential in containing global warming to safer levels. Among the various mitigation techniques, post-combustion capture setups may be installed onto pre-existing industrial or power plants with minimal disruption to operation, showing obvious potential for CO_2 emission reduction from stationary sources. However, the high temperatures and low CO_2 concentrations of flue gases mandate the choice of sorbents with good selectivity and thermal stability, in addition to suitable performance at elevated temperatures which excludes common solid adsorbents such as zeolites and activated carbons. In contrast, layered double oxides (LDOs) obtained through the thermal activation of hydrotalcite and other layered double hydroxides (LDHs) were shown to readily adsorb CO_2 at temperatures as high as 500°C making them promising candidates for post-combustion carbon capture processes.

In this study, porous geopolymer-hydrotalcite composite scaffolds with 40wt% active phase were produced by Direct Ink Writing and evaluated for CO_2 adsorption at 300°C. Geopolymers are attractive matrix candidates for composite adsorbents due to their low cost and facile synthesis route, good mechanical properties and significant porosity which improves access to the active phase. Furthermore, they can act as adsorbents themselves due to their mesoporous nature and moderate Specific Surface Area (SSA). Sodium- and potassium-based geopolymers (NaGPs and KGPs respectively) were characterised individually in terms of their textural properties and CO_2 capacity in order to select suitable candidates for the matrix of the composite adsorbents. KGPs displayed superior SSA and performance overall, however during optimisation of the printing slurry they were found to require the use of organic additives to obtain a stable dispersion of the hydrotalcite filler.

The composites were tested for CO_2 adsorption at 300°C after thermal activation at 400°C to induce the LDH-LDO transformation in the hydrotalcite active phase. Both NaGP- and KGP-based composites showed higher CO_2 capacity compared to the expected value for 40wt% hydrotalcite, indicating that the geopolymer matrices assume simultaneous structural and functional roles in the composites. The organic fraction in KGP-hydrotalcite composites could not be completely removed by heat treatment and resulted in a significant performance loss compared to the entirely inorganic NaGP-hydrotalcite formulation; moreover, the latter displayed substantially better mechanical properties. Scaffolds printed with finer struts were found to expose a larger geometric contact area resulting in higher performance, while simultaneously allowing for a better load distribution and mechanical strength. Regeneration strategies were evaluated in order to obtain a stable performance throughout several CO_2 adsorption cycles.

Effect of dopant concentration in ITO nanoparticles: a Solid-State NMR study

Elisa Della Latta[1], Francesca Martini[1,2], Silvia Borsacchi[3,2], Alessio Gabbani[1], Ananthakrishnan Mohan[1], Fabio Scattareggia Marchese Di Giovanni[1], Francesco Pineider[1], Marco Geppi[1,2]
[1]*Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Giuseppe Moruzzi 13, 56123 Pisa, Italy*
[2]*CISUP, Centro per l'Integrazione della Strumentazione dell'Università di Pisa, Lungarno Pacinotti 43, I-56126, Pisa, Italy*
[3]*Istituto di Chimica dei Composti Organo Metallici, Consiglio Nazionale delle Ricerche (CNR-ICCOM), Via Giuseppe Moruzzi, 1, 56124, Pisa, Italy*

In last decades, nanomaterials have attracted particular interest thanks to their potential application in many different fields, such as optoelectronics and sensing [1,2]. In particular, plasmonic nanoparticles have been subject of intense research due to their optical response when irradiated with light. Indeed, the electric field of light induces a coherent oscillation of conduction electrons, known as "Local Surface Plasmon Resonance" (LSPR), which leads to a strong absorption band typically in the UV-Vis – near IR (NIR) regions [3,4]. A sub-class of plasmonic nanocrystals is that of plasmonic degenerately doped *semiconductor* nanocrystals, where conduction electrons are generated by introducing aliovalent dopants. Among them, Tin-doped Indium Oxide (ITO) is an n-type semiconductor that shows a resonant peak in the NIR region, tunable by varying the content of dopant (Sn%) [2]. Understanding the structural and electronic properties of these complex plasmonic nanoparticles is an important but not an easy task, and Solid-State NMR (SSNMR) appears particularly attractive for this scope [5,6,7,8]. In this work, we present a SSNMR investigation on ITO nanoparticles stabilized with oleic acid, with increasing percentage of Sn. ^{119}Sn Cross Polarization (CP) and Direct Excitation (DE) spectra under Magic Angle Spinning (MAS) allowed us to investigate the effect of Sn content on the structural and electronic features of the nanoparticles. Further information about electronic properties of these systems was obtained by measuring ^{119}Sn spin-lattice relaxation times (T_1) at different temperatures.

[1] W. Seo et al. Adv. Mater. 15(2003) 795
[2] M. Kanehara et al. J. Am. Chem. Soc. 131 (2009) 17736
[3] H. Fang et al. Chem. Mater. 29 (2017) 4970
[4] I. Kriegel et al. Phys. Rep. 674 (2017) 1
[5] L. Casabianca Solid State Nucl. Magn. Reson. 107 (2020) 101664
[6] L. Marbella Nano Lett. 17 (2017) 2414
[7] Y. Avadhut Phys. Chem. Chem. Phys. 14 (2012) 11610
[8] G. Strouse J. Phys. Chem. C 124 (2020) 28220

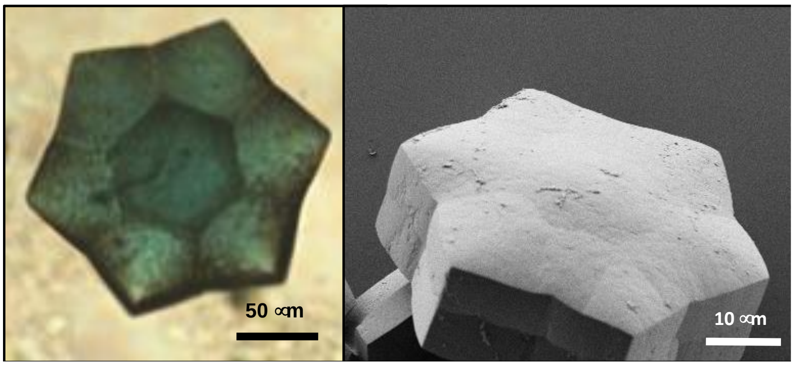
Crystallographic–Morphological Paradoxes in Metal–Organic Frameworks

Maria Chiara di Gregorio[1], Vivek Singh[2], Linda J. W. Shimon[3], Michal Lahav[2], Milko E. van der Boom[2]
[1]Department of Chemistry, Sapienza University, Rome 00185, Italy
[2]Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Rehovot 7610001, Israel
[3]Department of Chemical Research Support, Weizmann Institute of Science, Rehovot 7610001, Israel
mariachiara.digregorio@uniroma1.it

The symmetry of a crystal's morphology usually reflects the symmetry of the crystallographic packing. For single-crystals, the space and point groups allow only a limited number of mathematical descriptions of the morphology (forms), all of which are convex polyhedrons. In contrast, multidomain appearance and concave polyhedrons are hallmarks of polycrystallinity and twinning and are inconsistent with single crystallinity. [1]

Here we report a metal organic- framework with a new type of structure: a concave stellated polyhedron single crystal having a multidomain appearance and a rare space group (*P*622)(Figure).[2-4]

Despite these contradictions, it is puzzling that the symmetry of these crystals is linked at different hierarchies, from the molecular to the microscopic levels. They exhibit a deceptive combination of the three characteristics that define a crystal at different length scales: the unit cell, the organization of these unit cells, and morphology. The structural properties of this system are intrinsic, as no other materials (additives) were used to shape the facets. The unusual concave morphology of the crystals can be a direct consequence of the open molecular packing often found in metal-organic frameworks. This fact has not been recognized before in these and other porous materials. Such crystals offer new opportunities for the formation of 3D objects where the physical properties can be designed and predicted based on the point group symmetry.



.

[1] T. Hahn International Tables for Crystallography, 5th rev. ed.; Kluwer Academic: Dordrecht, 2002.
[2] M. C. di Gregorio et al. J. Am. Chem. Soc., 144 (2022) 22838
[3] M. C. di Gregorio et al. Nat. Commun. 11 (2020) 380
[4] M. C. di Gregorio et al. Nat. Commun. 12 (2021) 957

Thermal analysis and calorimetry to fingerprint the oxidative behaviour of oils in paint films.

Celia Duce[1], Silvia Pizzimenti[1], Giulia Caroti[1], Luca Bernazzani[1], Maria Rosaria Tné[1], Ilaria Bonaduce[1]
[1]*Department of Chemistry and Industrial Chemistry, University of Pisa, Via Giuseppe Moruzzi 13, I-56124, Pisa, Italy*

Lipids, when exposed to atmospheric oxygen, are subject to a complex series of reactions that may evolve toward two main competitive pathways: oxidative degradation, resulting in the formation of polar species, including volatile compounds (such as short chain carboxylic acids, aldehydes, and ketones), and cross-linking, resulting in the formation of higher molecular weight species. [1]
All these reactions occur simultaneously during the air drying of an oil paint The prevalence of one reaction over the other is influenced by the presence of pigments, dryers, and additives in the paint layer and it determines the molecular composition of the paint film and, consequently, its stability, hydrophobicity, polar nature, and durability. [1]
The molecular characterization of a paint film is a very complex task, due to its insolubility, and often its molecular analysis is argued from the analysis of the unpolymerized fraction of the oil binder.
Our idea is to study the degree of cross-linking/oxidationtaking place in the oil binder (such as linseed oil and safflower oil) during the early stage of a paint curing and how and how much the presence of historically and artistically relevant inorganic pigments (i. e. lead white [2], synthetic ultramarine blue [2], carbon black, [3] and cadmium red) or the presence of a co -binder can modify it [4]. The results obtained can be used to suggest the final composition of a fully cured paint network. [3]
This communication aims at discussing the main information that can be obtained on the chemistry of the oil paint curing by means of a methodological approach based on thermogravimetric analysis (TG), differential scanning calorimetry (DSC), and analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS).

[1] I. Bonaduce, et al .Acc. Chem. Res., 52 (2019) 3397-3406
[2] S. Pizzimenti et al. ACS Appl. Polym. Mater3, 4 (2021) 1912–1922
[3] S. Pizzimenti et al. J. Therm. Anal. Calorim. 147, (2022) 5451
[4] O. Ranquet et al. Nature Communications | (2023) 14:1534

Silica-cyclodextrin hybrid materials

Marta Gallo[1], Luigi Manna[1], Mauro Banchero[1], Silvia Ronchetti[1], Barbara Onida[1]
[1]*Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129 Torino, Italy*
marta.gallo@polito.it

Porous silicas and cyclodextrins (CDs) are known for their properties and widely studied as promising supports on one hand for adsorption of pollutants in the environmental field and on the other hand for release of active principles in the pharmaceutical sector. With these premises, silica-CD hybrids could offer a synergic action of the two constituents representing an interesting support for both drug delivery and molecules adsorption. Indeed, in view of the removal of organic compounds, silica could stabilize the CDs without recurring to the currently used cross-linking procedure which is known to weaken the adsorption capacity of the CD cavity [1]. Similarly, for drug delivery purposes, silica could stabilize the drug-CD complex and, in case of topical drug release, would also give an added value since silicic acid has a beneficial effect for the skin [2].

In this perspective the present work aims at developing a hybrid material made of silica and cyclodextrin for the delivery of active principles on skin or the adsorption of pollutants.

A first kind of hybrid is obtained through a one-pot sol-gel synthesis in acid aqueous solution where the CD is used as a templating agent [3]. After preliminary tests, β-methyl-cyclodextrin (βMCD) is selected as the most promising CD for this purpose. The βMCD-silica hybrid obtained by sol-gel process is a bulk material containing a considerable amount of CD (around 45 wt.%) in amorphous form and represents, therefore, a promising support. However, since a high specific surface area is desirable for increasing the release/adsorption properties of the hybrid, an attempt is made to produce the hybrid material in form of aerogel. Different preliminary trials are done in order to optimize both the synthesis of the gel and its drying in super-critical carbon dioxide.

The obtained samples are characterized in terms of physico-chemical properties and microstructure (by means of infra-red spectroscopy, termogravimetry, X-ray diffraction electron microscopy) in order to investigate their composition and the interaction between the organic component (CD) and the inorganic one (silica).

[1] F. Amran et al., Front. Chem. Sci. Eng. 16 (2022) 1407
[2] C.D. Seaborn et al., Biol Trace Elem Res. 89 (2002) 251
[3] S. Polarz et al., Angew. Chem. Int. Ed. 40 (2001) 4417

Sustainable processing routes to development of new Eco-friendly Piezoceramics

Sebastiano Garroni[1], Marzia Mureddu[1], Maria Dore[1], Costantino Cau[1], Fabrizio Murgia[1], Gabriele Mulas[1], Stefano Enzo[1], Antonio Iacomini[2], José F. Bartolomé[3], Sonia Lopez-Esteban[3], Álvaro García[3], and Lorena Pardo[3]
[1] Department of Chemical, Physical, Mathematical, and Natural Sciences, University of Sassari, Via Vienna 2, I-07100 Sassari, Italy.
[2] Electronic Ceramics Department, Jožef Stefan Institute, 1000 Ljubljana, Slovenia
10 point type, centered, italicized
[3]Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas (CSIC), c/ Sor Juana Inés de la Cruz, 3, Cantoblanco, 28049 Madrid, Spain
Presenter’s e-mail address: sgarroni@uniss.it

Piezoelectric materials are a key technology for a wide range of industrial and consumer products, including applications on actuators, ultrasonic motors, transformers, micro-energy harvesting devices, hydrophones, high resolution ultrasonic medical imaging, and accelerometers in mobile phones and notebooks. Lead zirconate titanate (PZT) based ceramics, due to their consolidate properties, are the dominant class of materials for manufacturing piezoelectric devices. However, the replacement of lead-base piezoceramics is nowadays mandatory because the PZT fabrications require the use of lead oxide (PbO), a high toxic and hazardous material [1]. Therefore, tremendous efforts are necessary for the development of competitive ecological, lead-free, piezoelectric material with properties comparable with PZT and transfer it to specific applications. In this context, promising lead-free candidates include Barium Titanate ($BaTiO_3$ (BT))-modified systems, such as $(Ba,Ca)(Zr,Ti)O_3$ (BCZT), which shows, at particular nominal compositions, higher piezoelectric performance than PZT. On the other hand, BCZT systems suffer of a relatively low Curie point ($\simeq$100°C) and severe synthesis (up to 1350°C) and sintering temperatures (up to 1500°C), making the whole processing not appealing for up scaling purpose [2, 3].

The present contribution aims at providing a short overview of the experimental attempts performed to reduce the synthesis and sintering temperatures and to deepen the insight into the fundamental mechanisms governing the formation of BCZT. Starting from a new representative examples of mechanical activations combined with thermal treatments approaches, it is shown that optimal electromechanical properties (d33 = 455 pC/N, kp = 35%, Qm = 155) can be achieved while the synthesis (<900 °C) and sintering temperatures (<1300°C) were drastically reduced [4]. The potential of these new routes for the fabrication of ecological lead-free piezoceramics, and some of the related challenges, are also briefly discussed.

[1] Eu-Directive 2002/96/Ec: Waste electrical and electronic equipment (WEEE). Off J Eur Union 2003, 46: 24-38.
[2] Y. Saito et al., Lead-free piezoceramics. Nature 2004; 432:84-7.
[3] Villafuerte-Castrejón, M.E.; Morán, E.; Reyes-Montero, A.; Vivar-Ocampo, R.; Peña-Jiménez, J.A.; Rea-López, S.O.; Pardo, L. Towards Lead-Free Piezoceramics: Facing a Synthesis Challenge. Materials 2016, 9, 21. https://doi.org/10.3390/ma9010021.
[4] Mureddu. M. et al.; Solid State Processing of BCZT Piezoceramics Using Ultra Low Synthesis and Sintering Temperatures, Materials 2023, 16(3), 945.

Abstract ID. T1O13

Ag nanoparticles decorated reduced graphene oxide based hybrid nanocomposites for textile coatings with superior antibacterial characteristics

A. Grandolfo[1,2], G. Mandriota[2], I. De Pasquale[2], G. V. Bianco[3], E. Fanizza[4], R. Comparelli[2], M. Striccoli[2], M. L. Curri[2,4], C. Ingrosso[2]
1) Dept. of Electrical and Information Engineering, Polytechnic of Bari, Bari, Italy
2) CNR-IPCF c/o Dept. of Chemistry, University of Bari, Bari, Italy
3) CNR-NANOTEC, c/o Dept. of Chemistry, University of Bari, Bari, Italy
4) Dept. of Chemistry, University of Bari, Bari, Italy
*adriana.grandolfo@poliba.it

The application of nanostructures in manufacturing of textiles featuring specific properties (i.e. flame retardancy, thermal and electrical conductivity, self-cleaning, antimicrobial) [1], has been recently attracting increasing attention both for fundamental studies and textile industry applications, where the ability of conveying functionalities to traditional fabrics may fulfil specific technological needs and issues of textile industry. Hybrid nanocomposites based on graphene (G) and inorganic nanoparticles (NPs) have demonstrated exceptional interest for this technology purpose due to their enhanced functionalities resulting from the merging of the intrinsic chemical and physical properties of the two components [1]. G is a carbon scaffold with high chemical reactivity, thermal and electrical conductivity and (electro)catalytic activity. Inorganic NPs present unique size dependent properties and their high surface-active area that amplifies their potential with respect to bulk traditional additives and materials [1]. In this work, original hybrid nanocomposites based on a G derivative, Reduced Graphene Oxide (RGO) have been decorated by plasmonic Ag NPs by means of a facile *in situ* colloidal approach carried out in aqueous solution[2]. At first, RGO has been exfoliated and functionalized with histidine (His), a biocompatible aromatic linker capable to bind both RGO, via π-π interactions, and the Ag NPs through coordination bonds. The Ag NPs have ben synthesized on His-RGO from aqueous solutions by reduction of silver nitrate ($AgNO_3$) with sodium citrate ($C_6H_5O_7Na_3$) and sodium borohydride ($NaBH_4$). The exfoliation and functionalization of RGO have been performed in His solutions, systematically investigating the effect of relevant experimental parameters, as RGO:$AgNO_3$ w/w, $AgNO_3$:$C_6H_5O_7Na_3$ and $NaBH_4$:$C_6H_5O_7Na_3$ molar ratio and pH was systematically investigated by tuning on the characteristic of the final product. The spectroscopic and morphologic characteristics of the obtained nanocomposites have been comprehensively investigated by means of UV-Vis absorption and Raman spectroscopy, TEM and SEM-EDS in order to assess the synthetic path and thus control the characteristics of the final product, in terms of Ag NPs size distribution and coating density. The obtained His-RGO/Au NPs nanocomposites have demonstrated high colloidal stability in aqueous medium. In particular, the nanocomposite formed of His-RGO sheets decorated by a dense layer of monodisperse spherical Ag NPs, ca. 24 ± 4 nm in size, with a Localized Surface Plasmon Resonance absorption at 366 nm has been considered, due to the narrow NPs size distribution and high RGO coverage, for the further antimicrobial test. The antimicrobial activity of this His-RGO/Ag NPs nanocomposite, deposited by impregnation on cotton fabrics, has been assessed by following the standard EN ISO 20743:2021 protocol showed a superior antibacterial activity against *Escherichia coli*.

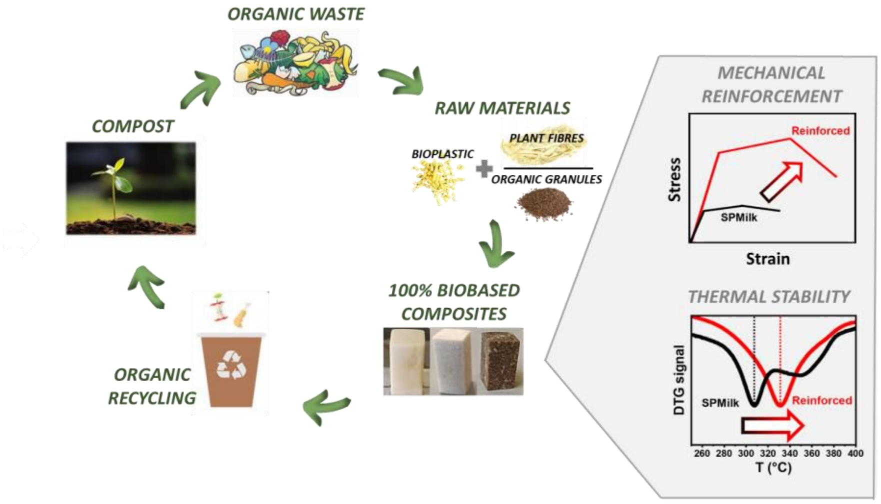
Acknowledgments: the work has been partially supported by TRANSISTOR Project (BRIC 2019 ID:33) and Italian PON Ricerca e Innovazione (2014-2020) ECOTEC (ARS 01_00951) project.

---

[1] P. J. Rivero et al. Nanoscale Research Letters (2015) 10: 501
[2] Ingrosso, C.; et al. Carbon (2021) 182, 57-69

From dairy product waste to plastic: preparation and characterization of new fully biobased composite materials

Raffaella Lettieri[1,2], Veronica Fazio[1], Donato Abruzzese[3], Elisabetta Di Bartolomeo[1], Cadia D'Ottavi[1], Andrea Micheletti[3], Alessandro Tiero[3], Leonardo Duranti[1], Valentina Armuzza[2], Silvia Licoccia[1,4], Emanuela Gatto[1,2]
[1]University of Rome Tor Vergata Department of Chemical Science and Technologies, Via della Ricerca Scientifica, 00133 Rome (Italy)
[2]Splastica Srl, Via della Ricerca Scientifica, 00133 Rome (Italy)
[3]University of Rome Tor Vergata Department of Civil and Computer Science Engineering, Via del Politecnico, 1, 00133 Rome (Italy)
[4]NAST Centre for Nanoscience, Nanotechnology and Instrumentation, University of Rome Tor Vergata Physics Department, Via della Ricerca Scientifica, 00133 Rome (Italy).
raffaella.lettieri@uniroma2.it

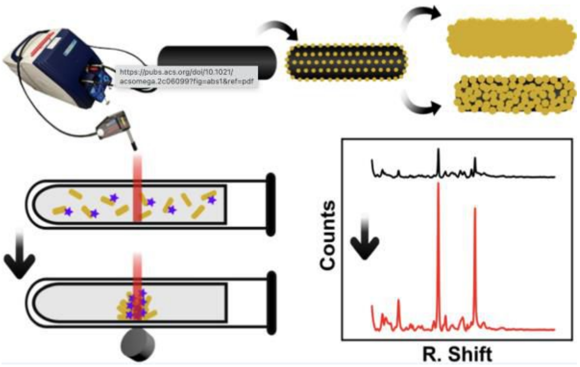


Organic waste is a virtually unlimited and inexpensive source of raw materials and represents a powerful matrix for the development of biobased materials due to the abundance of important biomolecules. This study investigates the influence of the addition of different organic-based additives on the physical-mechanical properties of a new biomass-derived material. The investigated samples are made of a bulk innovative biomaterial named SP-milk® that is a 100% biobased, biodegradable and compostable material produced from dairy waste by Splastica®srl through a sustainable process. Plant fibres and inert organic particulate were used to improve the material characteristics. Compression and flexural tests were performed to study the mechanical characteristics. The addition of short randomly orientated fibres increases flexibility with a slight improvement in hardening resistance obtained with the higher percentage tested (1 wt%). Longer fibres led to a more effective reinforcement as a result of the effect of residual resistances. The addition of 20 wt% inert granules gave a harder and more resistant material, although with concomitant loss of ductility. The combination of fibres and granules resulted in the preservation of the positive effects of both components. The surface morphology was examined by scanning electron microscopy, focusing on the failure zones after flexural tests. Thermal analysis demonstrated the improved thermal stability of the composites with respect to the parent matrix. The results obtained here demonstrate that the use of suitable natural reinforcement agents is effective in improving a biobased and biodegradable material while preserving its sustainability.

Magnetic-Plasmonic Fe_3O_4@Au Nanorods for Surface-Enhanced Raman Scattering Analysis of Antibiotics in Water

Leixuri B. Berganza, Lucio Litti, Moreno Meneghetti, Senentxu Lanceros-Méndez, and Javier Reguera
[1] *BCMaterials, Basque Center for Materials, Applications, and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain*
[2] *Department of Chemical Sciences, University of Padova, 35131 Padova, Italy*
lucio.litti@unipd.it

Surface-enhanced Raman scattering (SERS) has become a promising method for the detection of contaminants or biomolecules in aqueous media. The low interference of water, the unique spectral fingerprint, and the development of portable and handheld equipment for in situ measurements underpin its predominance among other spectroscopic techniques. Among the SERS nanoparticle substrates, those composed of plasmonic and magnetic components are prominent examples of versatility and efficiency. These substrates harness the ability to capture the target analyte, concentrate it, and generate unique hotspots for superior enhancement. Here, we have evaluated the use of gold-coated magnetite nanorods as a novel multifunctional magnetic−plasmonic SERS substrate. The nanostructures were synthesized starting from core-satellite structures. A series of variants with different degrees of Au coatings were then prepared by seed-mediated growth of gold, from core-satellite structures to core−shell with partial and complete shells. All of them were tested, using a portable Raman instrument, with the model molecule 4-mercaptobenzoic acid in colloidal suspension and after magnetic separation. Experimental results were compared with the boundary element method to establish the mechanism of Raman enhancement. The results show a quick magnetic separation of the nanoparticles and excellent Raman enhancement for all the nanoparticles both in dispersion and magnetically concentrated with limits of detection up to the nM range (~50 nM) and a quantitative calibration curve. The nanostructures were then tested for the sensing of the antibiotic ciprofloxacin, highly relevant in preventing antibiotic contaminants in water reservoirs and drug monitoring, showing that ciprofloxacin can be detected using a portable Raman instrument at a concentration as low as 100 nM in a few minutes, which makes it highly relevant in practical point-of-care devices and in situ use.



[1] Leixuri B. Berganza, Lucio Litti, Moreno Meneghetti, Senentxu Lanceros-Méndez, and Javier Reguera ACS Omega 7 (2022) 45493–45503

The enigmatic case of emissive hybrid manganese metal halides

Federico Locardi, Marta Campolucci, Chiara Maria Solinas, Maurizio Ferretti
Department of Chemistry and Industrial Chemistry, Università degli Studi di Genova, Via Dodecaneso 31, 16146 Genova, Italy
Presenter's e-mail address: federico.locardi@unige.it

Nowadays, metal halide perovskites are one of the most investigated materials for optoelectronic applications, with $CsPbBr_3$ that stands out for its high photoluminescence quantum yield, high carrier mobility and defects tolerance. Many studies have attempted to substitute the Pb^{2+} with other metals both for reducing the toxicity of lead and to explore new material properties. Besides the use of Sn^{2+} or the formation of double perovskites (*i.e.* two Pb^{2+} are replaced with a monovalent and a trivalent metal cation), a promising strategy involves the fabrication of metal halides with lower dimensionalities. In these structures, the metal-halides octahedra originally connected in a 3D structure in the perovskites are stacked along one, two or three crystallographic planes. This process is facilitated by the substitution of Cs^+ with an organic cation, leading to hybrid organic – inorganic materials. Recently, Mn^{2+} is emerged as promising candidates thank to its capability to coordinate halides both in an octahedra and tetrahedra coordination, inducing orange-red or green emission, respectively [1,2].

Here, we report our achievements in the preparation of hybrid Mn – based halides contain methylammonium ($CH_3NH_3^+$, MA), butyl ammonium ($C_4H_9NH_3^+$, BA) or benzyl ammonium ($C_6H_5CH_2NH_3^+$, BZ) in different crystals structures. By a careful modification of the organic cations and/or the synthesis conditions, it is possible to control the Mn^{2+} coordination and to obtain materials with a high green or red emission. Moreover, the X – ray diffraction analysis showed a reversible phase change around room temperature. This study confirms the great potential of the hybrid Mn halides as materials for optoelectronic applications; besides, the numerous stable phases that can form are still puzzling.

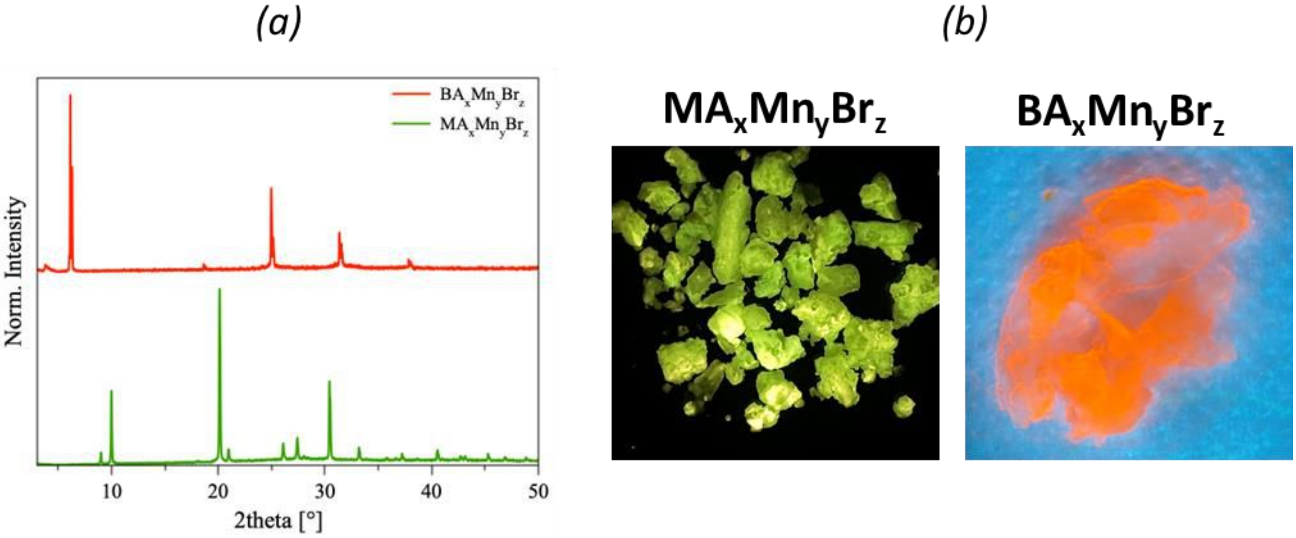


Figure. (a) XRD pattern and (b) photoemission under UV light of MA and BA hybrid manganese bromide

[1] H.B. Jalali et al. ACS Energy Lett. 7 (2022) 1850-1858
[2] K. Dave et al. Crystals 13 (2023) 499

Abstract ID. T1O17

Local dynamics in triptycene-based porous polymers by multi-nuclear and multi-technique solid-state NMR

Francesca Martini[1,2], Elisa Della Latta[1], Silvia Borsacchi[3,2], Molly C. Warndorf[4], Kayla R. Storme[4], Timothy M. Swager[4], Marco Geppi[1,2]
[1]*Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Giuseppe Moruzzi 13, 56123 Pisa*
[2]*CISUP, Centro per l'Integrazione della Strumentazione dell'Università di Pisa, Lungarno Pacinotti 43, I-56126, Pisa, Italy*
[3]*Istituto di Chimica dei Composti Organo Metallici, Consiglio Nazionale delle Ricerche (CNR-ICCOM), Via Giuseppe Moruzzi, 1, 56124, Pisa, Italy*
[4] *Department of Chemistry, Massachusetts Institute of Technology (MIT), Cambridge, Massachusetts 02139, United States*
Presenter's e-mail address: *francesca.martini@unipi.it*

Polymer-based membranes are object of a considerable research interest for many applications of key relevance to energy and the environment, including gas separation, sensing, energy storage and conversion technologies. In this frame, Polymers with Intrinsic Microporosity (PIMs) [1,2] have been assessed as promising materials for the development of energy efficient gas-separation membranes with high CO_2 permeability and selectivity [3,4], even if critical limitations, such as the trade-off between permeability and selectivity, plasticization, and physical aging, still need to be overcome [5]. The characterization of the structural and dynamic properties at the molecular and supramolecular level is of upmost importance to understand the origin of the final properties of these polymers, and to shed light on the gas adsorption and transport mechanisms. Indeed, such a knowledge is crucial for the development of materials with improved and optimized performances. To this end, solid-state NMR spectroscopy (ssNMR) provides a wide variety of tools able to disclose information on structure and dynamics on wide ranges of spatial lengths and motion time scales [6]. In this work, a multi-nuclear and multi-technique ssNMR approach has been used to characterize the local structure and dynamics of PIMs constituted by benzo-triptycene structural units and perfluorinated biphenyl linkers (Figure 1a). Selective information on the dynamics of t-butyl, triptycene and biphenyl moieties have been obtained by the combined analysis of ^{1}H, ^{19}F and ^{13}C spin-lattice relaxation times (T_1) recorded at different Larmor frequencies and at variable temperatures (Figure 1b). The analysis of ^{2}H static spectra of a sample deuterated on the t-Butyl groups has also been performed. The presence of fast motions with characteristic frequencies in the MHz regime involving the perfluorinated biphenyl linkers and the t-Butyl groups has been detected, while the triptycene unit seems to be frozen in the investigated time scale.

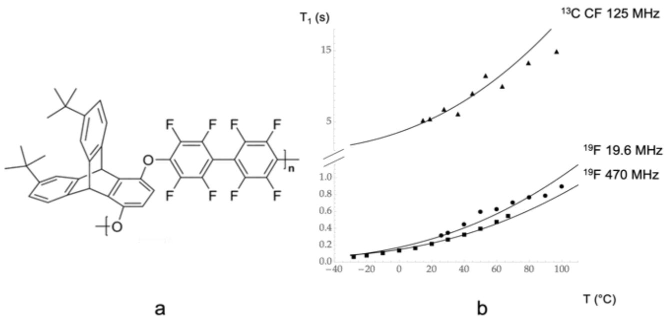


Figure SEQ Figure * ARABIC 1 (a) Structure of the investigated PIM. (b) Analysis of the variable temperature ^{19}F and ^{13}C T_1 data.

[1] P.M. Budd et al. Adv. Mater. 16 (2004) 456
[2] T. M. Long et al. Adv. Mater. 13 (2001) 601
[3] A. Fuoco et al. ACS Appl. Mater. Interfaces 10 (2018) 36475
[4] N. B. McKeown Polymer 202 (2020) 122736
[5] Z.-X. Low et al. Chem. Rev. 118 (2018) 5871
[6] M. Geppi et al. App. Spectrosc. Rev. 44 (2008) 1

Structure and reactivity of bismuth vanadate-water interfaces

Giacomo Melani[1], Wennie Wang[1,2], Chenyu Zhou[3], Mingzhao Liu[3], Kyoung-Shin Choi[4], Giulia Galli[1,5,6]
[1]Pritzker School of Molecular Engineering, University of Chicago, IL, USA
[2]McKetta Department of Chemical Engineering, University of Texas-Austin, TX, USA
[3]Center for Functional Nanomaterials, Brookhaven National Laboratory, NY, USA
[4]Department of Chemistry, University of Wisconsin-Madison, WI, USA
[5]Department of Chemistry, University of Chicago, IL, USA
[6]Materials Science Division, Argonne National Laboratory, IL, USA
giacomomelani@uchicago.edu

Bismuth vanadate (BVO) is a promising photoanode for photoelectrochemical cells, due to its tunable band gap (~2.4 – 2.6 eV), favorable alignment of its valence band with the water oxidation potential, stability in aqueous environments, and its relative easiness of preparation [1]. In a recent study [2], we showed that tuning surface termination/composition and hence surface energetics is critical to improve the efficiency of the oxygen evolution reaction (OER) [2]. In addition, we highlighted [3] the importance of surface defects in altering the reactivity of BVO toward water, concomitant to water modifications to the electronic structure of the photoanode. However, a complete atomistic description of the interface between defective facets of BVO and water is not yet available, and yet it is necessary for the optimization of the OER efficiency. Here we carry out first principles molecular dynamics simulations with the Qbox code (http://qboxcode.org/) of BVO-water interfaces with different composition, as well as measurements of the electronic (XPS) and vibrational (IRRAS) spectra of water-covered BVO thin films. We combine theoretical and experimental results on spectra and computed electronic properties to characterize the interplay between surface hydroxylation and metal oxidation states at the surface, and to understand their impact on surface reactivity.

[1] T. W. Kim and K.-S. Choi, Science (2014).
[2] D. Lee, W. Wang et al. Nat. Energy 2020
[3] W. Wang et al. J. Am. Chem. Soc., 2022.

Synthesis of maghemite nanoparticles by self-combustion: the atmosphere effect

Jean Pierre Miranda Murillo[1], Alexander Omelyanchik[2], Diego Colombara[1] and Davide Peddis[1-3]
[1]Department of Chemistry and Industrial Chemistry & INSTM , University of Genova, nM2-Lab, 16146 Genova
[2]Immanuel Kant Baltic Federal University, 236041 Kaliningrad, Russia
[3]Institute of Structure of Matter, National Research Council, nM2-Lab, Via Salaria km 29.300, Monterotondo Scalo 00015, Roma, Italy
Jeanpierre.mirandamurillo@edu.unige.it

Generally, the sol-gel self-combustion method is a facile, inexpensive, and green synthetic approach, enabling to obtain the desired nanostructured oxide with a high degree of homogeneity and purity [1]. Iron oxide features two main allotropic phases with different magnetic nature: the antiferromagnetic hematite α-Fe_2O_3 and ferrimagnetic maghemite γ-Fe_2O_3 [2]. This communication illustrates the effect of the reaction atmosphere on the formation of these magnetic phases. Here, a thick gel of Fe(III)-citrate(III) network, is turned into crystalline powder in (**A**) air atmosphere or in (**B**) a closed line of Argon flow. The X-Ray Powder Diffraction (XRPD) shows the typical pattern of hematite (**A**) or the cubic reflexes of the tetragonal γ-Fe_2O_3 (**B**). The magnetic saturation M_s of 2.1 Am^2kg^{-1} (**A**) and 70 Am^2kg^{-1} (**B**) are ascribed to traces of γ-Fe_2O_3 for sample (**A**) and a total presence of γ-Fe_2O_3 for sample (**B**), respectively.

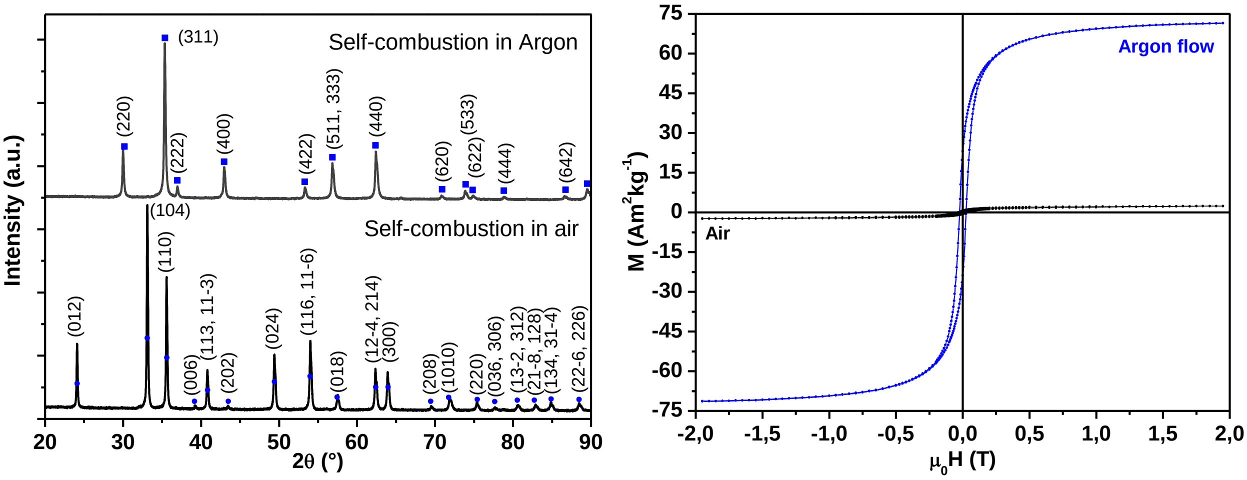


Figure 1. Left, XRPD pattern of the sample **A** (bottom, α-Fe_2O_3, $R\underline{3}ch$) and **B** (top, γ-Fe_2O_3, $P4_12_12$). Right, hysteresis loop of sample **A** and **B**.

[1] Danks et al., Mater. Horizons 3 (2016) 91-112
[2] J. M. D. Coey, Magnetism and Magnetic Materials (2010)

"Preparation and characterization of PET (Polyethylene terephthalate) nanoparticles by using Hexafluoro Isopropanol: Chloroform (1:1)"

Muhammad Mudassir, Andrea Salina, Raffaella Lettieri, Mariano Venanzi, Cadia D'Ottavi, Elisabetta Di Bartolomeo, Emanuela Gatto
Department of Chemical Science and Technologies, University of Rome Tor Vergata, Rome, Italy
viking_md@hotmail.com

Nano- and microplastic toxicology has appealing global consideration. As a matter of fact, the plastic materials are disposed in the environment and degrade by releasing micro- and nano plastic, which are very dangerous, due to their potential to penetrate biological membranes. In order to perform toxicological studies on human cells, it is necessary to produce particles with nanometric dimension, which can be hardly extracted and characterized from environmental matrices. [1,2] In this work, we have produced PET nanoparticles from commercial grade PET resin, by grinding the PET pellets and dissolving the powder in a solution of hexafluoro isopropanol: chloroform (1:1)v/v. By using this feasible method, PET nanoparticles have been characterized by UV-Vis absorption, optical microscopy (bright field), scan electron microscopy (SEM) and dynamic light scattering (DLS). Furthermore, PET fluorescence properties have also been characterized by spectrofluorometric techniques.

This approach demonstrates a simple and easy way for producing PET nanoparticles, which can be very useful for analyzing the cell toxicity of this kind of plastics. We also showed that spectroscopic techniques can be easily applied for the evaluation and quantification of PET nano- and microparticles in environmental samples.

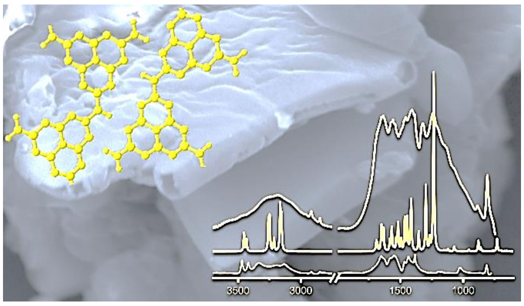
[1]-Rodríguez-Hernández, A. G.; Muñoz-Tabares, J. A.; Aguilar-Guzmán, J. C.; Vazquez-Duhalt, R. A novel and simple method for polyethylene terephthalate (PET) nanoparticle production. Environmental Science: Nano. 2019, 6(7), 2031-2036. DOI:org/10.1039/C9EN00365G

[2]-Li, Y.; Wang, Z.; Guan, B. Separation and identification of nanoplastics in tap water. Environmental Research.2022, 204, 112134. DOI:org/10.1016/j.envres.2021.112134

New insight into structure, optical and vibrational properties of g-C_3N_4 as building block for innovative architectures.

Paolo Negro[1], Federico Cesano[1], Silvia Casassa[1], Domenica Scarano[1]
[1]*Department of Chemistry and NIS (Nanostructured Interfaces and Surfaces) Interdepartmental Centre, University of Torino & INSTM-UdR Torino, Via P. Giuria 7, 10125 Torino, Italy*
pa.negro@unito.it

Graphitic carbon nitride (g-C_3N_4), a polymeric metal-free semiconductor, has been considered a challenging material, due to its thermal and chemical stability, non-toxicity, tunable band gap and visible light activity, but also due to its environmentally friendly and sustainable properties. Hence, it comes out that widespread applications, including degradation of dye pollutants, photocatalysis for hydrogen production, carbon dioxide reduction, water splitting, solar light-driven photo-redox catalysis, photoelectric conversion as well fuel cells have been developed [1] However, concerning the *g*-C_3N_4 photocatalytic activity, some drawbacks are worthy of mention, including the high recombination rate of the photoinduced electron–hole pairs, the chemical inertness itself, the poor charge carrier mobility, the low specific surface area. To overcome the aforementioned drawbacks, g-C_3N_4/g-C_3N_4 or g-C_3N_4/graphene metal-free homojunctions, or heterojunctions made by coupling *g*-C_3N_4 with metals or other semiconductors have been developed, aiming at improving the surface properties, the surface area, *etc.,* then the charge separation at the interfaces and the increased lifetime of photoinduced charge carriers [2]. Concerning this, it is well known that the peculiar properties of g-C_3N_4/g-C_3N_4 homojunctions or g-C_3N_4 /semiconductor heterojunctions depend strongly on the synthesis processes, which are affecting condensation degree, stacking order, formation of defects, as well as the band gap junctions. Despide the many efforts focused either on experimental (*i.e.* neutron and X-ray diffraction patterns) and on computational approaches, which predict amazing properties and applications, the complex structure of g-C_3N_4 systems is still a matter of a controversial debate. Along this theme, our aim was to give some insights into the more proper and stable configurations of the g-C_3N_4 polymerized structures, by combining the results obtained from X-ray diffraction patterns, UV-visible and FTIR spectra with the Density Functional Theory (DFT) calculations, using the CRYSTAL code [3]. This approach allowed us to highlight a mixture of highly condensed g-C_3N_4 domains embedded in a less condensed "melon-like" framework [4], as a starting point to develop more complex heterostructures. Therefore, in this contribution preliminary results on g-C_3N_4/g-C_3N_4 isotype junctions and on a case study g-C_3N_4 / TiO_2 heterojunction will be described, with the aim to highlight the role of morphology, structure, surface and bulk properties on the photocatalytic performance.



[1] Thomas, A.; Fischer, A.; Goettmann, F.; Antonietti, M.; Müller, J.-O.; Schlögl, R.; Carlsson, J. M., *Journal of Materials Chemistry* 2008, *18* (41), 4893-4908

[2] Akhundi, A.; Zaker Moshfegh, A.; Habibi-Yangjeh, A.; Sillanpää, M.,. *ACS ES&T Engineering* 2022**,** *2* (4), 564-585.

[3] Erba, A; Desmarais, J.K.; Casassa, S.; Civalleri, B.; Donà, L.; Bush, I. J.; Searle, V.; Maschio, L.; Daga, L.-E.; Cossard, A.; Ribaldone, C.; Ascrizzi, E.; Marana, N. L.; Flament, J.-P.; Kirtman, B., *J. Chem. Theory Comput.* 2022. https://doi.org/10.1021/acs.jctc.2c00958.

[4] Negro P., Cesano F., Casassa S., Scarano D., *under publication on Materials 2023.*

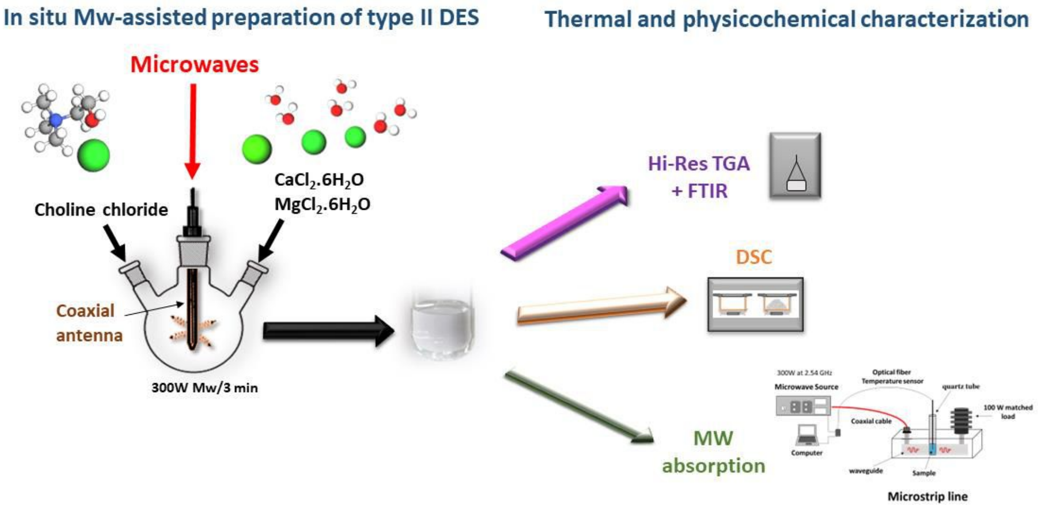
Insights into the microwave-assisted preparation and physicochemical characterization of type-II Deep Eutectic Solvents

Chiara Pelosi,[1] Celia Duce,[1,2] José Gonzalez-Rivera,[2] Maria Rosaria Tinè, [1,2] Gianluca Ciancaleoni,[1] Luca Bernazzani.[1]

[1]Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via G. Moruzzi 13, 56124, Pisa, Italy.
[2]National Institute of Optics (INO-CNR) Pisa, Via G. Moruzzi 1, 56124 Pisa, Italy.
chiara.pelosi@unipi.it

Deep Eutectic Solvents (DESs) are a versatile and green class of mixtures formed by two or more compounds linked by a strong hydrogen or halogen bond network, with a melting point strongly lower respect to their precursors [1]. They have attracted a lot of interest in the recent years due to their green features (they usually have low toxicity, low vapor pressure, low flammability), the ease of preparation, their inexpensiveness, and the wide range of applications in which they can be used. For example, they can be used for the trapping of CO_2, for extraction processes from biomasses, as solvents/catalyst of reactions and many others [2].

Here, we present the preparation of type-II DESs made by choline chloride and calcium (or magnesium) hydrated chloride using a coaxial microwave antenna as an energy- and time-saving method to heat the precursors. After the preparation, we analyzed extensively the thermal and physicochemical properties of the samples, in order to obtain more information for their applicability and on the sample nanostructure. More in detail, the density, viscosity, and conductivity of the samples at different temperatures were measured, and their thermal degradation and thermal properties were evaluated by thermogravimetry coupled with FTIR spectroscopy and Differential Scanning Calorimetry. The addition of water as cosolvent, and its effect on the system properties, was also evaluated.



[1] Martins, M. A. R.; Pinho, S. P.; Coutinho, J. A. P. *J. Solution Chem.* **2019**, *48* (7), 962–982.
[2] Smith, E. L.; Abbott, A. P.; Ryder, K. S. *Chem. Rev.* **2014**, *114* (21), 11060–11082.

Improving the thermoelectric performance of Fe/Ni-based skutterudite by multi-filling

Cecilia Piscino[1,*], *Pietro Manfrinetti*[1,2], *Nadia Parodi*[1], *Roberto Spotorno*[1], *Carlo Fanciulli*[3], *Ketan Lohani*[4], *Paolo Scardi*[4], *Cristina Artini*[1,5]
[1] *DCCI, University of Genova, Via Dodecaneso 31, 16146 Genova Italy*
[2] *SPIN-CNR, Corso Perrone 24, 16152 Genova, Italy*
[3] *CNR-ICMATE, Via Previati 1/E, 23900 Lecco, Italy*
[4] *DICAM, University of Trento, Via Mesiano 77, 38123 Trento, Italy*
[5] *CNR-ICMATE, Via De Marini 6, 16149 Genova, Italy*
**cecilia.piscino@edu.unige.it*

Due to the growing demand for energy in recent decades, the search for materials and devices capable of providing sustainable energy has become the focus of many studies. Particularly, in the field of energy recovery, thermoelectricity represents a useful technology to harvest waste heat.

In order to maximize the conversion of thermal into electric energy, thermoelectric devices need materials that comply the Phonon Glass Electron Crystal concept. This latter describes a good thermoelectric material as one with low thermal but high electric conductivities.

Among the different classes of thermoelectric materials, filled skutterudites (Fig. 1) with general formula $REyM_4X_{12}$ (RE ≡ rare earth, M ≡ transition metal, X ≡ pnicogen atom), if properly designed, can show the desired features to be used in this field [1]. In particular, by multifilling the cavities of the structure, or by doping the skutterudite crystallographic sites, lattice disorder can be increased, thus decreasing the phonon thermal conductivity.

Multifilling was attempted with Sm, Nd and La, while Sn was chosen to partly substitute Sb. The project is focused on several Fe/Ni-based systems with growing complexity and it entailed the synthesis of samples through the conventional melting-quenching-annealing technique and their crystallographic and thermoelectric characterization.

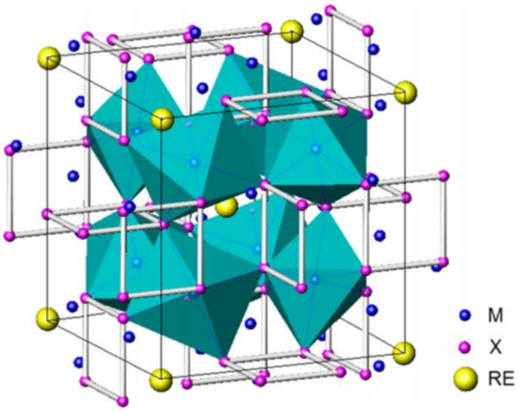


Figure 1. Crystal structure of a generic filled skutterudite [2]

[1] C. Artini, R. Carlini, R. Spotorno, F. Failamani, T. Mori, and P. Mele, "Structural properties and thermoelectric performance of the double-filled skutterudite $(Sm,Gd)_y(Fe_xNi_{1-x})_4Sb_{12}$," *Materials*, vol. 12, no. 15, Aug. 2019, doi: 10.3390/ma12152451.

[2] C. Artini, G. Zanicchi, G. A. Costa, M. M. Carnasciali, C. Fanciulli, and R. Carlini, "Correlations between Structural and Electronic Properties in the Filled Skutterudite $Sm_y(Fe_xNi_{1-x})_4Sb_{12}$," *Inorg. Chem.*, vol. 55, no. 5, pp. 2574–2583, Mar. 2016, doi: 10.1021/acs.inorgchem.5b02932.

Halides perovskites nanocrystals synthesized in *green* solvents

Davide Pratolongo[1,2], *Lorenzo Pugliesi*[1], *Sophia Victoria Ochoa Meza*[1], *Marta Campolucci*[1], *Chiara Lambruschini*[1], *Barbara Benedetti*[1], *Maurizio Ferretti*[1], *Federico Locardi*[1]
[1]Departement of Chemistry and Industrial Chemistry, Università degli studi di Genova, Via Dodecaneso 31, 16146 Genova, Italy
[2]Electron Microscopy Facility, Istituto Italiano di Tecnologia, Via Morego 30, Genova 16163, Italy
davide.pratolongo@edu .unige.it

Metal halide perovskites nanocrystals (MHP NCs) are really promising material due to their exceptional optoelectronic properties which could be controlled by the tuning of the shape (cubes, rods, platelets) and the thickness (monolayer, bilayers, etc.). Even if several syntheses could be performed to obtain MHP NCs, the best in term of shape and size control is the Hot Injection method (HInj)[1] (Figure 1, a). This procedure consists in a quick injection of one or more reactive into a solution of all the other ones at a definite temperature (usually between 100°C and 250°C). The reaction starts with a sudden nucleation followed by a growth step. The reaction finishes with a quench by a temperature-lowering[2,3]. Traditionally, HInj is performed in non-polar, high boiling point solvent such as 1-octadecene (ODE), decane, dioctyl ether (DOE), diphenyl ether etc. In this work, we report how is possible to use *green* solvents with high boiling point and dielectric constant similar to the aforementioned solvent to obtain MHP NCs retaining the optical properties. Limonene and α-pinene are being employed instead of ODE, DOE or decane as solvent in perovskites nanocrystal synthesis (Figure 1, b and c) both lead-based (*e.g.* $CsPbBr_3$) and lead-free (*e.g.* $Cs_2AgInCl_6$).

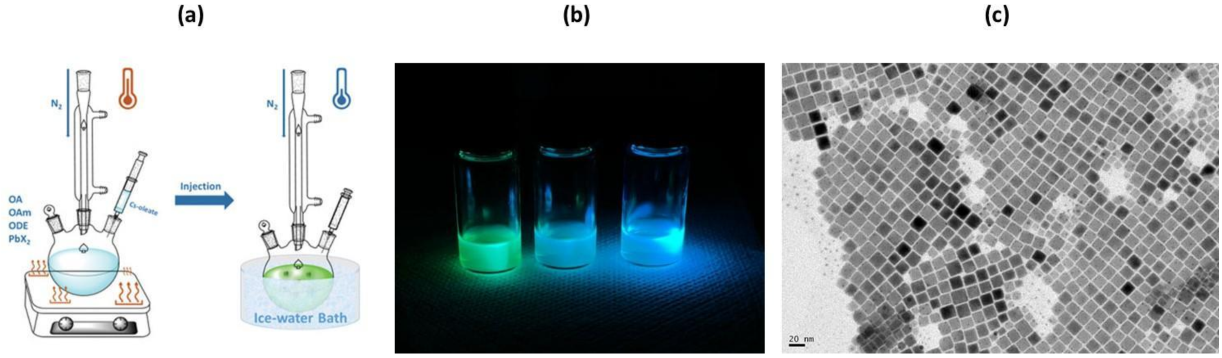


Figure 1: a) schematic illustration of HI method[3], b) luminescence and c) TEM image of NC synthetized in green solvent

[1] A. Dey et al. ACS Nano 2021, 15, 7, 10775–10981
[2] G. Li et al. Elsevier: 2019; 305-341.
[3] Y. Bai et al. Adv. Mater. 34 (2022) 2105958

Copper-binder complexes characterization in verdigris pigment by CW-EPR and ESEEM spectroscopies

Riccardo Punis[1] and Alfonso Zoleo[1]
[1]Dipartimento di Scienze Chimiche, Università degli Studi di Padova
riccardo.punis@phd.unipd.it

Copper pigments, especially the verdigris (copper acetate), have been known to be degradation-prone for many centuries. Therefore, the characterization of the species involved into the degradation processes is very relevant, but, so far, a comprehensive work has never been done. EPR spectroscopy is very sensitive towards the Cu(II) chemical surrounding, providing insights into the structure of Cu(II) complexes, and it has been proved efficient in detecting and identifying Cu(II) species from copper pigments [1,2]. The copper acetate is a bimetallic complex in which Cu(II) ions are bridged by four carboxylate ligands. Once the pigment is mixed with a binder (linseed oil, arabic gum, egg tempera, etc.), a clear monomeric complex signal arise in the EPR spectra, suggesting that the ligand has "extracted" the copper ions from the copper acetate complex breaking it. By plotting the $g_{//}$ vs. $A_{//}$ determined with the simulations, the number and the nature of the binding atoms of the monomeric complexes can be established [3]. This differentiation allows distinguishing oleaginous media from proteinaceous ones. Moreover, it is possible to evaluate the "extraction efficiency" of different binders by estimating the relative amount of the residual dimer and the monomer signals. Different EPR-pulse methods are also available. We performed ESEEM (Electron Spin Echo Envelope Modulation) experiments on the linseed oil – verdigris mock-up systems in order to obtain further information about the structure of complexes, combing the spectral data with theoretical calculations. It emerges that the unpaired electron is coupled with hydrogen and carbon as expected. It is shown that a combination of CW-EPR and pulsed EPR experiments is likely the best way to obtain information about pigment-ligand Cu(II) complexes in ancient materials.

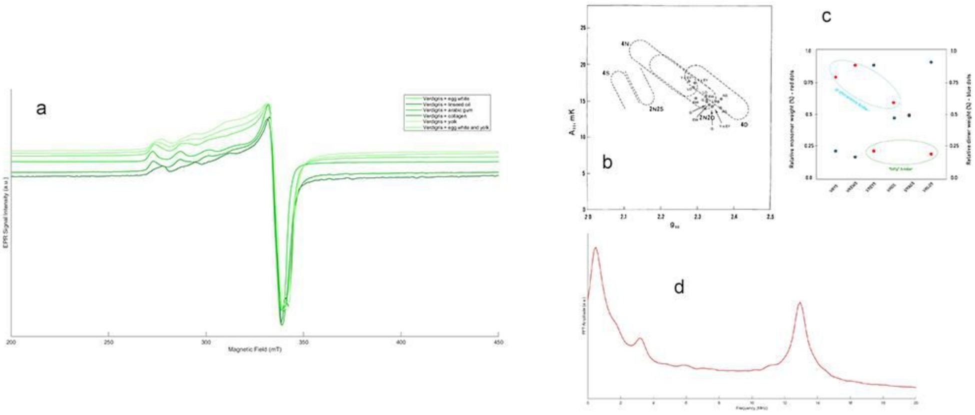


Figure SEQ Figure * ARABIC 1: CW-EPR spectra of verdigris-binder mixtures, b) Peisach-Blumberg diagram, c) Dimer-monomer relative weights and d) ESEEM spectrum of verdigris and linseed oil mixture.

[1] A. Zoleo et al. Archaeom. 56(3) (2015) 496-512
[2] M. Alter et al. Ino. Chem. 58(16) (2019) 13115-13128
[3] J. Peisach et al. Arch. Biochem. Biophys. 165(2) (1974) 691-708

Plasmonic nanoparticles as the scattering medium in colloidal random dye lasers

Luca Salemi[1], Marcello Condorelli[1], and Giuseppe Compagnini[1]
[1]Department of Chemistry, University of Catania, Viale Andrea Doria, 6, 95125 Catania (CT)
luca.salemi@phd.unict.it

Plasmonic nanoparticles as the scattering medium in random lasers have been first demonstrated in 2005 by Dice and coworkers [1], proving favorable in comparison to dielectric particles due to two effects: a much higher scattering cross-section (i.e. per particle or per unit volume), and potential unspecified plasmonic enhancement effects in the near field of the nanoparticles. The two mechanisms have been partially tested by Popov et al. [2] using Au nanospheres of varying diameter embedded in a dye-polymer film, explaining all the observations by the scattering only. Further literature has explored the effect of various different plasmonic nanoparticles and system geometry, proving both coherent and incoherent random lasing [3,4]. However, since the localized plasmons are highly sensitive to details in the nanoparticles' size and shape and to the surrounding environment, to get a meaningful comparison of different materials and shapes one has to handle the plasmonic system with great care. For instance, an inappropriate choice of material properties, or reshaping of anisotropic particles under the pump laser, may lead to a large difference between calculated scattering cross-sections and the actual experiment. In this work, we study the random lasing properties of Rhodamine 6G solutions with plasmonic nanoparticles, and attempt to carefully characterize the emission in relation to the properties of the plasmonic colloid, such as resonance wavelength, scattering cross section and efficiency, and electric field enhancement. To do so, we synthesize various plasmonic nanoparticles using a combination of chemical growth and pulsed laser techniques, characterizing the colloids experimentally and with numerical simulations. The R6G-plasmonic colloids are then placed in a quartz cuvette and pumped with a 532nm pulsed laser, and their emission spectra are recorded keeping the same configuration of the system across all experiments. The emission spectra are then acquired and the laser threshold and bandwidth are studied in relation to the characteristics of the plasmonic nanoparticles.

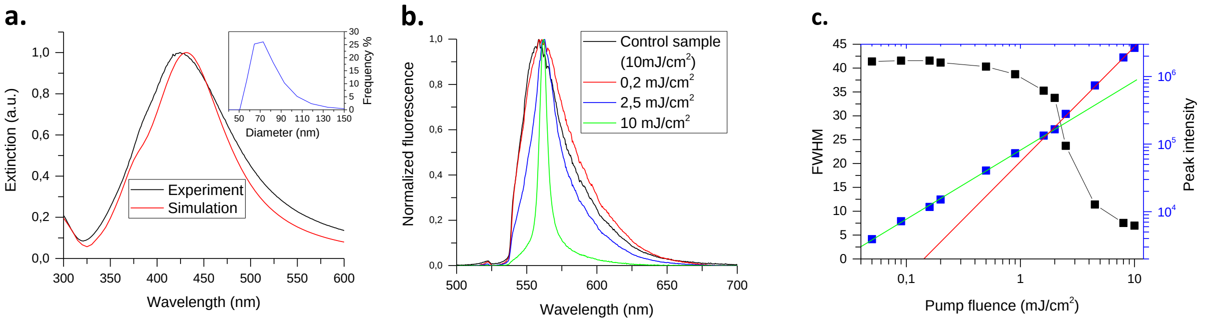


Figure 1: **a.** Experimental extinction spectrum and simulated extinction cross-section of Ag nanospheres of average diameter 70nm. The inset shows the DLS-measured size distribution. **b.** Normalized fluorescence spectra at various pump fluence, and **c.** bandwidth and peak intensity as a function of the pump fluence for the same Ag nanospheres suspended in a methanol solution of Rhodamine 6G 1mM. The control sample is the same solution without nanoparticles. Linear fits to the log-log plot of the peak intensity vs pump fluence are extended only to the points below (green) or above (red) threshold to aid visualization.

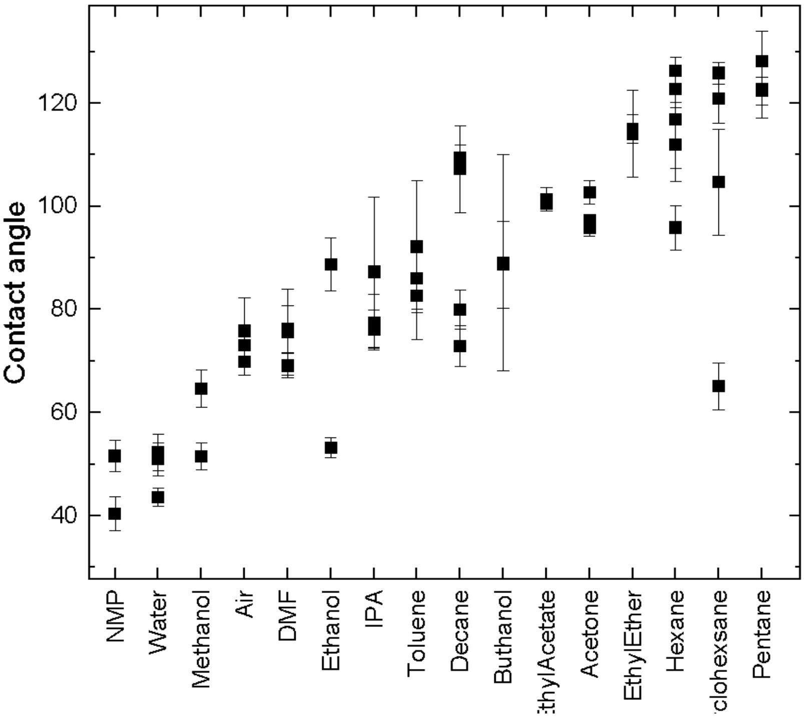
[1] G.D. Dice, S. Mujumdar, and A.Y. Elezzabi, Appl. Phys Lett. 86, 131105 (2005).
[2] O. Popov, A. Zilbershtein., and D. Davidov, Appl. Phys. Lett. 89, 191116 (2006)
[3] A.S.L. Gomes, A.L. Moura, C.B. de Araújo, and E.P. Raposo, Prog. Quantum Electron. 78, 100343 (2021)
[4] Z. Wang, X. Meng, A.V. Kildishev, A. Boltasseva, and V.M. Shalaev, Laser Photonics Rev. 11, 1700212 (2017).

Abstract ID. T1O27

Tuning Wettability of Graphene Oxide by Laser Induced Reduction in Liquids

Vittorio Scardaci[1], Giuseppe D'Arrigo[2], Guido Condorelli[1], Giuseppe Compagnini[1]
[1]*Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Catania, Italia*
[2]*CNR—Institute for Microsystems and Microelectronics, Catania, Italy*
vittorio.scardaci@unict.it

The ability to control the wettability of surfaces as well as their patterning is at the centre of technology development efforts due to the broad applicability of such type of surfaces in fields like self-cleaning surfaces, oil-water separation, microfluidics, to name a few. To achieve this, combinations of methods have been used, including lithography, plasma surface modifications, spray coating, and self assembly [1,2]. In this study, we report a method to both pattern and tune the wettability of a graphene oxide (GO) surface, from hydrophilic to hydrophobic. In this method, a GO film deposited onto a substrate is immersed into an organic solvent and patterned by laser scribing while in the liquid environment. The GO film, initially fully wetted by any solvent, is now reduced by the laser and can be characterized by contact angle measurements. In Figure 1 we can observe that by changing solvent we are able to continuously tune the contact angle of such surface, and thus its wettability. Further surface characterization includes Electron Microscopy, optical profilometry, Raman and FTIR spectroscopies and X-Ray Photoelectron Spectroscopy (XPS). We hypothesize that a combination of multiple factors determines the surface roughness of the surfaces, which in turn determines their wettability. Such factors may include solvent properties like boiling point, dipole moment, surface tension etc. and will be further investigated.



[1] S Y. Wang, et al., Small, 17, 2103322 (2021)
[2]] X. Gao, et al., Adv. Mater., 28, 168-173 (2016).

Morpho-Structural and Magnetic Properties of $CoFe_2O_4/SiO_2$ Nanocomposites: The Effect of the Molecular Coating

Sawssen Slimani[1,3*], Alessandro Talone[2,3], Maryam Abdolrahimi[2,3], Patrizia Imperatori[3], Gianni Barucca[4], Dino Fiorani[3], and Davide Peddis[1,3].
[1]Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, 1-16146 Genova, Italy.
[2]Dipartimento di Scienze, Università degli Studi 'Roma Tre', 00146 Roma, Italy.
[3]Istituto di Struttura della Materia-CNR, 00015 Monterotondo Scalo (RM), Italy.
[4]Dipartimento di Scienze e Ingegneria della Materia, dell'Ambiente ed Urbanistica-SIMAU, Università Politecnica delle Marche, 60131 Ancona, Italy.

Magnetic nanoparticles-based hybrid materials (MNP-HM) represent promising multifunctional systems with novel magnetic properties, due to interface effects, and superior performance in technological application[1,2]. In this framework, the design of a suitable synthetic approach represents a key point to obtain a MNP-HM with optimized physical properties. A key step in the synthesis of MNP-HM is definitively the molecular functionalization of MNP. Here, we report an investigation of the interparticle interactions by changing the molecular coating on $\sim$5 nm $CoFe_2O_4$ nanoparticles embedded in a silica structure. Cobalt ferrite-coated nanoparticles were prepared by the polyol method using triethylene glycol as a co-reagent (CFOT) and by the exchange ligand process using dihydroxyhydrocinnamic acid (CFOH). Then, magnetic mesoporous silica nanocomposites have been prepared starting from CFOT (CFOTS) and CFOH (CFOHS). The magnetic investigation at low temperature allows revealing the key role of organic ligands in tuning the morpho-structural properties of hybrid materials For the CFOTS sample, the interparticle distance did not change after coating, whereas the CFOHS sample showed an increase in the interparticle distance of 23%. This value has been obtained by investigating interparticle interactions by remanence techniques, which represent a good approach to determine the approximated values of interparticle distances in complex systems. The measurements showed that the silica coating produces a reduction of 47% in the dipolar interaction strength for the CFOHS sample, whereas no significant change was observed for the CFOTS sample. The differences in magnetic response upon varying the molecular coating of nanoparticles are due to the different interactions of the molecular ligands with silica, resulting in a change of interparticle distances and then magnetic interactions.

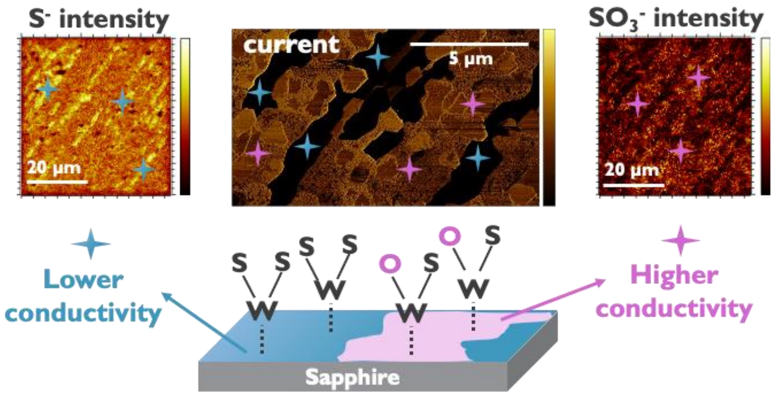
References

[1] Y. Piñeiro et al. Magnetochemistry. 6 (2020) 1–27.
[2] Y. Yang, et al. Mater. Today Adv. 17 (2023) 100338.

Correlated Intrinsic Electrical and Chemical Properties of Epitaxial WS_2 via Combined C-AFM and ToF-SIMS Characterization

Valentina Spampinato,[1,2] Yuanyuan Shi,[1,3] Jill Serron,[1] Albert Minj,[1] Benjamin Groven,[1] Thomas Hantschel,[1] Paul van der Heide[1] and Alexis Franquet[1]
[1]IMEC, Kapeldreef 75, 3001 Leuven, Belgium
[2]Università degli Studi di Catania, Dipartimento di Scienze Chimiche, Viale A. Doria 6, 95125 Catania, Italy
[3]School of Microelectronics, University of Science and Technology of China, Hefei, China
Valentina.spampinato@unict.it

2D transition metal dichalcogenides [1] are attracting great interest thanks to their atomic layer thickness, extraordinary (opto)electronic, chemical and thermal properties. However, it has become increasingly more difficult to characterize, chemically and electrically, this kind of materials and their interfaces. Indeed, conventional methodologies, including scanning probe microscopies, fail to capture insight in the chemical and electronic nature of the semiconductor, albeit vital to understand its impact on the semiconductor performance. Therefore, in this work, we present a unique and universal *in-situ* approach [2] to characterize thin WS_2 layers by combining time-of-flight secondary ion mass spectrometry (ToF-SIMS) and atomic force microscopy (AFM) in conductive mode. In this way it was possible to map chemical differences between regions of different electrical conductivity in the 2D material, thanks to the accurate chemical information achievable with ToF-SIMS combined with the atomic resolution attainable with AFM. Surprisingly, WS_2 regions of lower electrical conductivity possess a larger amount of sulfur compared to regions with higher conductivity, for which oxygen was also detected. Such difference in chemical composition likely roots from the non-homogeneously terminated sapphire starting surface, altering the WS_2 nucleation behavior and associated defect formation between neighboring sapphire terraces [3]. These resulting sapphire terrace-dependent doping effects in the WS_2 hamper its electrical conductivity. Thus, we demonstrated how accurate chemical assignment at sub-micrometer lateral resolution of atomically thin 2D semiconductors is vital to achieve a more detailed understanding on how the growth behavior affects the electrical properties.



WS_2 grown on sapphire with different surface terminations

[1] K. F. Mak et al. Nat. Photon. 10 (2016) 216
[2] V. Spampinato et al. Anal. Chem. 92 (2020) 11413
[3] Y. Shi et al. ACS Nano 15(6) (2021) 9482

Design, preparation and optical characterization of plexcitonic nanohybrids based on gold nanorods and J-aggregate of organic dyes

Federico Toffoletti[1], Fabrizio Mancin[1], Elisabetta Collini[1]
[1]*University of Padua, Department of Chemical Science, Via Marzolo 1*
Federico.toffoletti@studenti.unipd.it

The increasing ability to prepare systems with nanoscale resolution and address their optical properties with ultrashort time precision is revealing quantum phenomena with tremendous potential in quantum nanotechnologies.[1] Colloidal plexcitonic materials promise to play a pivotal role in this scenario.[2] Plexcitons are hybrid states originating from the mixing of the plasmon resonances of metal nanostructures with molecular excitons. They allow nanoscale confinement of electromagnetic fields and the establishment of strong couplings between light and matter, potentially giving rise to controllable and tunable coherent phenomena. However, the characterization of the ultrafast coherent and incoherent dynamics of colloidal plexciton nanohybrids remains highly unexplored. Therefore, in this work, plexcitonic nanohybrids based on organic dyes aggregated on gold nanorods' surface are designed, prepared, and characterized. Pump-Probe and 2D electronic spectroscopy are employed to explore in depth the ultrafast incoherent and coherent dynamics after photoexcitation of the uncoupled plasmonic systems and the plexcitonic nanohybrids. By comparing the response of the nanohybrids with the one of the uncoupled systems, the nonlinear photophysical processes at the base of the ultrafast dynamics were identified, allowing a step forward toward the effective understanding and exploitation of these nanomaterials.

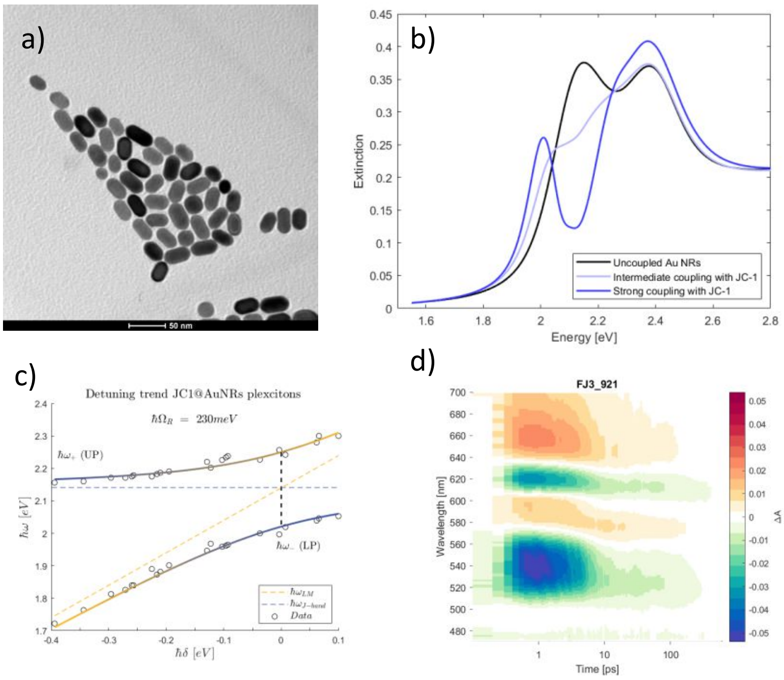


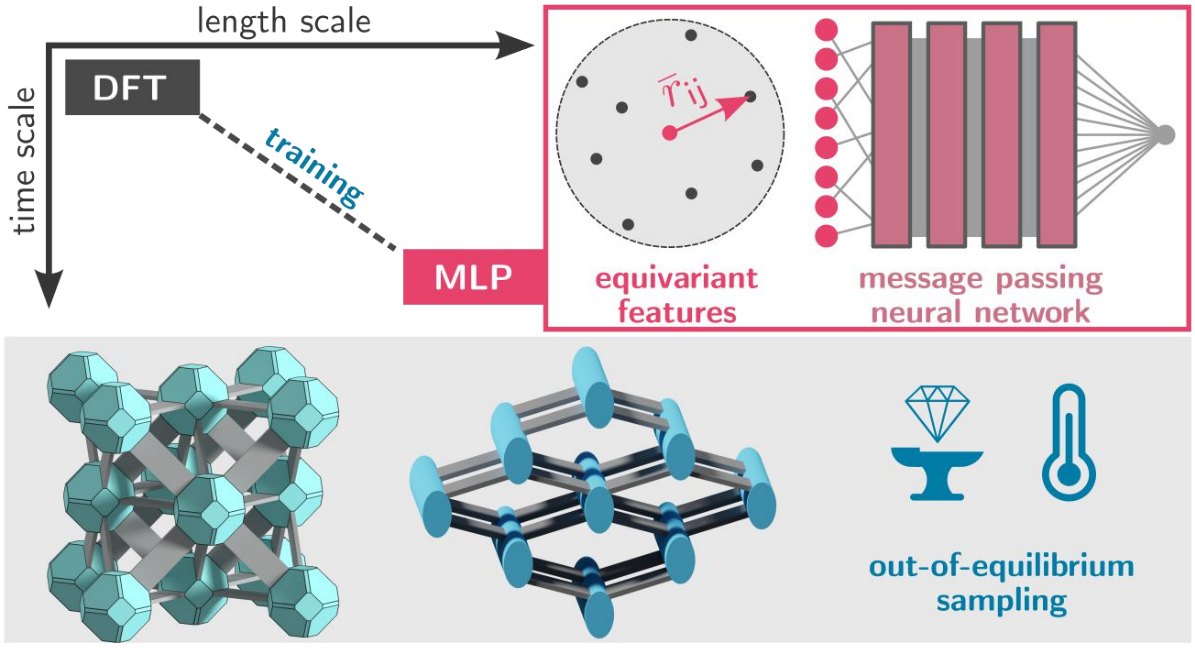
Figure 1 a) TEM image of gold nanorods. b) Extinction of bare gold nanorods before (black line) and after (blue lines) the addition of the dye. c) Detuning trend of upper and lower plexciton states obtained varying the plasmon resonance. d) Pump-Probe maps of the nanohybrid based on gold nanorods and JC-1 aggregates.

[1] N. Peruffo et al. J. Phys. Chem. Lett. (2022) 13, 28, 6412-6419
[2] N. Peruffo et al. Nanoscale (2021) 13, 6005-6015

Rare event sampling in nano-structured materials beyond standard DFT

Sander Vandenhaute[1], Pieter Dobbelaere[1], Tom Braeckevelt[1], Veronique Van Speybroeck[1]
[1]*Center for Molecular Modeling, Ghent University, Technologiepark 46, 9052 Zwijnaarde (Belgium)*
sander.vandenhaute@ugent.be

One of the biggest outstanding challenges in computational materials science relates to the ability to simulate and include both enthalpic as well as entropic contributions to the dynamics of activated processes in an accurate manner. The computational cost of highly accurate descriptions of the interatomic interactions has so far made it impossible to employ them in comprehensive enhanced sampling approaches. While machine-learned approximations to the interaction energy are becoming increasingly faster and more data-efficient [1, 2], their parameterization still depends on the availability of a large and diverse training set which includes the local atomic geometries encountered throughout the entire process. Efficient generation of this training dataset is highly nontrivial, especially when large free energy barriers are present. Here, we present a number of case studies in soft porous crystals (SPCs) and perovskite systems in which we exploit the efficacy of online learning to perform rare event sampling at an accuracy far beyond what is provided by 'standard' density functional theory (DFT) calculations within the generalized-gradient approximation [3]. Due to efficient parallelization and targeted enhanced sampling, the cost of parameterizing an accurate machine-learned interaction potential is greatly reduced, which gives us the ability to compute the quantum mechanical reference energy and forces in the training set at much higher accuracy (in this case with explicit inclusion of electron correlation using RPA or MP2). This greatly improves the predictive power of downstream inference of physical properties, such as relative phase stabilities, elastic moduli, or ion diffusion rates.



[1] S. Batzner et al. Nat. Commun. 13 (2022) 2453
[2] I. Batatia et al. NeurIPS 36 (2022)
[3] S. Vandenhaute et al. npj Comput. Mater. 9 (2023) 19

POSTERS

T1. PHYSICAL CHEMISTRY OF MATERIALS

Emissive 2D $(C_6H_5CH_2NH_3)_2(Pb,Mn)Br_4$ Hybrid Metal Halides

Marta Campolucci[1,2], Emanuela Sartori[1], Stefano Toso[2,3], Maurizio Ferretti[1], Liberato Manna[2], Zeger Hens[4], Federico Locardi[1,2]
[1]*Department of Chemistry and Industrial Chemistry, Università degli Studi di Genova, Via Dodecaneso 31, 16146 Genova, Italy*
[2]*Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy*
[3]*International Doctoral Program in Science, Università Cattolica del Sacro Cuore, 25121 Brescia, Italy*
[4]*Physics and Chemistry of Nanostructures group (PCN), Ghent University, Krijgslaan 281, Gent 9000, Belgium*
marta.campolucci@edu.unige.it

2D layered lead halide materials have recently gained attention having excellent emission comparable with the well-known 3D perovskites counterpart but with better electronic conductivity and quantum confinement effect observable even in the bulk materials [1]. In 2D structures, the A cation inserted in the 3D materials (traditionally Cs^+ or a small organic molecules) can be replaced by a multitude of bigger organic cations [2,3].

Here, we present our recent results on the preparation of emissive 2D (Pb,Mn)-based hybrid metal halide. Starting from the synthesis of Bz_2PbBr_4 ($Bz^+ = (C_6H_5CH_2NH_3)^+$), the Pb^{2+} was progressively replaced by Mn^{2+}. The XRF analyses demonstrated that the percentage of Pb substitution strongly depends on the metal ratio in the starting materials. The crystals morphologies are composition-dependent: Bz_2PbBr_4 crystallizes as white millimeter-sized layers, whereas an increase in the Mn amount causes the precipitation of a second phase with a needle shape, as also demonstrated by the XRD analyses. The presence of Bz cation in the structure is confirmed by FTIR analyses. The emission varies from the light blue of Bz_2PbBr_4 to the typical orange one of the Mn. The PL spectrum for the samples with intermediate compositions exhibits a weak emission for the excitonic peak at 410 nm and a strong Mn emission, centered at 610 nm, ascribable to the spin-forbidden Mn^{2+} d−d transition ($^4T_1 \rightarrow {}^6A_1$). The ABS and PLE spectra demonstrate an energy-transfer process from the Pb^{2+} to Mn^{2+} emitter, even at low Pb concentrations. The emission intensity reaches the maximum for the experimental Mn composition of 8.0% (PLQY » 47.9%).

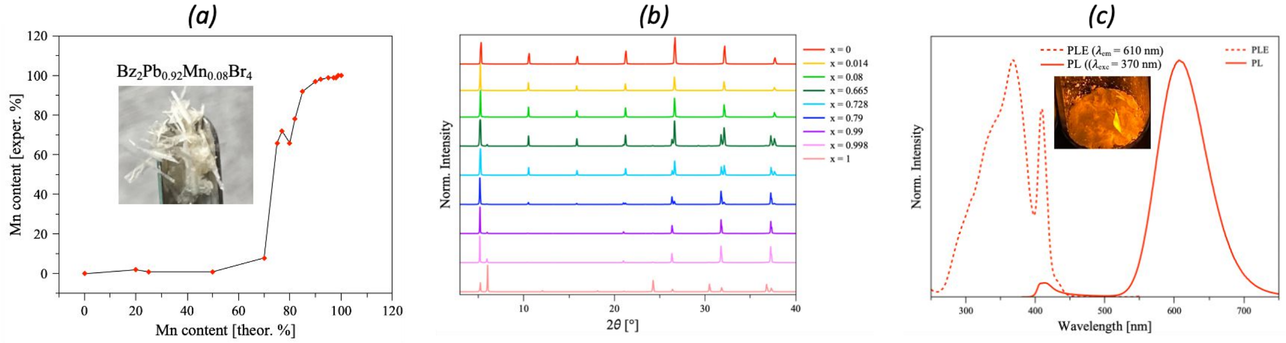


Figure 1: (a) XRF results, with the image of $Bz_2Pb_{0.92}Mn_{0.08}Br_4$ crystals, and (b) XRD patterns of $(C_6H_5CH_2NH_3)_2(Pb_{1-x}Mn_x)Br_4$ samples. (c) PLE and PL spectra, with the image under UV lamp (⍰ = 365 nm), of crystals' $Bz_2Pb_{0.92}Mn_{0.08}Br_4$.

[1] M. Jung Inorg. Chem. 58 (2019) 6748-6757

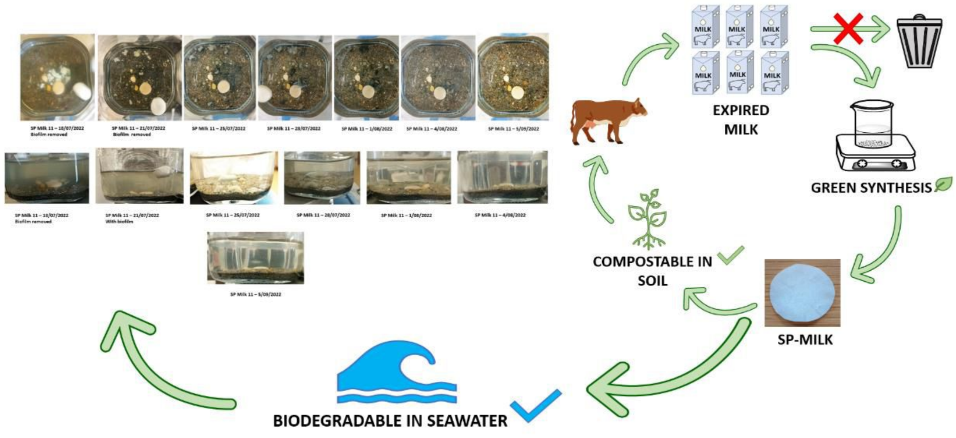
[2] Q. A. Akkerman ACS Energy Lett. 5 (2020) 604

[3] F. Meinardi et al. ACS Energy Lett. 2 (2017) 2368

Aerobic biodegradation at seawater-sediment interface of a compostable and food waste-based bioplastic.

Alice Caravella,[1] Raffaella Lettieri,[1,2] Rocco Vezza,[1] Emanuela Gatto[1,2]
[1] Department of Chemical Science and Technologies, Tor Vergata University, Via della Ricerca Scientifica 1, 00133, Rome Italy
[2] Splastica srl, spinoff of the University of Rome Tor Vergata, Via della Ricerca Scientifica 1, 00133, Rome Italy

Bioplastics are heterogeneous groups of material with multiple applications in different fields whose future production will increase more and more over the time. Currently their market presence in much lower than those conventional because of production costs. Bioplastics available nowadays are produced using 1st generation feedstock and they could generate ethical end environmental critical issues related to soil consumption not for human food production. Thus, efforts are made to develop these materials starting from waste, to increase their upstream sustainability reducing their production costs. [1] Another concern regard their compostability because they are not always compostable under home composting conditions. This causes the same injuries produced by the environmental dispersion of conventional plastics. Therefore, the present work was focused on the biodegradation in sea water of a bioplastic material produced By SPlastica srl ©, produced by expired milk and already tested for compostability according to EN 13432:2000. The experiment was carried out in aerobic and controlled laboratory conditions according to ISO 19679:2020 and [2] to simulate the biodegradation at sediment-water interface in sublittoral coastal zone. The bioplastic milk-based (SP-Milk) biodegradability was tested against positive control (filter paper), negative control (LDPE) and blank (seawater and sediment without any other material (blank). Its biodegradation percentage reaches, measuring the CO_2 developed, the 83.5% in just 52 days with respect to the endogenous respiration rate represented by the blank. Only few gelatinous-like residues of samples remained and were analyzed by optical microscope. The biodegradation data were supported by visual disappearance of the sample and by optical microscopy results that reveal an intense microorganism presence at water-SP Milk residues interface. To the best of our knowledge, comparable results were not obtained yet in a so tiny timeframe and represents a promising first result for further studies on ecotoxicological effects on marine biota.



[1] https://docs.european-bioplastics.org/publications/fs/EuBP_FS_Renewable_resources.pdf
[2] Briassoulis, Demetres & Pikasi, A. & Papardaki, N.G. & Mistriotis, Antonis. (2020). Aerobic biodegradation of bio-based plastics in the seawater/sediment interface (sublittoral) marine environment of the coastal zone – Test method under controlled laboratory conditions. Science of The Total Environment. 722. 137748. 10.1016/j.scitotenv.2020.137748.

Cd.ZnS photocatalytic activity in paintings: effect of structure, composition and particle size

Castagnotto Elena[1,2], Campolucci Marta[1], Locardi Federico[1], Ferretti Maurizio[1]
[1]Department of Chemistry and Industrial Chemistry (DCCI), Via Dodecaneso 31 16146, GE, Italy
[2]Swedish National Heritage Board, Artillerigatan 33A 62138, Visby, Sweden
elena.castagnotto@edu.unige.it

Cd.ZnS solid solutions are excellent photocatalyst materials and show tuneable efficiency: their performance can be influenced by the variation of morphology, stoichiometry, and micro crystal structure [1,2]. These compounds have been also employed as pigments in the art field since 1840s; unfortunately, the imperfection of earlier synthesis methods led to the commercialization of a variety of Cd/Zn sulphurs with great heterogeneities in the aforementioned characteristics. When employed by artists in combination with linseed oil, they resulted in a rather fast paint degradation, with every pigment presenting it's own peculiar conservation challenge [3]. In this study, a series of $Cd_xZn_{1-x}S$ nanocrystal solid solutions (x = 0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1) has been synthesized and characterized with the aim of studying and model their behaviour when employed with linseed oil in aged paint layers.

Initially, a synthesis method has been optimized in order to obtain compounds with controlled characteristic such as stoichiometry, crystal phase (cubic, hexagonal, amorphous or mixtures), and particle size. Powders have been characterized by means of X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and UV-Vis Reflectance Spectroscopy. To simulate, and accelerate, the ageing process that the paints may have undergone, oil-pigment thin films have been irradiated under a solar lamp for 8 weeks. The study of the effects of the various properties, especially structure, on the photocatalytic degradation of oil was carried out with a DoE model, using values extrapolated from Fourier-Transform Infrared Spectroscopy in Attenuated Total Reflectance (ATR-FTIR) spectra as a Response.

[1] Huang, H. B., Fang, Z. Bin, Yu, K., Lü, J. & Cao, R. Visible-light-driven photocatalytic H2 evolution over CdZnS nanocrystal solid solutions: Interplay of twin structures, sulfur vacancies and sacrificial agents. J. Mater. Chem. A 8, 3882–3891 (2020).
[2] Akyüz, D. & Koca, A. Photo-Induced Phase Transition of CdZnS Based Nanocomposite at Room Temperature Under Solar Irradiation. Catal. Letters 149, 876–881 (2019).
[3] Ghirardello, M. et al. Time-Resolved Photoluminescence Microscopy Combined with X-ray Analyses and Raman Spectroscopy Sheds Light on the Imperfect Synthesis of Historical Cadmium Pigments. Anal. Chem. 90, 10771–10779 (2018).

Pulsed Laser Deposition of solid electrolyte thin films for solid state microbatteries

A. De Bonis[1], M. Curcio[1], A. Galasso[1], A. Santagata[2], S. Brutti[3], A. Celeste[3], R. Teghil[1]
[1]Departmento of Science, University of Basilicata, Viale dell'Ateneo Lucano, 10, 85100 Potenza, Italy
[2]CNR-ISM, FemtoLAB, U.O.S. Tito Scalo, Zona Industriale, 85050 Tito Scalo, Italy
[3] Department of Chemistry, Sapienza University of Rome, p. le Aldo Moro 5, 00185 Roma (Italy)
Presenter's e-mail address: angela.debonis@unibas.it

The emerging needs for reliable and long-lasting energy storage systems require ventures beyond the classical Li-ion paradigm. Now the focus is primarily on safety, life, fast charging and high energy density. Lithium metal batteries with organic electrolyte solutions suffer of detrimental dendrite growth, on the other hand solid electrolytes help in suppressing the formation of dendrites thanks to their mechanical properties therefore they could be the ideal choice to develop safer, high energy density lithium metal batteries for those metals that are prone to dendrite formation.

Pulsed Laser Deposition (PLD) technique has been exploited to manufacture thin films of an advanced ceramic electrolyte based on mixed crystalline Li-La-Zr-Ta-oxides (LLZTO), starting from commercial precursors. The depositions were performed with a nanosecond laser source (Nd:YAG, 532nm, 10Hz, 7ns, 250 mW) and the deposition parameters (such as the substrate temperature and the pressure of the gas buffer) and nature of the substrate (silicon or metallic like stainless steel (SS), Al and Cu) were optimized to achieve careful control of the composition, crystallinity, morphology and growth rate of the produced mixed oxide.

The physicochemical characterization of the thin films was exploited by a multi-technique approach that includes several spectroscopies and microscopies (FTIR, micro-Raman, XRD, SEM, TEM).

The deposited LLZTO thin films will be tested as electrolyte for solid state microbatteries.

Exploring Persistent Luminescence in Halide Double Perovskites

Emmanuela Di Giorgio[1], Marta Campolucci [1,2], Sophia Ochoa Victoria Meza[1], Maurizio Ferretti[1], Federico Locardi[1,2]
[1] *Department of Chemistry and Industrial Chemistry, Università degli Studi di Genova Via Dodecaneso 31, 16146 Genova, Italy*
[2]*Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy*
emmanuela.digiorgio@outlook.it

Persistent Luminescence (PeL) is a peculiar type of luminescence in which a material, after a proper activation (by X-rays, electrons or ultraviolet/visible light), continues to emit radiation even for several hours once the excitation has ceased. The phenomenon of PeL is based on the existence of trap levels that can temporarily store excitation energy. PeL is well known in oxides generally doped with lanthanides ions [1]; yet, it has been also recently observed in halide-based perovskites compounds [2].

Here, we explore the influence of the synthesis conditions on the PeL behavior and the relationship with the particles size in halide double perovskites. $Cs_2NaInCl_6$:Mn^{2+} has been prepared in the form of single crystals, micrometric crystals and nanocrystals via a hydrothermal process, a reflux synthesis and a hot – injection method, respectively. The nominal Mn^{2+} percentage has been tuned according to the synthesis to obtain the longest PeL. The results showed that PeL lasts longer for micrometer materials (2500 s) than single crystals (1100 s) but disappears in nanocrystals (Figure 1a). This suggests the probable formation of trap defects that participate in the PeL mechanism in the micrometric particles, whose further increase quenches the luminescence in the nanocrystals. A similar effect has been also observed tuning the halides composition (Figure 1b).

This evidence highlights the potential of halide perovskites as a new class of persistent luminescence materials.

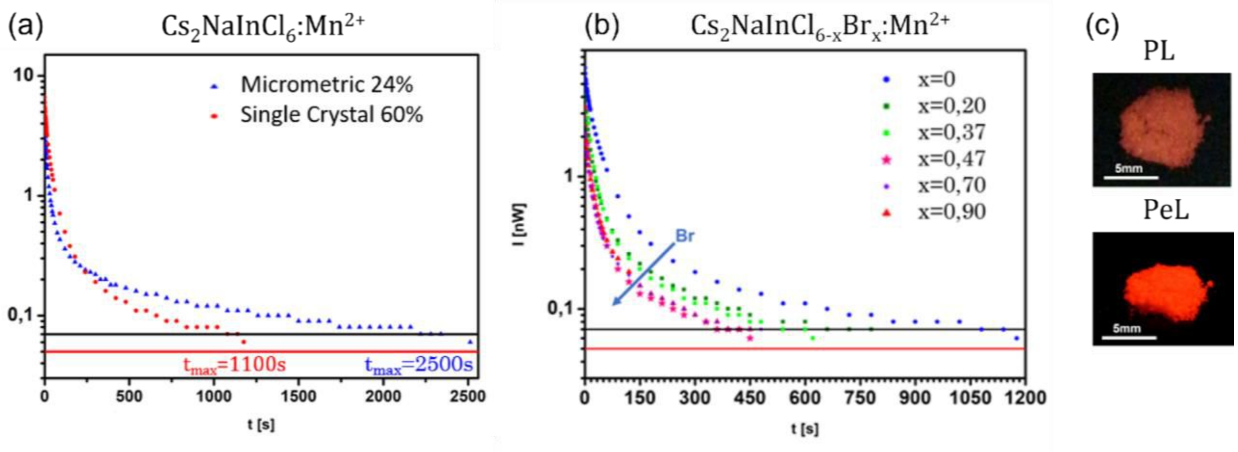


Figure 1. (a) PeL of longest-PeL micrometric and single crystal sample; (b) PeL of samples with halides composition tuning; (c) PL and PeL (after 30 seconds) photos of the longest-PeL sample.

[1] D. Poleman et al. J. Appl. Phys. 128 (2020) 240903
[2] X. Chen et al. J. Phys. Chem. Lett. 13 (2022) 8163–8168

Spectroscopic characterization of perovskite photoactive layers for PV applications: polaron formation and effects of reorientation for polyatomic cations

Danilo Dini[1], Valentina Carpenella[2], Claudia Fasolato[3], Caterina Petrillo[4], Jessica Barichello[5], Fabio Matteocci[5],
Diego Di Girolamo[1], Aldo Di Carlo[5], Paolo Postorino[6], Alessandro Nucara[6]
[1]Dept. of Chemistry, University of Rome "La Sapienza", p.le Aldo Moro 5, 00185 Rome (Italy)
[2]Dept. of Sciences, University of Rome "Roma Tre", via della Vasca Navale 84, 00146 Rome (Italy)
[3]ISC-CNR, Institute of the Complex Systems, , p.le Aldo Moro 5, 00185 Rome (Italy)
[4]Dept. of Physics and Geology, University of Perugia, via A. Pascoli, 06123 Perugia (Italy)
[5]Dept. of Electronic Engineering/CHOSE, University of Rome "Tor Vergata", via del Politecnico 1, 00133 Rome (Italy)
[6]Dept. of Physics/SPIN-CNR, University of Rome "La Sapienza", p.le Aldo Moro 5, 00185 Rome (Italy)
Presenter's e-mail address: *danilo.dini@uniroma1.it*

Perovskite systems of hybrid nature constitute the most promising class of materials for the realization of low-cost, lightweight and flexible photovoltaic devices.[1] Within this group Br-based perovskites attract particular attention because employable as photoactive thin films in semitransparent solar cells with relatively high conversion efficiency and good temporal stability.[2] In the present contribution it is considered the analysis of the spectroscopic features of the perovskite $CH_3NH_3PbBr_3$ when deposited onto different substrates with selective transmission in the IR and visible intervals,[3] together with a first evaluation of the light-to-current conversion properties in the corresponding device employing $CH_3NH_3PbBr_3$. The study, consisting in the realization of out-of-equilibrium spectroscopy experiments with above bandgap excitation in the perovskite of interest, evidences a correlation between the local strains generated by photogenerated electron-hole couples with the environment, and the dynamics of deformation of the polyatomic cation $CH_3NH_3^+$. The latter species is confined in the cavities created by vertex-sharing octahedral units $PbBr_6$ and senses the local structural changes brought about by the photoinduced polarons through the modification of the strength of the H-bonds the N-H moiety forms with Br^-. This is supported by simultaneous detection of absorbance diminution below 3200 cm^{-1} and an increase of absorbance at wavenumbers larger than 3200 cm^{-1} (in the region of where CH_3 and NH_3 stretching occur) upon variation of the pumping fluence at above bandgap energy. This combination of findings denotes that lattice distortion [consequent to the sequence of events: (a) exciton generation and (b) polaron formation] provokes indirectly the freezing of $CH_3NH_3^+$ in a stretched conformation with vibrational modes of higher energies.

[1] T.A. Chowdhury et al. RSC Adv. 13 (2023) 1787
[2] J. Barichello et al. Sol. RRL (2022) 2200739
[3] V. Carpenella et al. J. Phys. Chem. C, in press

The CO and CO_2 detection activity on the SiC graphenylene nanosheet

Nicolas Martins[1,2], Naiara Marana[2], Chiara Ribaldone[2], Julio Sambrano,[1] and Silvia Casassa[2]
[1]*Modeling and Molecular Simulation Group, São Paulo State University, Bauru, Brazil*
[2]*Dipartimento di Chimica, Università di Torino, Torino, Italy*
nicolas.ferreira@unesp.br

Since the discovery of graphene [1], two-dimensional (2D) carbon allotropes with different atomic configurations have been proposed, which bring different properties and applications for this material class. One of these proposed structures is graphenylene (GP), also called 4-6-12 biphenylene, a 2D material with a bandgap of 0.8 eV [2] and a special porous structure that could be ideal for energetic devices. In 2017, this shape was synthesized through a polymerization reaction [3], instigating more studies about this novel class of carbon-based 2D materials. Based on this, many researchers started to investigate different semiconductor materials with graphenylene-like structures, including silicon carbide (SiC) [4]. The inorganic graphenylene-like SiC (IGP-SiC) is a wide band gap semiconductor (3.22 eV), and its dodecagonal pore has 6.82 Å, which confers to its new application, such as a gas sensor. Regarding this, the present study aims to analyze the CO and CO_2 adsorption on the IGP-SiC, focusing on the gas detection activity of this novel monolayer. All simulations will be performed using the DFT framework via CRYSTAL23 code and by applying HSE06 hybrid functional with D3 dispersion, as implemented on the CRYSTAL environment. The adsorption energies, changes in the bandgap, and charge density will be analyzed to verify the gas detection efficiency by the IGP-SiC monolayer. In this sense, this work is expected to give important information about CO and CO_2 detection activity on the novel IGP-SiC nanosheet.

[1] A. K. Geim and K. S. Novoselov, *The Rise of Graphene*, Nat. Mater. 6, 183 (2007).
[2] G. Brunetto, P. A. S. Autreto, L. D. Machado, B. I. Santos, R. P. B. dos Santos, and D. S. Galvão, *Nonzero Gap Two-Dimensional Carbon Allotrope from Porous Graphene*, J. Phys. Chem. C 116, 12810 (2012).
[3] Q.-S. Du, P.-D. Tang, H.-L. Huang, F.-L. Du, K. Huang, N.-Z. Xie, S.-Y. Long, Y.-M. Li, J.-S. Qiu, and R.-B. Huang, *A New Type of Two-Dimensional Carbon Crystal Prepared from 1,3,5-Trihydroxybenzene*, Sci. Rep. 7, 40796 (2017).
[4] N. F. Martins, G. S. L. Fabris, A. R. Albuquerque, and J. R. Sambrano, *A New Multifunctional Two-Dimensional Monolayer Based on Silicon Carbide*, FlatChem 30, 100286 (2021).
[5] N. F. Martins, G. S. L. Fabris, A. S. Maia, A. R. Albuquerque, and J. R. Sambrano, *Inorganic Graphenylene-like Silicon Carbide as Anode Material for Na Batteries*, FlatChem 35, 100410 (2022).

Use of different synchrotron light techniques to evaluate the defects structure in doped ceria electrolytes for solid oxides cells

Sara Massardo[1], Cristina Artini[1,2], Alberto Martinelli[3], Maria M. Carnasciali[1,4], Marcella Pani[1,3]
[1] *DCCI, University of Genova, Via Dodecaneso 31, 16146 Genova Italy*
[2] *CNR-ICMATE, Via De Marini 6, 16149 Genova, Italy*
[3] *SPIN-CNR, Corso Perrone 24, 16152 Genova, Italy*
[4] *INSTM, Via Dodecaneso 31, 16146 Genova, Italy*
sara.massardo@edu.unige.it

Doped ceria systems are widely investigated electrolytes for IT-SOCs (Intermediate Temperatures - Solid Oxides Cells), crystallizing with a fluorite-type structure. In fact, in $Ce_{1-x}RE_xO_{2-x/2}$ compounds (RE= trivalent Rare Earth), the partial substitution of Ce^{4+} by RE causes the formation of not-associated oxygen vacancies, allowing the conduction of O^{2-} ions through the structure, thanks to a vacancy-hopping mechanism. In such compounds, the ionic conductivity is ruled by different quite complex factors, strictly related to the structure of the electrolyte and to the different types of defects occurring in it. In the last years, our research group extensively explored the structural and micro-structural properties of RE-doped ceria, through different techniques [1], both at ambient and non-ambient conditions [2, 3], thus gaining a deep knowledge on the structure of such compounds. We recently undertook a study on the defects architecture in co-doped ceria systems [4, 5], in which two RE doping ions with different dimensions are simultaneously used. On such systems, we already performed several experiments using synchrotron light, such as x-ray diffraction, also at high pressure (Xpress beamline, Elettra synchrotron, Trieste, IT). Moreover, to deepen our knowledge on the local structure in these compounds, X-ray absorption spectroscopy (EXAFS) and pair distribution function (PDF) studies were performed at the ESRF synchrotron of Grenoble, FR (beamlines BM08 and ID22, respectively, see Figure 1). The investigations were conducted on $Ce_{1-x}(Nd_{0.74}Tm_{0.26})_xO_{2-x/2}$ (NdTm system) and $Ce_{1-x}(Nd_{0.63}Dy_{0.37})_xO_{2-x/2}$ (NdDy system) samples with x≤ 0.6, obtained through a well-established co-precipitation synthetic protocol [1]. The analysis of the collected data provided information on the deformations taking place in the oxide with the increasing RE amount: with the present contribution, an overview on the acquired data and their implications on the electrolyte performances will be given.

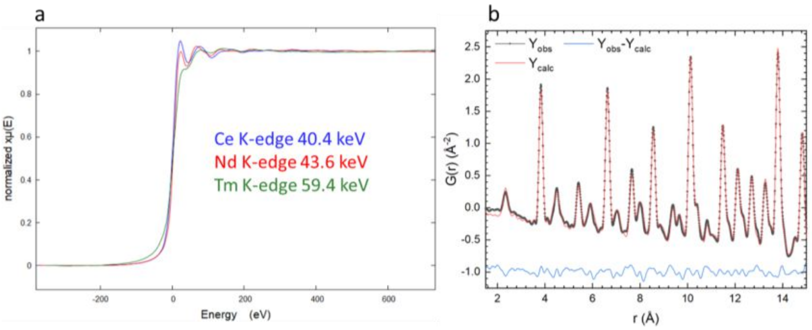


Figure 1 (a) aligned EXAFS spectra collected on the sample with x_{NdTm}= 0.6; (b) fit of the G(r) profile for a pure ceria sample.

[1] C. Artini et al. Inorg. Chem. 55 (2016) 10567
[2] S. Presto et al. Phys. Chem. Chem. Phys. 20 (2018) 28338
[3] S. Massardo et al. Coatings 11 (2021) 724
[4] C. Artini et al. J. Energy Chem. 60 (2021) 494
[5] C. Artini et al. Inorganics 7(8) (2019) 94

Dyes emission mediated by plasmonic nanostructures revealed by SNOM

Anna Mercedi[1], Lucio Litti[1]
[1] Department of Chemical Sciences, University of Padova, v. Marzolo 1, 35131 Padova, Italy
Presenter's e-mail address: anna.mercedi@studenti.unipd.it

The interaction between a fluorescent dye and a plasmonic surface, can lead to a variety of different phenomena, such as Surface Enhanced Raman Scattering (SERS) [1,2], Surface Enhanced Fluorescence (SEF) [3], or even Surface Plasmon Amplification by Stimulated Emission of Radiation (SPASER) [4]. All these effects are commonly studied in the far field regime, but they are strongly dependent on various local factors: the distance between the fluorophore and the nanoparticle, the particles aggregation, as well as shape and composition of the plasmonic substrate.

Scanning near field optical microscopy (SNOM) is a Scanning Probe Microscopy technique with unique characteristics that allow to shed light in the nanoscale, overcoming the diffraction limit, while simultaneously providing topographical images [5]. It is, therefore, a powerful tool to directly study the correlation of all the local structural factors with the emission properties, providing new insights about the complex mechanisms and structure/activity relationships of these systems and paving the way to new developments.

[1] E. Lenzi, L. Litti, D. Jimenez de Aberasturi, M. Henriksen-Lacey and L. M. Liz-Marzán, SERSTEM: An app for the statistical analysis of correlative SERS and TEM imaging and evaluation of SERS tags performance, Journal of Raman Spectroscopy, 2021, 52, 355–365.
[2] L. B. Berganza, L. Litti, M. Meneghetti, S. Lanceros-Méndez and J. Reguera, Enhancement of Magnetic Surface-Enhanced Raman Scattering Detection by Tailoring Fe3O4@Au Nanorod Shell Thickness and Its Application in the On-site Detection of Antibiotics in Water, ACS Omega, 2022, 7, 45493–45503.
[3] A. R. Guerrero and R. F. Aroca, Surface-Enhanced Fluorescence with Shell-Isolated Nanoparticles (SHINEF), Angewandte Chemie, 2011, 123, 691–694.
[4] M. A. Noginov, G. Zhu, A. M. Belgrave, R. Bakker, V. M. Shalaev, E. E. Narimanov, S. Stout, E. Herz, T. Suteewong and U. Wiesner, Demonstration of a spaser-based nanolaser, Nature, 2009, 460, 1110–1112.
[5] M. De Serio, R. Zenobi and V. Deckert, Looking at the nanoscale: scanning near-field optical microscopy, TrAC Trends in Analytical Chemistry, 2003, 22, 70–77.

Exchange coupled $CoFe_2O_4$/CoO/CoFe nanocomposites synthetized by colloidal chemistry

Jean Pierre Miranda Murillo[1], Farzane Talaee Shoar[2-3], Gianni Barucca[2-3], Gaspare Varvaro[3], Diego Colombara[1] and Davide Peddis[1]
[1]Dipartimento di Chimica e Chimica Industriale, via Dodecaneso 31, 16146, Italy
[2]Department SIMAU, University Politecnica delle Marche, Via Brecce Bianche, Ancona 60131, Italy & UdR INSTM Ancona, Italy
[3]Institute of Structure of Matter, National Research Council, nM2-LAB, Research Area Roma 1, Monterotondo Scalo (Roma), 00015, Italy
Jeanpierre.mirandamurillo@edu.unige.it

Several advanced magnetic devices (e.g., magneto-recording) rely on the phenomenon of exchange coupling occurring between different magnetic phases, since it gives the possibility of tuning the anisotropy of the overall material. The FeCo features an outstanding saturation magnetization (Ms) up to 246 Am^2kg^{-1} but a low anisotropy [1,2]. In this framework, $CoFe_2O_4$/CoO/CoFe magnetic nanocomposites (MNCs) have been produced by thermal decomposition of $Fe(acac)_3$ and $Co(acac)_2$ in a continuous H_2/N_2 flow. Different activation temperatures (T = 270°C, 295°C, 320°C and 350°C) and reducing times (t = 2h and 4h) have been explored, giving an insight on the reduction pathway of the $CoFe_2O_4$ to CoFe alloy (figure 1) [3]. These MNCs are intended to be used for green pattern deposition as part of the so-called *magnetorheological electrolytes* in the framework of the REMAP EIC-funded project (https://re-map.eu/) [4].

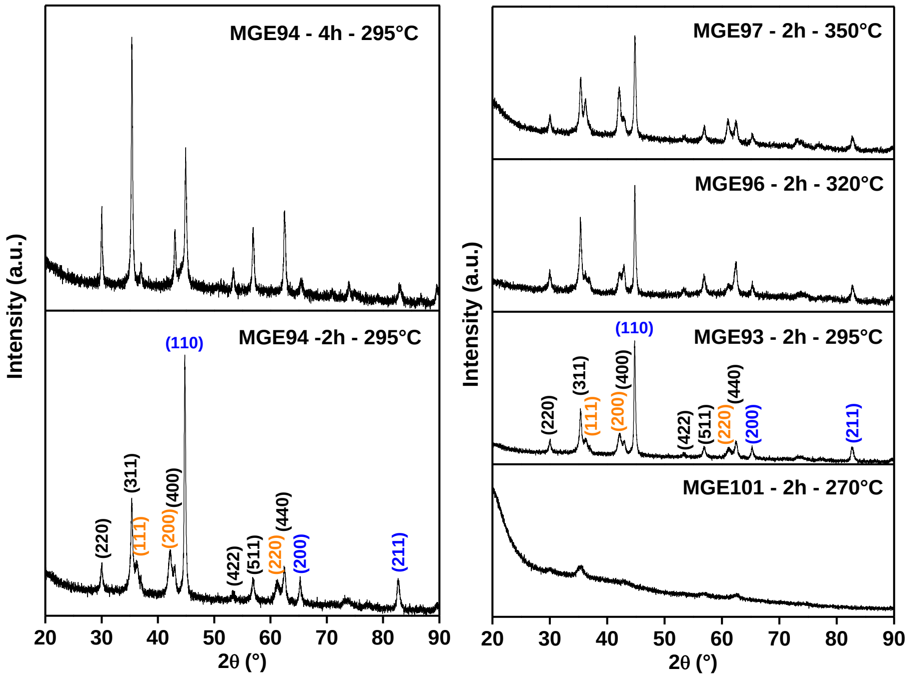


Figure 1. XRD patterns of the samples obtained at different temperatures (left) and times (right). The black ($CoFe_2O_4$, $Fd\underline{3}m$), orange (CoO, $Pm\underline{3}m$) and blue (CoFe, $Pm\underline{3}m$) miller indexes mark the different phases.

[1] J. M. D. Coey, Magnetism and Magnetic Materials (2010)
[2] A. Omelyanchik et al., MDPI 12 (2022) 1-10
[3] E. Lottini et al., Chem. Mater. 28 (2016) 4214
[4] D. Colombara, Patent No. PCT/EP2019/086023 (2020)

Synthesis and Structural Characterization of Mn-Doped Double Perovskite $Cs_2NaInCl_6$ Nanocrystals with Different Morphology

Sophia Victoria Ochoa Meza[1], Marta Campolucci[1,2], Emmanuela Di Giorgio[1], Emanuela Sartori[1], Maurizio Ferretti[1], Federico Locardi[1,2]
[1]Department of Chemistry and Industrial Chemistry, Università degli Studi di Genova, Via Dodecaneso 31, 16146 Genova, Italy
[2]Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy
Presenter's e-mail address: s4481490@studenti.unige.it

Lead-free halide perovskites have drawn attention as alternatives to their toxic and poorly stable lead-based counterparts [1]. In particular, double perovskites (DPs), where Pb^{2+} ions are replaced with a combination of a monovalent (B^+) and a trivalent (B^{3+}) metal cation, have been in the spotlight owing to their intriguing optical properties as the potential to be persistent phosphors. In fact, through doping with rare-earth or transition metal cations, it is possible to emit light after the excitation source vanishes [2]; this phenomenon is known as persistent luminescence. This interest has sparked different synthetic approaches towards both crystals and nanocrystals, and the exploration of effects related to different alloying, doping and size.

Motivated by the work of Chen *et al.* [3], we have prepared Mn-doped $Cs_2NaInCl_6$ nanocrystals with the aim to investigate the physical mechanisms occurring at the nanoscale and to propel the applicability of these materials. Following different synthetic approaches, we have synthesized $Cs_2NaInCl_6$: 60%Mn^{2+} nanocubes and nanoplates via a hot-injection solvothermal method and via a low temperature-induced crystallization method, respectively [4]. The samples have been characterized by X-ray diffraction (XRD), which indicates that the NCs crystallized in a cubic $Fm\overline{3}m$ DP structure. Transmission electron microscopy (TEM) micrographs of $Cs_2NaInCl_6$: 60%Mn^{2+} NCs evidenced the formation of NCs with a cuboidal shape and a mean size of 30-35 nm when employing the hot-injection method, while a larger rectangular morphology in the case of the nanoplates.

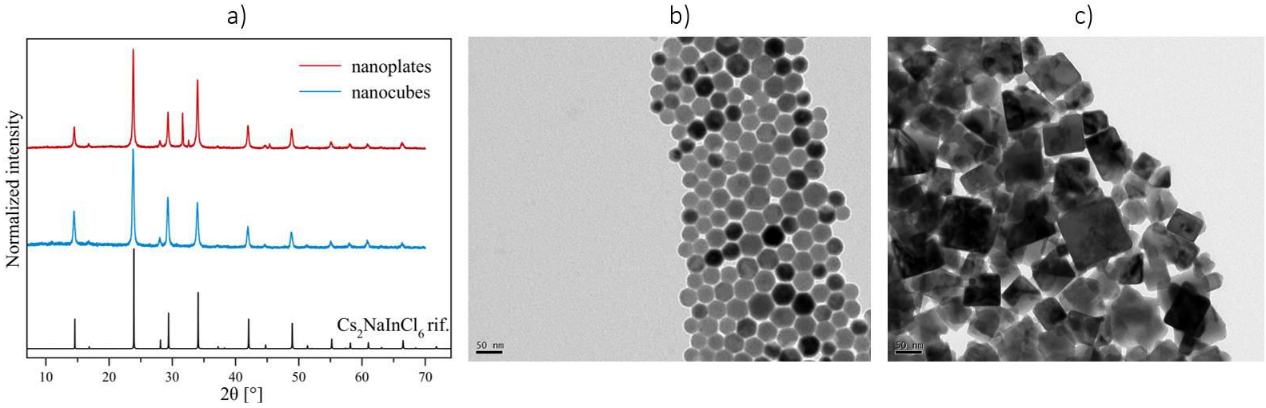


Figure 1: (a) XRD patterns of $Cs_2NaInCl_6$: 60%Mn^{2+} NCs. TEM image of (b) nanocubes and (c) nanoplates.

[1] Y. Liu et al. Angew. Chem. Int. Ed. Engl. (2021) 11592-11603
[2] V. Castaing et al. J. Appl. Phys. 130 (2021) 080902
[3] X. Chen et al. J. Phys. Chem. Lett. 13 (2022) 8163-8168
[4] S. Dror et al. Chem. Mater. 13 (2023) 1363-1372

Interplay between inter- and intraparticle interactions in bi-magnetic core/shell nanoparticles

A. Omelyanchik,[1,2] S. Villa[2], F. Canepa[1], G. Singh[3], M. Vasilakaki[4], G. Margaris[4], K. N. Trohidou[4] and D. Peddis[1,5]
[1]Department of Chemistry and Industrial Chemistry (DCIC) & INSTM, University of Genova, nM2-Lab, Genova, Italy;
[2]Immanuel Kant Baltic Federal University, Kaliningrad, Russia;
[3]Department of Materials Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway;
[4] Institute of Nanoscience and Nanotechnology, National Center for Scientific Research Demokritos, Athens 15310, Greece;
[5]Istituto di Struttura della Materia, CNR, nM2-Lab 00015 Monterotondo Scalo, (RM) Italy

Bi-magnetic nanoparticles of magnetic oxides with a core/shell structure are widely investigated due to their potential use in various applications, ranging from electronics to biomedicine [1]–[3]. The surface/interface effect and interparticle interactions strongly affect their magnetic properties and thus they should be considered to design materials with desired properties. However, all those effects have complex nature, and it is not trivial to consider them at the design step of materials. This work focuses on the study of the magnetic properties of bi-magnetic core/shell nanoparticles of cobalt ferrite (CFO) and nickel ferrite (NFO), also in the inverse configuration. The growth of a magnetically soft NFO shell affects the hard properties of the CFO seeds with a decrease of μ_0H_C from ~1.3 to 0.8 T. On the contrary, the magnetically harder shell increases the coercivity of the NFO seeds from ~0.025 to 0.03 T. These changes cannot be explained quantitatively by a classical additive rule: a strong influence of the architecture was revealed in a clear interplay among intraparticle (i.e., proximity effects) and interparticle interactions. This effect has been investigated by the remanent plot's technique. Then we applied the Monte Carlo simulation method to better understand the effect of different factors and for the first time in the core/shell system, the contribution of proximity effects in ΔM-plot has been highlighted. Implementation of this model allows one to design the material with desired magnetic properties.

[1] M. Estrader et al., "Robust antiferromagnetic coupling in hard-soft bi-magnetic core/shell nanoparticles," Nat. Commun., vol. 4 (2013), p. 2960.
[2] J. Kim, S. E. Chung, S.-E. Choi, H. Lee, J. Kim, and S. Kwon, "Programming magnetic anisotropy in polymeric microactuators," Nat. Mater., vol. 10 (2011), pp. 747–752.
[3] F. Fabris et al., "Tunnel Magnetoresistance in Self-Assemblies of Exchange-Coupled Core/Shell Nanoparticles," Phys. Rev. Appl., vol. 11 (2019), p. 054089

The ageing of the Verdigris pigment: influence of the binder and environmental conditions

Sara Pirovano, Elena Castagnotto, Silvia Vicini, Maurizio Ferretti, Federico Locardi
Department of Chemistry and Industrial Chemistry (DCCI), Università degli studi di Genova, Via Dodecaneso 31 16146, Genova, Italy
Presenter's e-mail address: sara.pirovano00@gmail.com

Verdigris is a copper – based green organometallic pigment widely used in the XVI and XVII centuries in oil paintings; however, it slowly disappeared due to its proclivity to darken and brown with ageing [1]. Interestingly, alterations are not systematic, and coexistence of altered and unaltered areas have been reported on the same painting. Several hypotheses have been formulated to address the colour changes, but the mechanism of degradation has not been fully yet elucidated [2]. The aim of this work is to better investigate the reactivity of Verdigris in relation to different environmental factors; thus, to propose a model that could help in the evaluation of the alteration path in the pictorial layers, and to find a solution to the browning of the pigment to limit its degradation. Various samples of Verdigris (namely $Cu(CH_3COO)_x \cdot xH_2O$) have been synthesized exposing copper thin sheets to the fume of an acetic acid solution at different concentrations. The monohydrate sample has been selected to be artificially aged. Its behaviour has been examined when mixed with oils having increasing amount of fatty acids, in order: walnut, linseed and poppyseed oil [3]. Artificial ageing conditions have been devised through a Design of Experiment (DoE) model, investigating influence and interaction of light, humidity, type of oil, time, and oil/pigment ratio. Pigment powders have been characterized by means of X-Ray Diffraction (XRD), Light Optical Microscopy (LOM), Fourier-Transform Infrared Spectroscopy in Attenuated Total Reflectance (ATR-FTIR) and UV-Vis spectroscopy; Verdigris paint films deterioration has been monitored through IR spectroscopic and colorimetric analysis. Moreover, the broad dataset obtained has been elaborated with Principal Component Analysis (PCA). The results showed that the color shift highly depends on humidity levels, but degradation occurs at RH% as low as 10%, change occurring in the pigment overtime outweigh the changes depending on binder deterioration, and it is possible to distinguish alteration based on exposure condition.

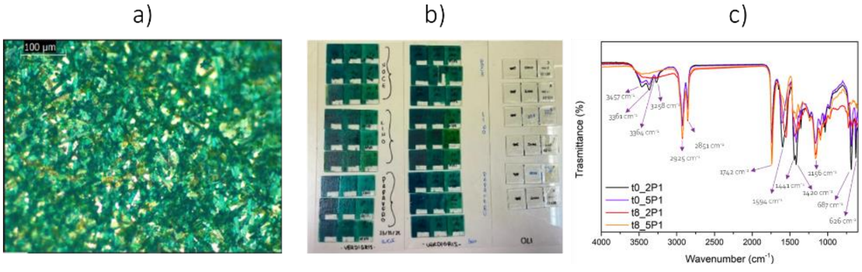


Figure. a) LOM image and; b) drafts of $Cu(CH_3COO)_2 \cdot H_2O$ with different types of oils ; c) FTIR-ATR spectra for comparison of samples of different times, exposed to different humidity conditions.

[1] M. San Andrés et. al. J. Raman Spectr. 41 (2010) 1468-1476.
[2] R.Wouhuysen-Keller, Historical Painting Techniques, Materials and Studio Practice, 26–29 June 1995, 65–69
[3] M.Gunn et al. Studies in Conservation, 47 (2002) 12-23.

Optimization of Lead Halides Perovskites Nanocubes' Synthesis in *Green* Solvents Through Experimental Design

Lorenzo Pugliesi[1], *Davide Pratolongo*[1,2], *Maurizio Ferretti*[1], *Barbara Benedetti*[1], *Federico Locardi*[1]
[1]*Department of Chemistry and Industrial Chemistry, Università degli Studi di Genova, Via Dodecaneso 31, 16146 Genova, Italy*
[2]*Electron Microscopy Facility, Istituto Italiano di Tecnologia, Via Morego 30, Genova 16163, Italy*
Presenter's e-mail address: *s4636378@studenti.unige.it*

To date, lead halide perovskites nanocrystals (LHPs NCs) are an established class of materials, catching rising attention due to their physical properties such as high electron mobility, low trap density, tunable and elevated emission[1]. The quantum confinement of the nanocrystal influences many LHPs NCs optoelectronic properties, for instance a lowering in the crystal dimension enhances the energy emission. One of the most used synthetic strategies is the Hot Injection Method (HInj), that allows a precise control over size and morphology, resulting in a control of the optoelectronic properties of the final material.

Briefly, HInj involves the rapid injection of the precursors (*e.g.* Cs^+ organic complex) into a hot solution of a non-polar solvent with high boiling point in presence of other metals (*e.g.* PbX_2) one or more organic ligands (alkyl carboxylic acids and amines), under inert atmosphere and at a temperature generally between 100°C and 200°C. The reaction starts immediately with a nucleation of the crystal and continues according to the desired final product and the interaction between the elements[2]. A relevant issue is that HInj is usually performed in toxic or petroleum–based solvents, such as octadecene (ODE), dioctyl ether (DOE), diphenyl ether (DPE) etc. Yet, some vegetable terpenes, such as limonene and α–pinene, have good characteristics, in terms of dielectric constant and boiling point, to be a substitute of the aforementioned solvents in the NCs synthesis. Here, we report the optimization of the synthesis of LHPs using *green* solvents. All the tests have been chosen according to a Plackett–Burman experimental design; through a following multivariate optimization, it would be possible to obtain the best conditions in terms of injection temperature, solvent type, amount of starting material and nanocrystal's growth time to have the product with a photoluminescence quantum yield and a shape control comparable to the traditional syntheses.

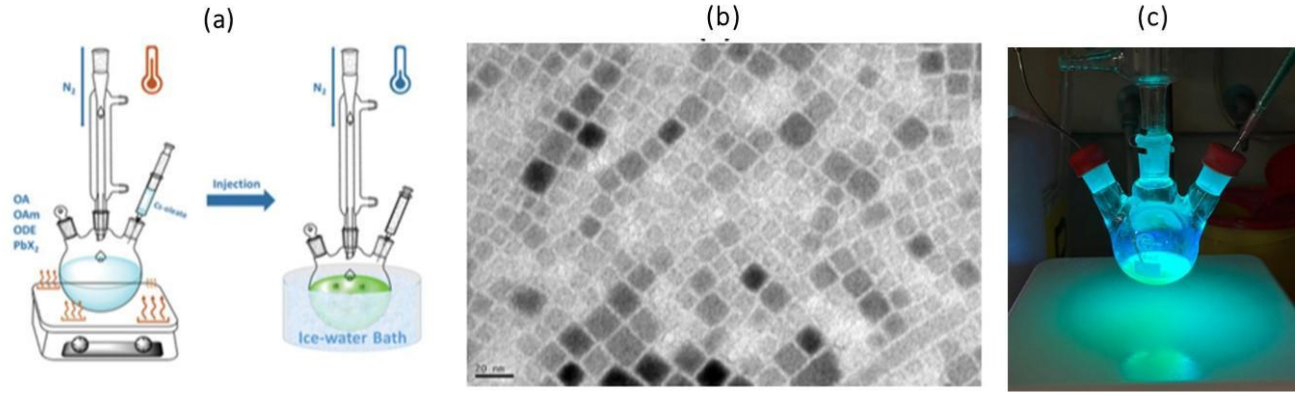


Figure 1: (a) Schematic illustration of HInj method[2]*; (b) TEM image of $CsPbBr_3$ nanocubes; (c) Green emission of nanocubes synthetized in limonene.*

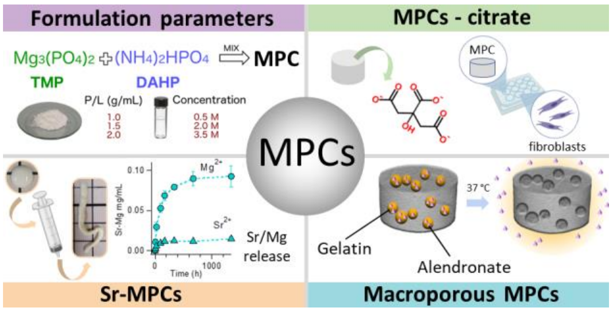
[1] X. Li et al. Chem. Rev. 121 (2021) 2230
[2] Y. Bai et al. Adv. Mater. 34 (2022) 2105958

Magnesium phosphate-based cements towards orthopedic applications

Rita Gelli [1], *Francesca Ridi* [1], *Piero Baglioni* [1]
[11]*Department of Chemistry "Ugo Schiff" and CSGI, University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino (Florence), Italy*
Presenter's e-mail address: francesca.ridi@unifi.it

Magnesium phosphate-based cements (MPCs) have recently attracted great attention as materials for bone repair due to their appealing features (fast setting, high early strength, good biocompatibility and degradation behavior) that represent an improvement with respect to the well-known calcium phosphate cements. This contribution showcases the most recent results from our group concerning the investigation of the physico-chemical characteristics of MPCs and the optimization of some of their features, aiming at the preparation of materials for bone repair. Four case studies will be presented. First, an investigation of the effect of the preparation conditions on the composition and the main physico-chemical and mechanical properties of MPCs will be presented [1]. Then, this contribution will show that MPCs can be successfully formulated to release active molecules and ions, namely citrate [2] and strontium [3]. Citrate is naturally present in bone and its inclusion in biomaterials has shown beneficial effects, whereas the role of strontium in promoting bone regeneration is well established. As a last example, this contribution will present an innovative strategy to prepare macroporous MPCs, taking advantage of gelatin microparticles as porogens [4].

As a general approach, such systems were studied in the early stages of setting in terms of cohesion, setting time and injectability, while the properties of the cement phase were assessed with X-Ray diffraction, thermal analyses, scanning electron/confocal Raman microscopy and compressive tests. The results showcase the versatility and the potential of these materials, whose properties can be tailored according to specific requirements in the bone repair field.



[1] R. Gelli, L. Mati, F. Ridi, P. Baglioni, *Materials Science and Engineering: C*, **2019**, 95, 248-255.
[2] R. Gelli, G. Di Pompo, G. Graziani, S. Avnet, N. Baldini, P. Baglioni, *ACS Biomaterials Science & Engineering*, **2020**, 6, 5538-5548.
[3] R. Gelli, G. Bernardini, F. Ridi, *manuscript submitted for publication.*
[4] R. Gelli, L. Sforzi, F. Montanari, F. Ridi, P. Baglioni, *Journal of Materials Science,* **2022**, 57(27), 12994-13010.

Ti doped zeolitic catalysts with MWW topology for partial oxidation of bulky alkenes

Francesca Rosso[1], Alessia Airi[1], Matteo Signorile[1], Silvia, Bordiga[1], Valentina Crocellà[1], Francesca Bonino[1]
[1] Department of Chemistry, NIS and INSTM Reference Centre, Università di Torino, Via G. Quarello 15, 10135 and Via P. Giuria 7, 10125, Torino, Italy.

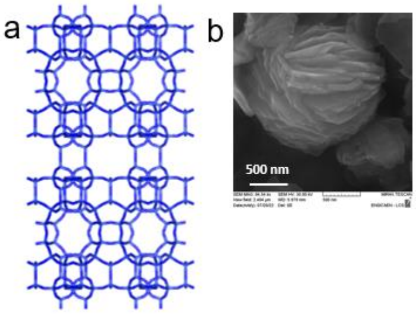


Figure 1. Projection of the MWW structure (a) and MWW zeolite micrograph (b). [4]

Partial oxidation reactions (e.g. alkenes epoxidation) are often catalyzed by Titanium Silicalite-1 (TS-1) [1], when small substrates are involved. Larger pores Ti-substituted zeolites, as the MWW framework (Ti-MWW) [2,3,4] (Figure 1) appears to be a promising alternative to TS-1 for the partial oxidation of bulkier substrates. The active sites in TS-1 consist in peroxo or hydroperoxo Ti(IV) complexes formed upon adsorption of a hydrogen peroxide (H_2O_2) molecule over the Ti atom. [5] The catalytic activity depends on the geometry of the interaction between H_2O_2 and Ti atom and it is increased when Ti is isolated in tetrahedral coordination. [5,6] When Ti sites presents distorted coordination the interaction with H_2O_2 may change, leading to species whose catalytic activity is debated. The Ti coordination in Ti-zeolites can spread from the tetrahedral (isomorphous substitution) to the octahedral (precipitated anatase), including all the “intermediate” species. [5]

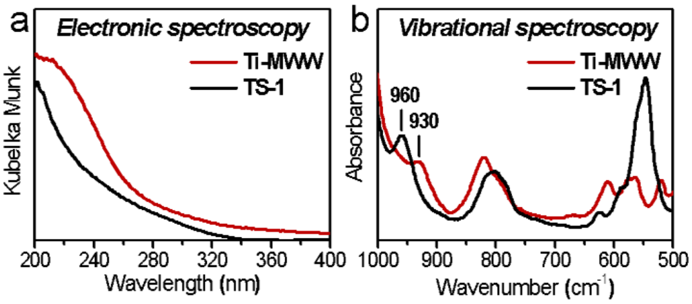


Figure 2. DR-UV-Vis (a) and ATR-IR (b) spectra of Ti-MWW and TS-1 samples.

This work is devoted to answer the questions: does a catalytically active Ti species form in Ti-MWW samples? Is it the same present in TS-1? Different Ti-MWW samples were synthesized to study the variation in Ti local environment depending on the preparation procedure. The preliminary results are reported in Figure 2 demonstrating slight differences between the two materials. The DR-UV-Vis spectra (Figure 2a) show that the Ligand to Metal Charge Transfer (LMCT) electronic transition, [7] sensitive to Ti coordination, is quite similar inTS-1 and Ti-MWW, while the ATR-IR spectrum of TS-1 (Figure 2b), on the contrary, shows a signal fingerprint of Ti in tetrahedral coordination, peaked at 960 cm^{-1}. [8] This signal is splitted (960 and 930 cm^{-1}) in Ti-MWW, [3] testifying a strong difference in Ti local environment. Finally, model conditions gas-phase catalytic tests were performed to compare Ti-MWW and TS-1 activity, using IR spectroscopy to follow the products formation in propylene and 1-hexene epoxidation.

[1] M. Taramasso et al. US Patent 4410501 (1983).
[2] P. Wu et al. J. Phys. Chem. B, 105 (2001) 2897-2905.
[3] H. Xu et al. ACS Catalysis, 10 (2020) 4813-4819.
[4] F. Rosso et al. in preparation.
[5] M. Signorile et al. J. Phys. Chem. C, 122 (2018) 9021-9034.
[6] X. Nie et al. Mol. Catal. 441 (2017) 150-167.
[7] F. Bonino et al. J. Phys. Chem. B 108 (2004) 3573-3583.
[8] G. Ricchiardi et al. J. Am. Chem. Soc. 123 (2001) 11409-11419.

Synthesis of PeL-supported doped-TiO_2-based photocatalysts for micro-contaminant degradation

Lorenzo Viacava[1], Nicolò Ghibaudo[1], Maurizio Ferretti[1], Federico Locardi[1], Barbara Benedetti[1], Stefano Alberti[1]
[1]*Chemistry and Industrial Chemistry Department, Via Dodecaneso 31, 16146, Genova (Ge), Italy*
lorenzo.viacava@gmail.com

TiO_2-based materials have been exploited in many fields of application; among them, environmental remediation for emerging contaminants in water bodies represents a significant topic. Extending the application of TiO_2 under sunlight and in turbid wastewater is currently an active research field. Nitrogen and Fluorine co-doped TiO_2 systems were synthesized by sol-gel method followed by hydrothermal treatment in an autoclave immersed in a silicone oil bath at 150°C for 3 hours. Tetraisopropoxide Titanium “TTIP” (97%), 2-propanol “2-PrOH” (99.9%) and distilled water were used as precursors agents while NH_4F as dopants source [1]. In order to optimize the synthesis, a multivariate approach was followed. A screening experimental design (Plackett-Burman design) was initially applied to find out which of the five investigated variables (temperature, time, pH, doping percentage, TTIP/2-PrOH ratio) had a significant effect on the energy gap (E_g) of the final product. Subsequently, another experimental design was applied to optimize the supporting synthesis of TiO_2 on a persistent luminescent material “PeL”: the main goal was to minimize the E_g of TiO_2 to make it compatible with the luminescent emission. PeL materials are a peculiar class of compounds that can emit light even after the external excitation has been removed and they can act as a light source for the activation of the photocatalyst even in dark conditions. As reported in literature [2], proper doping of TiO_2 can decrease the E_g of the semiconductor, which represents a favourable condition to match the emission of PeL with the absorption of TiO_2 (as highlighted by DRS spectra in Fig. 1). Eventually, the photocatalytic activity of the material was tested for the degradation of emerging contaminants (methylene blue, as a model pollutant) in both continuous and alternating irradiation conditions.

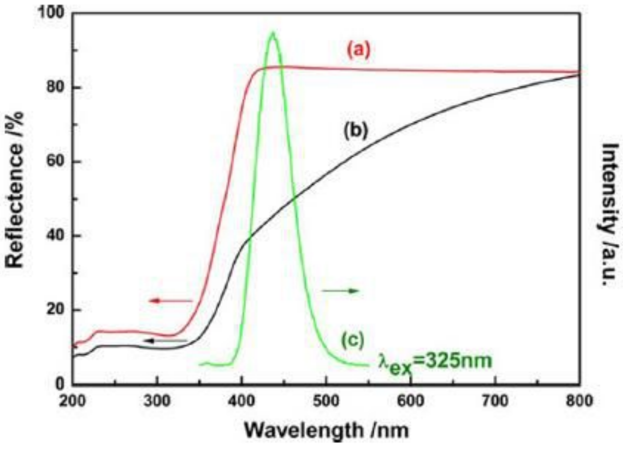


Figure 1. Overlap of diffuse reflectance spectra of (a) undoped TiO_2 (P25), (b) TiO_2:(N) and (c) emission spectrum of $CaAl_2O_4$: (Eu, Nd) [2]

[1] B. P. Dhamaniya et al. Res. Chem. Intermed. 43 (2017) 387
[2] H. Li et al. Nanoscale. Res. Lett. 6 (2011) 5

KEYNOTES

T2. PHYSICAL CHEMISTRY OF SOFT MATTER AND LIFE SCIENCE

Tracing a New Path in the Field of AI and Robotics: Mimicking Human Intelligence through Soft Matter

Pier Luigi Gentili[1]
[1]Department of Chemistry, Biology, and Biotechnology, Università degli Studi di Perugia, 06123 Perugia, Italy
pierluigi.gentili@unipg.it

Humanity is experiencing a technological revolution promoted by cutting-edge biotechnologies, nanotechnologies, Artificial Intelligence (AI), and Robotics. Specifically, AI and Robotics assist us in our daily mental and manual efforts; they augment our intelligence through powerful computing machines; they can even replace us in accomplishing specific tasks, sometimes going beyond human performances. Traditionally, AI is developed through software that can think rationally and humanly on current general-purpose electronic computers. Alternatively, AI is implemented in hardware by reverse engineering the brain, i.e., through neuromorphic engineering [1]. The awareness that a single cell is provided with a sort of nervous system (with sensors, a brain, and effectors) has opened up a new avenue for mimicking human intelligence: It is the so-called Chemical Artificial Intelligence (CAI) [2]. CAI exploits soft matter to imitate some performances of human intelligence and develop Chemical Robots [3]. A Chemical Robot (CR) looks like an artificial cell: it is a confined complex molecular assembly capable of reacting autonomously to its environment because it is equipped with the fundamental components of every living cell. First, it has sensors to collect data about the surrounding environment and its internal state. Then, it has an Artificial Neural Network (ANN), which processes the sensory data and makes decisions. ANN triggers the actions of Effectors, which are molecular machines and motors that act upon the CR's environment. Finally, the intelligent activities of any CR should be sustained energetically by a metabolic unit.

In this communication, it will be shown that ANNs can be made of proteins, and it is possible to mimic human power to "compute" with words [4, 5]. Alternatively, neural surrogates can be constituted by nonlinear chemical systems mimicking neural dynamics and originating synchronisation phenomena through chemical (based on diffusion, chemical waves, and advection) or optical communication [6, 7]. Synchronisation phenomena are at the core of any intelligent activity of the human brain [8].

CRs will allow humanity to control the microscopic world: they will perform biomedical actions and face challenges related to safeguarding the environment and exploiting energy and food resources. They will accompany and assist humanity in the future ahead. A successful CAI and Chemical Robotics will also help us understand more deeply two outstanding and mysterious emergent properties of Complex Systems: life and human intelligence [9].

[1] M. Mitchell "Artificial Intelligence. A guide for thinking humans. (2019) Farrar, Strauss and Giroux, New York (USA).
[2] P. L. Gentili. RSC Advances 3 (2013) 25523.
[3] M. Hagiya et al. Acc. Chem. Res. 47 (2014) 1681.
[4] P. L. Gentili, P. Stano. Frontiers in Bioengineering and Biotechnology 10 (2022) 927110.
[5] P. L. Gentili, J. Perez-Mercader. Frontiers in Chemistry 10 (2022) 950769.
[6] P. L. Gentili. Dyes and Pigments 205 (2022) 110547.
[7] P. L. Gentili et al. Angew. Chem. Int. Ed. 56 (2017) 7535.
[8] D. Buonomano "Your Brain is a Time Machine" (2018) Norton & Co.
[9] P. L. Gentili "Untangling Complex Systems: A Grand Challenge for Science" (2018) CRC Press, Boca Raton (FL, USA).

Steps towards Life: How inorganic surfaces may have been involved in the complexification of biomolecules

Jean-François Lambert[1], G. Berlier[2], O. El Samrout[1,2]
[1]Laboratoire de Réactivité de Surface (UMR 7197 CNRS), Sorbonne Université, Case 178, 4 Place Jussieu, 75252, Paris CEDEX 05, France
[2] Dipartimento di Chimica, Università di Torino, Via P. Giuria 7, 10125 Torino, Italy

Biomolecules have interacted with inorganic surfaces long before human scientists took an interest in the phenomenon. In fact, these interactions started as soon as our Earth was cold enough to harbour liquid water in contact with an already complex mineral surface and were so omnipresent that the mineral and biochemical worlds can be said to have co-evolved ever since. Organic building blocks of intermediate complexity such as amino acids were formed by reactions in the atmosphere or delivered by meteorites, while a wide array of mineral species was present, with the ability to adsorb molecules and catalyse different types of reactions.

It is therefore quite likely that inorganic surfaces accompanied or somehow directed the rise towards complexity of biomolecules that finally produced Life. A well-studied case is the polymerisation-condensation of amino acids to peptides (or nucleotides to nucleic acids). While this reaction is forbidden in solution, it does occur on surfaces such as silica or titania submitted to fluctuating conditions (wetting and drying cycles), with the record length for polypeptides (up to 20-mers) obtained in studies by G. Martra *et al*. [1]

We will discuss recent developments in this scenario, including the identification of surface sites responsible for this reactivity [2], the thermodynamic and kinetic dimensions of the amino acids polymerization scenario, and the information content of the polymers formed in this way. We will show that even apparently small changes in the mineral surface treatments can lead to very different reactivities [3], that protein-like elements of secondary structure are formed in the surface peptides [4], and that polymerisation is not random when mixtures of several amino acids are used. Finally, we will generalise the significance of surface reactivity by showing that condensation reactions on mineral surfaces also result in molecular transformations that could have taken part in proto-metabolic pathways such as the synthesis of nucleotides from simple precursors.

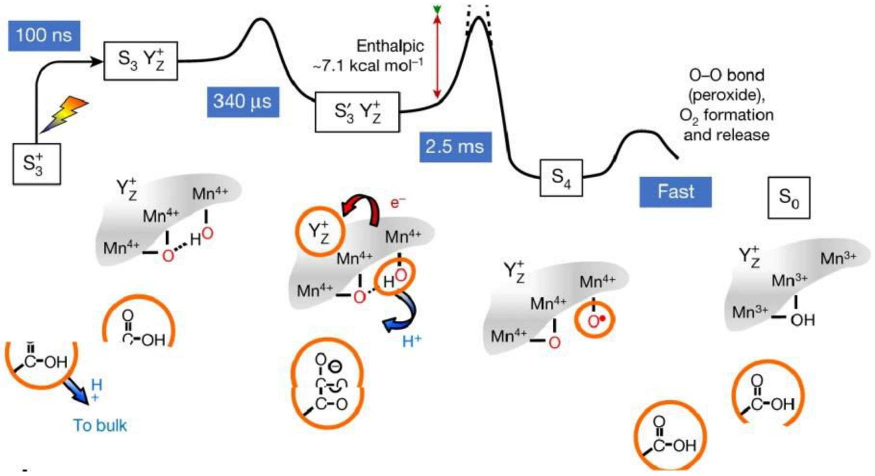
The picture that emerges from these studies is that of a complex and “creative” chemical reactivity of biomolecules on mineral surfaces, that can be oriented towards different outcomes by changes in reaction conditions, and thus could have played multiple roles in prebiotic chemistry. This constitutes a vast and exciting field of research, one that needs to be explored using a surface chemistry approach, as pioneered by G. Martra’s group.

[1] G. Martra et al. Angew. Chem. 53 (2014) 4671
[2] O. El Samrout et al., Langmuir 38 (2022) 15516
[3] O. El Samrout et al., Chem. Eur. J. 38 (2023), online publication, DOI : 10.1002/chem.202204010
[4] O. El Samrout et al., J. Phys. Chem. B 127 (2023), 673

The electron–proton bottleneck of photosynthetic oxygen evolution

Daniele Narzi[1], Matteo Capone[1,2], and Leonardo Guidoni[1]
[1]Department of Physical and Chemical Sciences, University of L'Aquila, L'Aquila, Italy.
[2]Department of Information Engineering, Computer Science and Mathematics, University of L'Aquila, L'Aquila, Italy
e-mail address: daniele.narzi@univaq.it

A key step in natural photosynthesis is the water-splitting reaction into molecular oxygen, electrons, and hydrogen equivalents. Understanding the molecular mechanisms behind this photoreaction will unravel the secrets of solar energy conversion in biochemistry and may inspire the design of artificial bio-mimetic materials for green energy production. Photosynthetic water oxidation occurs in the Mn_4Ca core of the Photosystem II complex where, through five subsequent steps (S_0-S_4) of the catalytic cycle, four electrons are sequentially removed until the oxidation of two water molecules. Using multiscale atomistic calculations, we investigated over the last ten years the molecular mechanism of the reaction catalyzed by Photosystem II, thus providing a clear structural and energetic description of different steps of the catalytic cycle [1-7]. Still, the rate limiting step of the water splitting reaction catalyzed by Photosystem II remained largely uncharacterized all this time.



Here, combining DFT-based calculations and classical MD simulations, we interpret experimental results based on microsecond infrared spectroscopy carried out by the group of Prof. Holger Dau, giving a detailed atomistic picture of the photosynthetic O_2 formation [8]. This study identified for the first time the slowest step in photosynthetic O_2 evolution consisting of a reactive oxygen radical formation occurring in a single-electron multi-proton transfer event involving the protonation of a carboxylate protein sidechain close to the Mn_4Ca cluster, as shown in the figure above. Our results provide insights into a biological process that is likely to have occurred unchanged for the past three billion years, which we expect to support the knowledge-based design of artificial water-splitting systems.

[1] D. Bovi, D. Narzi and L. Guidoni. Ang. Chem. Int. Ed. 52 (2013) 11744
[2] D. Narzi, D. Bovi and L. Guidoni. Proc. Natl. Acad. Sci. 111 (2014) 8723
[3] M. Capone, D. Narzi, D. Bovi and L. Guidoni. J. Phys. Chem. Lett. 7 (2016) 592
[4] D. Narzi, G. Mattioli, D. Bovi and L. Guidoni. Chem. – Eur. J. 23 (2017) 6969
[5] D. Narzi, M. Capone, D. Bovi and L. Guidoni. L. Chem – Eur. J. 24 (2018) 10820
[6] M. Capone, L. Guidoni and D. Narzi. Chem. Phys. Lett. 742 (2020) 137111
[7] M. Capone, D. Narzi and L. Guidoni. Biochemistry 60, 2341 (2021)
[8] P. Greife *et al*. Nature (2023) https://doi.org/10.1038/s41586-023-06008-5

ORALS

T2. PHYSICAL CHEMISTRY OF SOFT MATTER AND LIFE SCIENCE

Synthesis and characterization of hybrid magnetic/polymeric nanocomposites

Stefano Alberti[1], Ibtissame Sidane[1], Sawssen Slimani[1,2], Maurizio Ferretti[1], Davide Peddis[1,2]
[1]Chemistry and Industrial Chemistry Department, University of Genova, Via Dodecaneso 31, 16146, Genova (Ge), Italy
[2]Institute of Structure of Matter, National Research Council, nM^2-Lab, Via Salaria km 29.300, Monterotondo Scalo 00015, Roma, Italy
Presenter's e-mail address: stefano.alberti@unige,it

Nanocomposites are devices composed of multifunctional components that have attracted great interest in recent years. Research into novel nanocomposites has made it possible to combine the properties of the structural materials with those of the nanoscale filler, to create clever and useful materials that meet the requirements of specific applications [1]. In this work, the synthesis of magnetic nanocomposites based on spinel iron oxide nanostructures ($MeFe_2O_4$; Me: Fe^{2+} and Co^{2+}) functionalized with an organic capping (oleic acid) and silicon-based polymer (polydimethylsiloxane, PDMS) has been optimized. Spinel ferrite nanoparticles are particularly attractive for biomedical applications due to their tunable magnetic properties (i.e., saturation magnetization and magnetic anisotropy). In addition, the synthesis of the proposed hybrid nanocomposite was carried out by means of electrospinning, which is an innovative technique exploiting a high electric potential applied between a metallic needle, linked to a syringe, and a metallic collector, to create a solid material out of viscous solutions. Fibers are withdrawn towards the collector, creating a membrane with a three-dimensional fibrous network in the micro- or nano-scale (Fig. 1) [2]. The aim of this work is to compare the magnetic and physical-chemical properties of different electrospun membranes, in which different types of magnetic nanoparticles were embedded in different concentrations. This type of investigation is carried out by means of morpho-structural (X-ray diffraction, XRD, Transmission electron microscopy, TEM) and magnetic (Vibrating Sample Magnetometer, VSM) measurements. In addition, other methods (Fourier Transform Infrared Spectroscopy, FTIR, Thermogravimetric analysis, TGA, and Dynamic light scattering, DLS) have been used to determine the presence and the stability of magnetic nanoparticles within the polymer matrix. The results of this study could provide valuable insights into the synthesis and optimization of magnetic hybrid nanocomposites for various applications.

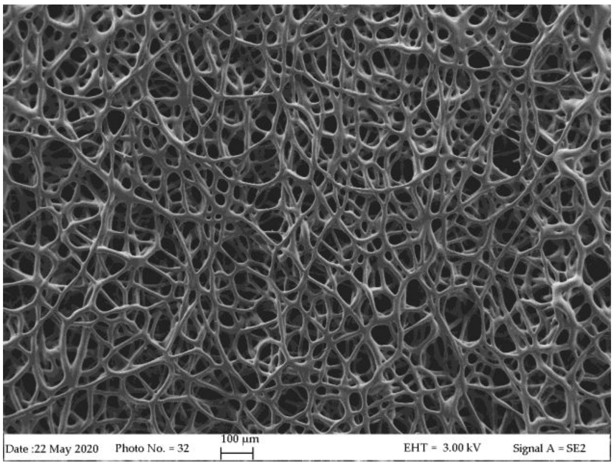


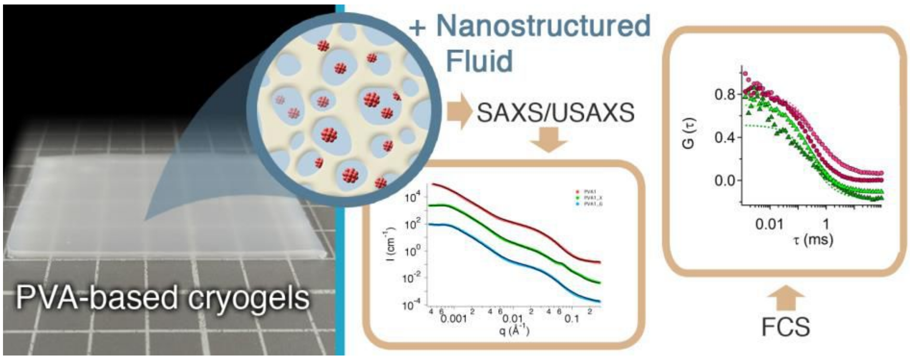
Figure 1: FeSEM image of a PDMS electrospun membrane

[1] S. Behrens and I. Appel. Current Opinion in Biotechnology, 39 (2016) 89-96
[2] Xue J. et al. Chem. Rev. 119 (2019) 5298-5415

PVA-Based Cryogels Loaded with Nanostructured Fluids for the Cleaning of Art: a SAXS-USAXS Study

Michele Baglioni[1,2]°, Rosangela Mastrangelo[2,3], Paolo Tempesti[2,3], Taku Ogura[4,5], Piero Baglioni[2,3]°
[1]*Department of Biotechnology, chemistry and pharmacy and CSGI, Via Aldo Moro 2, 53100 Siena, Italy.*
[2]*CSGI - Via della Lastruccia 3, Sesto Fiorentino, 50019 Florence, Italy.*
[3]*Department of Chemistry "Ugo Schiff" and CSGI, University of Florence, Via della Lastruccia 3, Sesto Fiorentino, 50019 Florence, Italy.*
[4]*NIKKOL GROUP Nikko Chemicals Co., Ltd., 1-4-8, Nihonbashi-Bakurocho, Chuo-ku, 103-0002, Tokyo, Japan.*
[5]*Research Institute for Science & Technology, Tokyo University of Science, 2641, Yamazaki, Noda-shi, Chiba 278-8510, Japan.*
michele.baglioni@unisi.it

The combination of nanostructured fluids (NSFs), such as micellar solutions or microemulsions, and highly-retentive hydrogels, such as PVA-based cryogels, represents nowadays a promising and innovative approach in the field of conservation of cultural heritage, as it enables the highest control available during cleaning interventions. However, at present, little is known about the confinement of NSFs into PVA-based cryogels. In the present contribution, small-angle X-ray scattering (SAXS) and ultra-small-angle X-ray scattering (USAXS), combined with fluorescence correlation spectroscopy (FCS), were used to address this issue. Two significantly different NSFs were selected for this purpose, based respectively on anionic or nonionic surfactants, and they were confined into four different gels: two single PVA and two semi-interpenetrated PVA/PVA "twin-chain polymer networks" (TC-PNs). The analysis of the experimental results shows that surfactant nature is crucial in determining i) the interaction of NSFs, i.e. the cleaning fluid, with the gels' polymer network [1], i.e. the vehicle for the cleaning fluid; and ii) the interaction of NSFs with the target material to be removed from works of art [2,3] (which can range from small oily compounds to hydrophobic polymeric coatings).



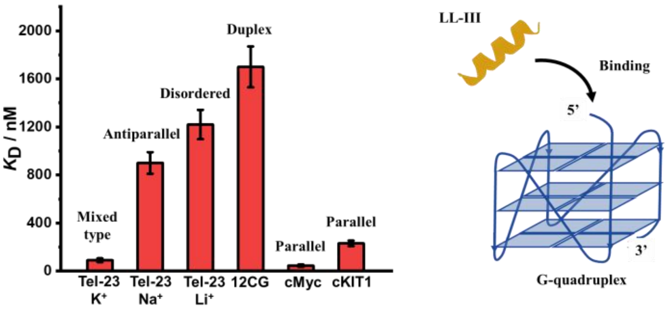
This study highlights that loading NSFs on PVA-based cryogels does not significantly affect the nanostructure of neither the NSFs nor the gels, and this is the physico-chemical reason behind the excellent cleaning performances of this combined system, which is being growingly considered as one of the most promising and innovative cleaning tools in art conservation.

[1] M. Baglioni et al. ACS Appl. Mater. Interfaces. 10 (2018) 19162–19172.
[2] M. Baglioni et al. J. Colloid Interface Sci. 606 (2022) 124–134.
[3] M. Baglioni et al. ACS Appl. Mater. Interfaces. 12 (2020) 26704–26716.

The anticancer peptide LL-III selectively recognizes the human telomere and cMyc G-quadruplexes: new frontiers in the development of effective peptide-based drugs

M. Campanile[1], R. Oliva[1], P. Del Vecchio[1], R. Winter[2], L. Petraccone[1]
[1]Department of Chemical Sciences, University of Naples Federico II, Via Cintia 4, 80126, Naples, Italy
[2] Department of Chemistry and Chemical Biology, TU Dortmund, Otto-Hahn Str. 4a, 44227 Dortmund, Germany
marco.campanile@unina.it

Anticancer peptides (ACPs) are a promising class of compounds for the development of novel drugs due to their low toxicity and high selectivity. Although most ACPs act by targeting the lipid bilayer of cancer cells, some peptides have been shown to translocate into the cell cytoplasm interacting with intracellular targets. [1] The ACP LL-III, a natural cationic peptide from the family of *Lasioglossins*, was found to selectively recognize and cross the negatively charged tumor membrane, localizing in the nucleolus and suggesting that nuclear DNA could be an intracellular target. [2,3,4] In this study, we explored the ability of LL-III to interact with cancer-relevant DNA sequences known to adopt G-quadruplex (GQ) structure, non-canonical conformations characterized by the stacking of planar guanine tetrads (G-tetrads) stabilized by a cation. [5] Using biophysical techniques such as fluorescence, circular dichroism (CD), and isothermal titration calorimetry (ITC), we investigated the molecular basis underpinning the binding of LL-III to different GQ structures, including the human telomeric sequence (Tel-23), cMyc, and cKIT1. Our results showed that LL-III discriminates among different DNA structures, in terms of sequence and topology, with a marked preference towards GQs when compared to duplex and disordered DNA. Interestingly, we measured the highest affinity (K_D ~ nM, see Figure) for the parallel cMyc and the mixed-type Tel-23, two well-known relevant anticancer targets. The binding process was found to be endothermic and entropically driven for all GQs, with the higher $\Delta_b H°$ values observed in the complexes where LL-III adopts a partially helical conformation, suggesting that the peptide/DNA recognition occurs through hydrophobic interactions between the most solvent-exposed G-tetrads and the peptide aromatic and apolar residues. Our findings support the idea that GQs recognition could be involved in the mechanism of action of LL-III, and that this peptide could represent a lead sequence for the development of new and highly selective peptide-based anticancer drugs.



Column bar reporting the K_D values determined for the DNA sequences employed in this study.

[1] F. Harris et al. Med. Res. Rev. 33 (2013) 190-234
[2] V. Čeřovský et al. ChemBioChem 10 (2009) 2089-2099
[3] J. Slaninová et al. Peptides 33 (2012) 18-26
[4] M. Campanile et al. Phys. Chem. Chem. Phys. 25 (2023) 3639-3650
[5] S. Neidle et al. Nat. Rev. Chem. 1 (2017) 0041

Polymeric electroactive P3HT-MWCNT composites for bioelectronic applications

Paola Campione[1,2,3], Grazia M.L. Messina[1], Francesca Santoro[2,3], Giovanni Marletta[1]
[1] Laboratory for Molecular Surfaces and Nanotechnology (LAMSUN), Department of Chemical Sciences, University of Catania and CSGI, Italy
[2] Institute of Biological Information Processing-Bioelectronics, IBI-3, Forschungszentrum Juelich, Germany
[3]Faculty of Electrical Engineering and IT, RWTH Aachen, Germany
Presenter's e-mail address: paola.campione@phd.unict.it

One of the main challenges in bioelectronics concerns the development of materials able to respond to external stimuli and that are compatible with neuronal tissues. In the last decades, conductive polymers (CPs) have been widely studied and developed as electroactive materials for applications in interfacing with biological systems [1]. Their conductive properties allow cells or tissues growth upon stimulation, and their "soft" nature allows to reduce the mechanical mismatch between material and cells thanks to the elasticity of polymeric films that is similar to biological tissues [2]. CPs' physical and electrical properties can be optimized through the formation of composites enriched with carbon nanotubes [3] or graphene in order to improve electron transport capacity, decrease impedance and increase flexibility. Their biocompatibility can be improved using functionalization methods with biologically active molecules [4,5], even if the influence of blending agents is still under investigation. The precise control of CP films nano-topography may have interesting effects for biointerfacing in terms of protein adsorption and cell adhesion. In this work, we report on how to deposit electroactive nanocomposites using semiconducting regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT), with small percentages in weight of multi- and single-walled carbon nanotubes (MWCNT, SWCNT) and reduced graphene-oxide (rGO). As the P3HT-MWCNT-based film systems appear to be the most promising ones for the conductivity properties, the attention has been focused on them. In particular, their morphology and mechanical properties (Young's Modulus) have been investigated by means of atomic force microscopy (AFM) and scanning electron microscopy (SEM), while their interaction with different extracellular matrix proteins were investigated by means of quartz crystal microbalance with dissipation monitoring (QCM-D). Noteworthy, it has been found that proteins are adsorbed in a very different way with respect to the bare semiconducting P3HT. Indeed, both the adsorption kinetics and the adsorbed mass are specific for each different extracellular matrix proteins. The biocompatibility of the systems with different cell lines has been investigated. These results pave the way to the unravelling of the role of the electrical properties of substrates on the interaction with biological moieties for future applications as platform for electrochemical devices in bioelectronics.

[1] Nezakati, T. et al. Chem. Rev. 118 (2018) 6766–6843
[2] Malliaras, G. Biochimica et Biophysica Acta 1830 (2013) 4286–4287
[3] Yao, Y. et al. Anal. Bioanal. Chem. 387 (2007) 303-309
[4] Scarpa, G. et al. Macromol. Biosci 10 (2010) 378–383
[5] Scarpa, G. et al. IEEE (2009) 265-268

Effect of external magnetic fields on the contact angle of magneto-responsive fluids

Michael Casale[1,*], Yassine Bentahar[2], Silvia Vicini[1],Marco Piccinni[1,*], Sawssen Slimani[1,4],
Pavel Kuzhir[2], Pauline Rulliere[3], Davide Peddis[1,4], Diego Colombara[1]
[1] Dipartimento di Chimica e Chimica Industriale &INSTM, Università degli Studi di Genova, Via Dodecaneso, 31, 16126 Genova, Italy
[2]Laboratoire de Physique de la Matière Condensée, CNRS UMR 6622 Université de Nice, Parc Valrose, 06108 Nice Cedex 2, France
[3]Laboratoire SOLVIONIC, 11 Chemin des Silos, 31100 Toulouse, France
[4]Institute of Structure of Matter, National Research Council, nM2-Lab, Via Salaria km 29.300, Monterotondo Scalo 00015, Roma, Italy

michael.casale@edu.unige.it
marco.piccinni@edu.unige.it

The increasing demand of technological devices and fabrication thereof has led to the development of so-called smart materials (SMs). SMs can change their chemical and physical properties upon various external stimuli (electric, mechanical, magnetic, thermal, luminous). The use of magneto-responsive fluids could enable novel technological applications if it were possible to control the contact angle by tuning the amplitude and gradient of an external magnetic field. In this contribution, we focus on the magneto-response of two separate systems: a ferrofluid based on γ-Fe_2O_3 and magnetic ionic liquids (MILs, i.e. liquid salts at room temperature where one of the ions is magnetic, such as iron, cobalt, nickel). γ-Fe_2O_3 ferrofluids have been extensively investigated in the literature and some studies reported that their wettability (i.e. contact angle) varies under magnetic field gradients. For what concerns MILs, several studies reported their synthesis and their characterization, but their wettability under a magnetic field has not been investigated yet. However, contact angles depend on the balance between surface tension, i.e. those of the substrate, of the fluid drop being investigated, and on the other surrounding phase (be it vacuum, air or a second liquid). Hence, in this study we also investigate the effect of a second immiscible liquid on the wettability of γ-Fe_2O_3 ferrofluid and MILs. Lastly, we correlate the contact angle measured experimentally with the magnitude of the magnetic field gradient generated in our custom-made setup, as reconstructed by Hall probe 3D-mapping.

[1] Z. Zhang, K. G. Demir, and G. X. Gu, "Developments in 4D-printing: a review on current smart materials, technologies, and applications," Int J Smart Nano Mater, vol. 10, no. 3, pp. 205–224, Jul. 2019, doi: 10.1080/19475411.2019.1591541.

[2] J. Wang, H. Yao, Y. Nie, X. Zhang, and J. Li, "Synthesis and characterization of the iron-containing magnetic ionic liquids," J Mol Liq, vol. 169, pp. 152–155, May 2012, doi: 10.1016/j.molliq.2012.02.005.

[3] S. Guba, B. Horváth, and I. Szalai, "Examination of contact angles of magnetic fluid droplets on different surfaces in uniform magnetic field," J Magn Magn Mater, vol. 498, Mar. 2020, doi: 10.1016/j.jmmm.2019.166181.

[4] A. Stammitti-Scarpone and E. J. Acosta, "Solid-liquid-liquid wettability and its prediction with surface free energy models," Advances in Colloid and Interface Science, vol. 264. Elsevier B.V., pp. 28–46, Feb. 01, 2019. doi: 10.1016/j.cis.2018.10.003.

G-quadruplex/ligand interaction in anticancer therapy: a physico-chemical study

Federica D’Aria[1], Bruno Pagano[1], Jussara Amato[1], Luigi Petraccone[2], Concetta Giancola[1]
[1] *Department of Pharmacy, University of Naples Federico II, Naples 80131, Italy*
[2] *Department of Chemical Sciences, University of Naples Federico II, Via Cintia 4, 80126 Naples, Italy*
federica.daria@unina.it

The structural polymorphism of DNA allows for the formation of non-canonical secondary structures, such as G-quadruplexes (G4s). G4s are formed by guanine-rich sequences that build-up into guanine tetrads stabilized by Hoogsteen hydrogen bonds and monovalent cations [1]. G4 structures are located in key functional regions of human genome, such as telomeres and oncogene promoters, therefore representing promising anticancer drug targets [2]. Several evidence has shown that G4 formation in oncogene promoters and their stabilization with G4-ligands can downregulate the expression of the corresponding oncoproteins [3]. In this context, the deep understanding of the energetics of G4 structures and their complexes with ligands is of enormous importance, in order to design molecules with highest affinity for G4s, and consequently increased biological activity [4]. Regardless of their function, efficient and controlled formation and unwinding of G4s are very important, because ‘mis’-regulated G4 structures cause genome instability and diseases. In particular, numerous helicases have been shown to target and regulate G4 structures, and hence play a key role in G4 metabolism [5]. Therefore, G4-helicase complexes are attractive anticancer targets and this area significantly overlaps the general field of G4-binders. Although there is information on the impact of G4-binders on helicase-G4 recognition/interaction, little is known on the interaction modes and energetics. Here, we applied physicochemical methodologies in combination with biochemical and biological assays to gain information on the G4/drug [3,6] and G4/helicase interactions *in vitro* and *in-cell* [7].

References

[1] D. Sen, W. Gilbert, Nature 334 (1988) 364–366.
[2] H. Tateishi-Karimata, N. Sugimoto, Chem. Commun. 56 (2020) 2379–2390.
[3] S. Balasubramanian, L.H. Hurley, S. Neidle, Nat. Rev. Drug Discov. 10 (2011) 261–275.
[4] F. D'Aria, B. Pagano, L. Petraccone, C. Giancola, Int J Mol Sci. 22 (2021) 448-460.
[5] O. Mendoza, A. Bourdoncle, J.B. Boulé, R.M. Brosh, Jr, J.L. Mergny, Nucleic Acids Res. 44 (2016) 1989–2006.
[6] F. D'Aria, V.M. D'Amore, F.S. Di Leva, J. Amato, M. Caterino, P. Russomanno, S. Salerno, E. Barresi, M. De Leo, A.M. Marini, S. Taliani, F. Da Settimo, G.F. Salgado, L. Pompili, P. Zizza, S. Shirasawa, E. Novellino, A. Biroccio, L. Marinelli, C. Giancola, Eur. J. Pharm. Sci. 149 (2020)105337-105350.
[7] F. D'Aria, E. De Piante, L.M.R. Napolitano, J. Amato, S. Pirrello, S. Onesti, C. Giancola, *Submitted*.

Polydopamine-coated liposomes: preparation, characterization, and evaluation of their behavior in biological fluids

Vincenzo De Leo[1], Anna Maria Maurelli[1], Valeria Daniello[2], Cosima Damiana Calvano[1], Sante Di Gioia[2], Massimo Conese[2], Francesco Milano[3], Fulvio Ciriaco[1], Chiara Ingrosso[4], Lucia Catucci[1]
[1]Department of Chemistry, University of Bari Aldo Moro, Via Orabona 4, 70126 Bari, Italy
[2]Department of Medical and Surgical Sciences, University of Foggia, Viale L. Pinto 1, 71122 Foggia, Italy
[3]Institute of Sciences of Food Production of National Research Council (CNR-ISPA),
S.P. Lecce-Monteroni, Lecce, 73100, Italy
[4]Institute for Chemical and Physical Processes of National Research Council (CNR-IPCF), S.S. Bari,
c/o Department of Chemistry, University of Bari, via Orabona 4, 70126 Bari, Italy
vincenzo.deleo@uniba.it

Polydopamine (PDA) is a bio-inspired synthetic polymer characterized by strong adhesive properties. It is a polymer easily obtainable in water and under oxidizing mild conditions, fully biocompatible and biodegradable. For this reason, it has often applications in the biomedical field. Despite its promising characteristics and the numerous studies that have involved it, the behavior of PDA in biological fluids has so far been little investigated.

In our laboratories we have developed a simple procedure to obtain a nanocarrier made up of liposomes stabilized by a layer of PDA (Lipo@PDA) potentially useful for applications in the field of drug delivery [1]. We have carried out a complete characterization of the prepared systems by TEM, DLS and Zeta potential analysis, and we have studied the experimental parameters (concentration of the monomer, temperature, polymerization time) which determine the growth of the polymer around the lipid vesicles. The stability of the Lipo@PDA vesicles in buffer was monitored at different temperatures. Subsequently the behavior of the nanocarriers was studied in Fetal Bovine Serum to simulate the interaction of Lipo@PDA with biological fluids. In particular, the stability of Lipo@PDA vesicles under these conditions and the formation of the so-called Protein Corona [2], i.e. the layer of proteins that interact with the surface of the material, were studied. For this purpose, the proteins were separated by means of SDS PAGE, quantified with the Bradford assay, and then analyzed by means of LC-ESI-MSMS. In addition, the Lipo@PDAs were subjected to a hemolysis assay with the red blood cells obtained from the human plasma. Finally, cytotoxicity tests with respect human respiratory epithelial cells were performed. The data obtained from all experiments were compared with those of PEG-stabilized liposomes, which are already normally used for the delivery of different drugs in clinical practice. Overall, the results obtained show that the behavior of the Lipo@PDA is partly influenced by the thickness of the polymerized PDA around the vesicles. Furthermore, by controlling the polymerization parameters of the PDA it is possible to obtain systems with behavior in biological fluids similar to that found for PEG-coated liposomes. We believe that these results can pave the way for real applications of Lipo@PDAs in the biomedical field.

[1] V. De Leo et al. Int. J. Mol. Sci. 22(21) (2021), 11916
[2] T. Cedervall et al. PNAS 104 (2007) 2050

Cyclodextrins: how to face an open challenge with state-of-the-art computational methods

R. Ferrero[1], S. Pantaleone[1], F. Caldera[1], F. Trotta[1], V. Brunella[1], M. Corno[1]
[1]*Department of Chemistry and Nanostructured Interfaces and Surfaces (NIS) Centre, University of Turin, Turin, Italy*
riccardo.ferrero@unito.it

Cyclodextrins (CDs) are cyclic oligosaccharides made up of α-D-glucopyranose monomeric units connected by α-(1-4) glycosidic bonds and characterized by a non-symmetric toroidal structure that gives to the molecule a truncated hollow cone shape.

CDs have received much attention in different applicative fields, from the Drug Delivery to the environmental sector, thanks to the marked tendency to form inclusion complexes with a large variety of substrates (e.g., pharmacologically active molecules, metal cations, vitamins…)[1]. Among several possible guest molecules, melatonin plays an essential role as a radical inhibitor and treater of sleeping disorders[2]. Therefore, many computational works were performed on these systems to clarify the structural, energetic and vibrational properties of the CDs as itself or in complexation with a guest molecule[3]. The choice of methods represents a crucial step in the modeling of CDs and vary from the molecular mechanics level, that allows the study of solvation without reaching a high-level of accuracy, to the DFT studies, generally limited to arbitrary selected conformations and using implicit solvation model.

Our focus has thus been to investigate the possible conformations of the three most used CDs, labelled α-, β- and γ-cyclodextrin, with 6, 7 and 8 units of monomer, respectively. A benchmark study was performed starting with a semiempirical methodology to explore the potential energy surface. To do so, simulations were carried out with xTB code at GFN2 level of theory, employing the submodule CREST[4]. Then, the lowest-energy structures were re-optimized with two recently released DFT composite methods, B97-3c and r^2-SCAN-3c[5], and the results compared with three double-hybrid DFT functionals. The presence of water was simulated using the ALPB implicit solvation model and the submodule QCG to treat the CDs structures with explicit solvation.

Results have shown that α- and β-cyclodextrins prefer the closed conformation in gas phase and the open one in implicit water, while the open conformation of γ-cyclodextrin is the most stable one in both cases. r^2-SCAN-3c has demonstrated to be very robust even against more accurate DFT methods, so representing the election method for the CDs modeling.

After the validation of the abovementioned approach, an analogous workflow has been applied to the inclusion complex between β-cyclodextrin and melatonin. Conformational researches performed with CREST constituted the starting point, followed by re-optimization of the structures with r^2-SCAN-3c. Binding energies and vibrational properties were computed for the most stable structures, highlighting the preferred orientation of complexation.

These recent and ever faster functionals have allowed us to model cyclodextrins and their inclusion complexes with good accuracy, so as to suggest that ongoing work on CDs is far from finished not only on the single complex but also to achieve the description of periodic or amorphous CD-based structures.

[1] P. Jansook et al. Int J Pharm 535 (2018) 1-2
[2] S. Tordjman et al. 15 (2017) 3
[3] S. Muzaffar et al J Mol Struct 1217 (2020)
[4] C. Bannwarth et al J Chem Theory Comput 15 (2019) 3
[5] S. Grimme et al Journal of Chemical Physics 154 (2021) 6

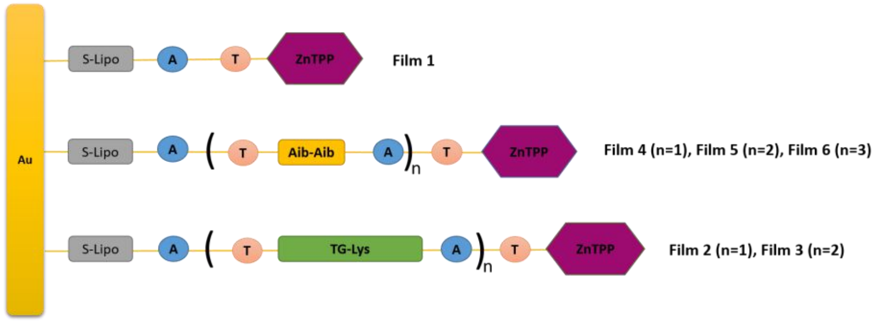
Abstract ID. T2O08

Photocurrent Generation in Supramolecular Bio-Inspired Nanoarchitectures on Gold Surface

Emanuela Gatto,[1] Sascha Kubitzky,[1] Elena Passaretti, [1] Mariano Venanzi,[1] Raffaella Lettieri,[1] Marta De Zotti[2]

[1]Department of Chemical Science and Technologies, University of Rome Tor Vergata, 00133 Rome (Italy)
[2]Institute of Biomolecular Chemistry, Padova Unit, CNR, Department of Chemistry, University of Padova, 35131 Padova (Italy)

Fabrication of ordered three-dimensional nanostructures on surface is an ongoing challenge in the field of materials science. In particular, molecular order and perfect positioning of different redox centers are of fundamental importance in building-up artificial photosynthetic systems, to control the direction of the electronic flow. Different systems with all subunits covalently linked have been reported in the literature, but the synthetic effort to obtain these multicomponent molecules is considerable. In Nature all supramolecular architectures are built up by non-covalent interactions [1], between them hydrogen bonds. In particular, DNA molecules are engineered using pair up of nucleobases. In this lecture, studies on photocurrent generating supramolecular components built with an unprecedented approach will be shown: using the thymine-adenine DNA base pairs approach to construct supramolecular films in 3D, composed of different 2D layers. To this end, we have engineered three types of photocurrent generating films on gold surfaces [2]. Film **1-6** consists of multilayered systems where the light absorbing group (ZnTPP chromophore) is noncovalently linked to a gold surface through thymine-adenine hydrogen bond. These films are assembled by consecutive deposition of each layer. In film **1**, two components are used: adenine linked to a lipoic acid molecule (Lipo-A) to covalently bind the gold surface, and ZnTPP linked to a thymine molecule (T-ZnTPP). Film **2-6** have additional noncovalently linked layers. In film **2** and **3**, respectively, one or two layers of a helical undecapeptide analogue of the trichogin GA IV peptide were inserted (TG-Lys). In this peptide four glycine were replaced by four lysine residues to favor helical conformation and reduce conformational flexibility. The presence of Lys residues also confers pH sensitivity to the peptide secondary structure [3]. In film **4, 5** and **6**, respectively, one, two or three layers of a dipeptide, (Aib)$_2$, were inserted, in order to control the film length. The peptide termini were functionalized with thymine and adenine, respectively, to enable Lipo-A and T-ZnTPP conjugation. These films have been characterized by electrochemical and spectroscopic techniques, and have been found to be very stable over time, also in contact with a solution. They were also able to generate current under illumination, with an efficiency higher than the one recorded in similar systems.



[1] Gatto E. et al. *Langmuir 28* (2012) 2817
[2] Gatto E. et al. *Angew. Chem. Int. Ed.* 58 (2019), 7308
[3] Gatto, E. et al. *Chemistry Eur. J.* 27(2021), 2810

Modeling Complex Spectroscopies of Systems in Complex Environments

Sara Gómez, Piero Lafiosca, Tommaso Giovannini, Chiara Cappelli
Scuola Normale Superiore, Piazza dei Cavalieri, 7 I-56126 Pisa (Italy)
sara.gomezmaya@sns.it

Resonance Raman (RR) spectroscopy and especially UVRR has a large potential to unveil the structural and electronic properties of systems embedded in different environments.[1] RR provides selectivity and sensitivity through the enhancement of particular vibrations associated with specific chromophores when the incident wavelength is tuned to match a specific electronic transition of the system[2]. Experimentally, many biological systems are studied by using this technique, but its computational simulation is far from trivial[3,4]. Indeed, computing the property in a complex environment requires that the effects arising from electronic and vibrational parts (electronic transitions, normal modes, and polarizabilities) be coherently inserted into the model. In addition, there are two key points to consider when modeling RR in complex systems: (i) treating large systems implies including hundreds of vibrations in the calculation of the final spectra, and (ii) obtaining a reliable spectroscopic signal needs an adequate sampling of the configurational phase space of the target-environment system, which means that the vibrational analysis has to be performed on each configuration, thus further increasing the computational complexity.

We have extended our atomistic multiscale computational protocol, which has been proven successful to model spectral signals in aqueous solutions[5,6,7], to more complex systems, such as chromophores embedded in biological matrices by proposing a series of strategies to compute the normal modes at different levels of sophistication. In particular, we focus on Doxorubicin, a widely used chemotherapy agent, intercalated into DNA[8]. For that system, the good agreement between computed and experimental data allows us to easily identify the main features of RR spectra in both aqueous and DNA solutions, confirming the reliability of our methods. This methodology is very versatile and thus suitable for promising applications to complex biosystems.

[1] S. A. Oladepo et al. J. Phys. Chem. Lett. 2 (2011) 334–344
[2] I. López-Peña et al. Biochemistry 54 (2015) 4770−4783
[3] A. Baiardi et al. J. Chem. Phys. 141 (2014) 114108
[4] F. Egidi et al. J. Chem. Theory Comput. 10 (2014) 346−363
[5] T. Giovannini et al. Chem. Soc. Rev. 49 (2020) 5664−5677
[6] S. Gómez et al. J. Phys. Chem. Lett. 13 (2022) 6200−6207
[7] S. Gómez et al. J. Mol. Liq. 346 (2022) 117841
[8] S. Gómez et al. J. Chem. Inf. Model. 63 (2023) 1208−1217

Photosynthetic Bacteria Biohybrid Systems for Self-Powered Pollutants Detection

Jefferson Honorio Franco[1], Paolo Stufano[2], Dario Lacalamita[1], Massimo Trotta[3], Matteo Grattieri[1,3]
1 Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Bari, 70125, Italy
2 CNR-NANOTEC, Consiglio Nazionale delle Ricerche, Bari, 70125, Italy
3 IPCF-CNR, Consiglio Nazionale delle Ricerche, Bari, 70125, Italy
jeffersonhfranco@gmail.com

Industrial waste streams are the main source of heavy metals contamination in water environments as they can be found in several industrial effluents.[1] Purple bacteria have been employed as a versatile, well characterized photosynthetic system able to perform sun-powered decontamination of water environments.[2] *Rhodobacter capsulatus* (*R. capsulatus*) is a purple non-sulfur photosynthetic bacterium (PNSB) that is able to grow under diverse environmental conditions, ensuring an outstanding metabolic versatility.[2] Remarkably, PNSB bacteria have shown unique metabolic characteristics towards several organic compounds, which opens up opportunities for the development of hybrid electrochemical systems for pollutants biosensing. Specifically, their implementation in biohybrid systems to obtain portable self-powered biosensors devices is particularly appealing.[3] In this work, we report the effects of various pollutants on a hybrid biophotoelectrode, using a home-made poly-hydroxybutyrate (PHB)-carbon nanofibers (CF) electrode modified with a redox-adhesive matrix based on purple bacteria and polydopamine (PDA).[4] The possibility to combine this biohybrid electrode with a sustainable carbon-based cathode was also explored to obtain a self-powered biosensor for in-situ monitoring of contaminants. The performance of the biohybrid system, evaluated by electrochemical and spectroscopic techniques in the presence and absence of both light and pollutants will be presented. Finally, the future challenges to obtain photobioelectrocatalytic system capable of long-term operation to produce enhanced, portable, self-powered biosensor for environmental remediation purposes will be pointed out.

Reference

(1) V. Kumar et al. J. Water Process. Eng. (2022) 47.
(2) L. D. Torquato et al. Curr. Opin. Electrochem. (2022) 34.
(3) M. Grattieri, Photochem. Photobiol. Sci. (2020) 424.
(4) G. Buscemi et al. ACS Appl. Mater. Interfaces (2022) 26631.

Characterization of a 3D Bioprinted Tumor Model by Scanning Electrochemical Microscopy

Marco Malferrari[1], Maila Becconi[1], Simona De Zio[1], Francesco Falciani[1], Marzia Santamaria[1], Stefania Rapino[1]
[1] Department of Chemistry "Giacomo Ciamician", University of Bologna, via Francesco Selmi 2,
40126 Bologna, Italy
e-mail: marco.malferrari2@unibo.it

The cell microenvironment is a fundamental determinant of cellular physiology; its role is crucial in many pathologies and its influence key in therapy resistance and morbidity relapse [1].

3D bioprinting emerged as an attractive technique to create *in vitro* tridimensional models that approach the complexity of tissues. In particular, 3D-bioprinting of *in vitro* tumor models is an extremely promising approach for studying cancer cell biology [2]. However, despite an increasing number of 3D cellular culture types available, a fine and quantitative characterization of the microenvironment established in 3D cultures and 3D-bioprinted models is still lacking.

We recently fabricated a cervical tumor model by 3D-bioprinting HeLa cells in an alginate-based matrix [3]; phase-contrast and confocal fluorescence microscopies have been used to describe the spheroid population as a function of the post printing culturing time. We finely measured a key component of the cell microenvironment in the 3D model, i.e., oxygen concentration, with a high spatial resolution by employing scanning electrochemical microscopy and nanoelectrodes as probes of this technique [3]. We also quantitatively studied the diffusion of a molecule in the 3D bioprinted model over time to model drug diffusion in the 3D construct [3]. The combination of 3D bioprinting and characterization by scanning electrochemical microscopy have been shown to be a valuable approach for the development of *in vitro* 3D cancer models with quantifiable characteristics of the cell microenvironment.

[1] M.R. Junttila et al., Nature 501 (2013) 346
[2] M. Ravi et al., J. Cell Physiol. 230 (2015) 16
[3] M. Becconi et al., Cancers 15 (2023) 1327

Water-based Deep Eutectic Solvents: a new generation of green solvents

Emanuela Mangiacapre[1*], Franca Castiglione[2], Fabrizio Lo Celso[3], Martin Brehm[4], Alessandro Triolo[5], and Olga Russina[1]
[1]*Chemistry Dept. - University of Rome Sapienza, Rome, Italy*
[2]*Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Italy.*
[3]*Physics and Chemistry Dept. - University of Palermo, Palermo, Italy*
[4]*Institut für Chemie, Martin-Luther-Universität Halle–Wittenberg, Halle (Saale), Germany*
[5]*Istituto Struttura della Materia – Consiglio Nazionale delle Ricerche (ISM-CNR), Rome, Italy*
[*]*emanuela.mangiacapre@uniroma1.it*

Deep Eutectic Solvents (DESs) are promising sustainable media for a variety of applications. They can be defined as low-freezing mixtures formed by a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), with melting point below the ideal mixture one. Currently, research is focused on modulating of new DESs made up of eco-friendly components and with properties of practical interest, where water is typically present as either a contaminant or an additive. Only recently water was employed as an active component in DESs, thus leading to water-based DES (WB-DES) concept.

In this context, choline chloride:water (ChCl:W) mixtures were recently introduced as auspicious and low-viscosity WB-DESs. Solid-liquid equilibrium analysis shed light on the Deep Eutectic behavior of 1:4 mixture (termed as *aquoline*). Indeed, when approaching $X_{ChCl}=0.2$, melting point drastically drops, leading to a deep eutectic state at conditions completely different from the ideal behaviour (ca. $X_{ChCl}=0.27$ and $T_m=240$ K) [1,2].

Nevertheless, information on the role of water in WB-DES is lacking yet. To contribute to this issue, the behavior of different ChCl:W and other WB-DES was investigated in terms of different physicochemical properties (density, viscosity and refractive index), thermal behavior and structural investigations.

Temperature and concentration dependence of density and viscosity of eutectic mixtures were modelled. The temperature dependence of the isobaric thermal expansion coefficient α was monitored. Experimental X-ray analysis highlighted no existence of a mesoscale aggregation for the probed systems. Furthermore, for the ChCl:W system, NMR studies and ab initio-MD simulations suggested the presence of a clathrate-like structures, where chloride and water form a cage around choline hydroxyl. The reported WB-DES systems represent new media, which will pave the way to a new class of solvents with smart and eco-friendly features.

[1] A. Triolo, F. Lo Celso, M. Brehm, V. Di Lisio, O. Russina, Liquid structure of a choline chloride-water natural deep eutectic solvent: A molecular dynamics characterization, J Mol Liq. 331 (2021). https://doi.org/10.1016/j.molliq.2021.115750.

[2] E. Mangiacapre, F. Castiglione, M. D'Aristotile, V. Di Lisio, A. Triolo and O. Russina, Choline Chloride-water mixtures as new generation of green solvents: a comprehensive physico-chemical study. Journal of Molecular Liquids (accepted).

First detection of µ-plastics in human urines and kidneys using µ-Raman spectroscopy

Sara Massardo[1], Edoardo La Porta[2], Enrico Verrina[2], Stefano Alberti[1], Claudia Caboni[1], Matteo Santostefano[3], Daniela Verzola[4], Pasquale Esposito[4,5], Francesca Viazzi[4,5], G. Zaza[6], Cristina Artini[1,7]
[1] *DCCI, University of Genova, Via Dodecaneso 31, 16146 Genova Italy*
[2] *UOC Nephrology, IRCCS Istituto Giannina Gaslini, Via G. Gaslini 5, 16147 Genova Italy*
[3] *PM_TEN Srl, P.zza della Vittoria 7/14, 16121 Genova, Italy*
[4] *Department of Internal Medicine, University of Genoa, Viale Benedetto XV 6, 16132 Genova, Italy*
[5] *IRCCS Ospedale Policlinico San Martino, Largo R. Benzi 10, 16132 Genova, Italy*
[6] *Nephrology and Dialysis Unit, Department of Medical and Surgical Sciences, University of Foggia, 71121 Foggia, Italy*
[7] *CNR-ICMATE, Via De Marini 6, 16149 Genova, Italy*
sara.massardo@edu.unige.it

Microplastics (MPs) are defined as small plastic particles, measuring less than 5mm [1]; it is possible to distinguish between primary MPs, produced as such, and secondary MPs, resulting from the breakdown of larger plastic products, or from the shedding of synthetic fibers, or the release from personal care products, in the form of microbeads. Due to their ubiquitous presence in different environments, such as oceans [2], freshwater, and even the air we breathe, MPs became one of the environmental issues of highest concern of the XXI century.

Due to our constant exposure to the such contaminants, microplastics were already detected in human lung, liver, placenta [3], blood and breastmilk, thus pointing at an easy absorption and distribution of such particles in human body. However, health risks related to the assumption of MPs by mammals are still not well clarified, but it is commonly believed that, acting as foreign bodies, they could work as triggers for emerging diseases of unknown etiology, whose correlation with environmental exposure cannot be excluded. An epidemic of Chronic Kidney Disease (CKD) of uncertain etiology is emerging worldwide and then, to evaluate a possible involvement of MPs is crucial. To this end, in human urines and kidney the presence of MPs was investigated. We therefore analyzed properly digested urines (health individuals) and kidneys tissues (1-4 g from nephrectomies), looking for polymers or plastics additives, such as pigments. Analyses were performed using microRaman spectroscopy, a technique of election for the detection of microplastics, thanks to its high spatial resolution and sensitivity towards the presence of polymers and pigments. Our study confirmed the presence of plastic fragments (*e.g. Figure* 1) in both urines and kidneys, but also the presence of commonly employed pigments, such as hematite, laying the basis for further investigations on the mechanisms of excretion of these particles, and on their possible role in promoting kidney damage.

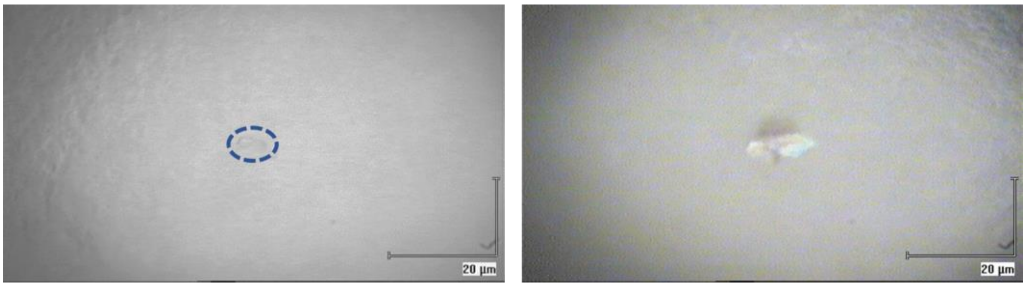


Figure 1 – Polyethylene (left) and polystyrene (right) fragment detected in the samples.

[1] C. Arthur et al. Proceedings of the international research workshop on the occurrence, effects, and fate of microplastic marine debris. NOAA marine debris program. Technical memorandum NOS-OR&R-30 (2009)
[2] D. Ita-Nagy et al. J. Haz. Mater. Adv. 5 (2022) 100037
[3] A. Ragusa et al. Envir. Int. 146 (2021) 106274

Synthesis, characterization, *in vitro* and *in vivo* studies on antibody decorated liposomes encapsulating MCC950 for the treatment of fatty liver disease.

Rita Mastrogiacomo[1-2], Roberto Negro[3], Livianna Carrieri[3], Federica Rizzi[2], Valentina Arrè[3], Gianluca Minervini[2,4], Elisabetta Fanizza[1-2], Giusy Bianco[5], Annamaria Panniello[2], Marinella Striccoli[2], Angela Agostiano[2], Maria Lucia Curri[1-2], Gianluigi Giannelli[6], Maria Principia Scavo[3] and Nicoletta Depalo[2]

1. Chemistry Department, University of Bari Aldo Moro, Via Orabona 4, 70125 Bari, Italy;
2. Institute for Chemical-Physical Processes, Italian National Research Council (IPCF-CNR)-CNR SS Bari, Via Orabona 4, 70125 Bari, Italy;
3. Laboratory of Personalized Medicine, National Institute of Gastroenterology "S. de Bellis" Research Hospital, Via Turi 27, Castellana Grotte, 70013 Bari, Italy;
4. Department of Electrical and Information Engineering, Polytechnic of Bari, Via E. Orabona 4, Bari, 70126, Italy;
5. National Institute of Gastroenterology "S. de Bellis," Personalized Medicine Laboratory, Via Turi 27 Castellana Grotte, Bari, Italy;
6. Scientific Direction, National Institute of Gastroenterology "S. de Bellis," Via Turi 27 Castellana Grotte, Bari, Italy.
e-mail address: *rita.mastrogiacomo@uniba.it*

The inflammatory state represents the hallmark of the Non-Alcoholic Steatohepatitis (NASH): the chronic inflammation together with the deposition of fibrotic tissue lead to more severe stages of the Non-Alcoholic Fatty Liver Disease (NAFLD) up to cirrhosis and hepatocellular carcinoma. The interaction between the inflammatory microenvironment and immune cells is mediated by the activation of the inflammasome NLRP3, a multi-protein complex, whose uncontrolled activation leads to the development of immunosuppression, cancer and metastases. Indeed, the inhibition of NLRP3 inflammasome in immune cells represents a promising therapeutic approach for selectively targeting macrophages that, when activated, are directly involved in the Non-alcoholic fatty liver disease (NAFLD) progression to NASH. MCC950 is a well-known inhibitor of the NLRP3 inflammasome, characterized by a short plasmatic half-life and by the lack of target capability, thus the clinical use of MCC950 could benefit from its encapsulation in nanocarriers. Among synthetic nanovectors, liposomes (LPs) are highly biocompatible, scalable and versatile nanodelivery systems that, due to their structure, can embed hydrophilic, lipophilic and amphiphilic compounds and/or nanoparticles (NPs) for different purposes[1]. Recently, Carbon Dots (CDs) have emerged as a new class of luminescent NPs that, thanks to their easy surface-functionalization and excellent biocompatibility, can serve as effective imaging tool in visual monitoring of biological processes. Hence, polyethylene glycol (PEG)-LPs (co-)loaded with MCC950 and luminescent synthesized CDs[2] have been prepared to obtain optically traceable nanovectors for the treatment of NLRP3. LPs have been prepared by means of a micro-emulsive approach and characterized in terms of morphology, colloidal stability, optical properties and drug loading. The nanoformulations have been finally conjugated with an anti-Frizzled1 antibody, overexpressed on the macrophages membrane, to obtain a targeted nanodelivery system. *In vitro* and *in vivo* studies have been carried out to evaluate the use of the new LP-based formulations, as efficient therapeutic nanovectors able to selectively target macrophages that, when activated, are directly involved in NAFLD disease to prevent the worsening of the liver damage.

This work was partially supported by RC2021-2024 project funded by Ministry of Health, PON TITAN 2021–2023 ARS01_00906 and bilateral project CNR-RFBR (Russia) 2021-2023, joint research project.

[1] Scavo, M. P., et al., Pharmaceutics 2020, 12 (7), 650
[2] Panniello, A., et al., J. Phys. Chem. C 2018, 122 (1), 839-849

Pluronic micelles for curcumin extraction: characterization and potential applications in the biomedical field

Anna Maria Maurelli[1], Vincenzo De Leo[1], Marzia Gariboldi[2], Emanuela Marras[2], Chiara Ingrosso[3], Francesco Milano[4], Lucia Catucci[1]
[1]*Department of Chemistry, University of Bari Aldo Moro, Via Orabona 4, 70126 Bari, Italy*
[2]*Department of Biotechnology and Life Sciences (DBSV), University of Insubria, Via J.H. Dunant 3, 21100 Varese, Italy*
[3]*Institute for Chemical and Physical Processes of National Research Council (CNR-IPCF), S.S. Bari,*
c/o Department of Chemistry, University of Bari, via Orabona 4, 70126 Bari, Italy
[4]*Institute of Sciences of Food Production of National Research Council (CNR-ISPA),*
S.P. Lecce-Monteroni, Lecce, 73100, Italy
anna.maurelli@uniba.it

Curcumin is the main polyphenol extracted from the rhizome of *Curcuma longa*, known for its antioxidant and anti-inflammatory properties. Curcumin is a hydrophobic molecule and requires organic solvents and large amounts of energy to be extracted from the plant matrix. Furthermore, it requires a suitable carrier to increase its bioavailability in a biological environment [1-2].

In this work Pluronic PF127 was used to extract curcumin from turmeric without the use of organic solvents and directly obtain curcumin in a water-soluble form, which can be used in the nutraceutical and biomedical fields. Ultrasound has been used to increase extraction efficiency and decrease the environmental impact of the process. The variation of the CMC of PF127with the temperature was exploited to remove the excess of free surfactant by centrifugal membrane filtration. The effect of the operating parameters on the yield and extraction kinetics was analyzed while the *frozen* micelles were characterized and tested for their antioxidant properties. Peleg's model was used to describe the extraction of curcumin from turmeric under various experimental conditions.

Ultrasounds have led to more performing extractions both in terms of speed and in terms of yield. The micelles have been fully characterized from a chemical-physical point of view by electronic microscopy, spectroscopic and DLS techniques. The antioxidant activity of curcumin in PF127 micelles was evaluated by ABTS assay and it found to be superior to that obtained with commercial curcumin. Finally, biological tests conducted on hct116 colon cancer cell line showed that the IC_{50} values measured for the micelles containing curcumin were lower than that of commercial free curcumin.

[1] De Leo et al. Molecules 23(4) (2018) 739
[2] De Leo et al. Int J Mol Sci. 24(1) (2023) 790

Green selenium nanoparticles in an innovative confined environment: synthesis, characterization, and size prediction

Elena Piacenza[1], Filippo Vitale[1], Delia F. Chillura Martino[1]
[1]Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF), Università degli Studi di Palermo, Viale delle Scienze – Edificio 16, 90128 Palermo (IT)
elena.piacenza@unipa.it

Selenium (Se) nanomaterials captivate researchers due to their biocompatibility, low toxicity, therapeutic potential, and unique optical and semiconductor properties [1,2]. They hold tremendous promise as antimicrobial, antioxidative, and anticancer agents, food supplements, or for renewable energy production, sensor design and function, and optoelectronic device generation [1-3]. However, the challenge impeding their practical application is the limited understanding of their structure-to-property relationship.

Selenium, traditionally classified as a non-metal, tends to crystallize even at room temperature in micro- or macro-aggregates; hence, producing stable SeNPs is imperative for justifying their use. Several synthetic approaches have been explored to overcome this issue, yet most either rely on toxic and harmful compounds and dangerous and energy-demanding operational procedures or yield limited NP stabilization [4]. Surfactants are commonly used as templates to produce metal or metal oxide NPs, although most are toxic or generally harmful. Moreover, only a few studies reported using these surfactants for SeNP production [1].

Given these premises, this study focuses on developing an innovative bio- and eco-compatible confined environment constituted by a safe surfactant (sodium oleate) and a reducing amino acid (L-cysteine) to synthesize stable SeNPs. Firstly, the confined environment was characterized by exploring the impact of an excess of either substance on its overall physical-chemical behavior and interactions between the surfactant and the amino acid. Subsequently, this confined environment was used for SeNP synthesis, exploring diverse concentrations and ratios and focusing on the NP size, shape, and stability. The resulting SeNPs are smaller than those obtained through conventional reduction processes and remained stable for more than two months at room temperature. Using the abovementioned confined environment, we also improve (up to 3-fold) the SeNP amount compared to those obtained in an aqueous environment. This study also introduces a novel SeNP size prediction model based on UV-Visible spectroscopy and Mie's scattering theory, which, although commonly used for metal NPs, was never reported for SeNPs. We efficiently implemented a model that allows us to predict the size of selenium nanoparticles obtained in an aqueous or confined environment, overcoming prediction issues related to other techniques or models (i.e., DLS or Tauc plot). The model is validated by comparing the estimated size distributions with those obtained through STEM microscopy, and it efficiently predicts SeNP size ranging from 20 to 90 nm in diameter.

[1] N. Bisht et al. Mater. Adv. 3 (2022) 1415-1431
[2] S. Chaudhary and S.K. Metha. J. Nanosci. Nanotechnol. 14 (2014) 1658-1674
[3] E. Piacenza, et al. Nanophotonics 9 (2020) 3615-3628.
[4] E. Piacenza et al. Phys. Sci. Rev. 3 (2018) 20170100

Vibrational Spectroscopy for the Detection and Identification of Myocardial Chemical Alterations in Heart-Failure with Preserved Ejection Fraction

Leonardo Pioppi[1], Reza Parvan[2], Alan Samrend[2], Gustavo Jose Justo Da Silva[2], Marco Paolantoni[1], Alessandro Cataliotti[2], Paola Sassi[1]
[1]*Department of Chemistry, Biology and Biotechnology, University of Perugia, I-06123 Perugia, Italy*
[2]*Institute for Experimental Medical Research, Oslo University Hospital and University of Oslo, Oslo, Norway*
leonardo.pioppi@studenti.unipg.it

The use of spectroscopic techniques for characterizing biological specimens can represent a valid alternative to histopathology. In most cases, the interaction between electromagnetic radiation and matter allows fast, label-free, and chemical-specific analysis of biological samples overcoming the typical limitations of histological procedures. Classical histological methods require multiple time-consuming manipulation steps that need many chemicals for fixation, inclusion, and staining procedures that can significantly alter the structure and composition of the biological specimen of interest, increasing the risk of contamination [1]. Additionally, each histological protocol is suitable to monitor a few biomolecules at a time; a complete characterization requires serial staining and sectioning steps, resulting in bigger sample sizes and longer diagnostic times. In recent years, the spectroscopic investigation of biological samples has mostly focused on the diagnosis of several types of cancers and neurological disorders [2], but other pathologies, such as cardiovascular ones which affect the lives of millions of people in the world, require particular attention. Vibrational spectroscopy can be a valuable tool for monitoring the markers of cardiovascular diseases [3]. Heart Failure with Preserved Ejection Fraction (HFpEF) is a major clinical challenge that is associated with a markedly high risk of death. Its development is often the result of the contribution of severe comorbidities such as obesity, diabetes, and hypertension [4]. The challenging diagnosis of HFpEF is often belated and the treatment of this condition remains largely unsuccessful, with a five-year survival rate of 43% after a first diagnosis. In addition, the wide plethora of comorbidities associated with HFpEF makes the disease's progression mechanism unknown. In this work, we perform an ex-vivo micro-FTIR and micro-Raman scattering analysis of the cardiac ventricles of rats to detect biochemical alterations due to the progression of HFpEF and obesity and diabetes as comorbidities. Spectroscopic markers related to the severe clinical picture were identified and respectively attributed. Interesting results are presented and discussed.

[1] R. Zehbe et al. J. R. Soc. Interface 7 (2010) 49
[2] V. Balan et al. Materials. 12 (2019) 2284
[3] N. Tombolesi et al. Sci. Rep. 12 (2022) 3440
[4] R. Altara, M. et al. Front.Endocrinol. 8 (2017) 160

Dendritic mesoporous silica core@shell nanostructures with dahlia-like morphology as pH-responsive delivery systems of 5-Fluorouracil for colorectal cancer treatment

Federica Rizzi[1], Maria Principia Scavo[2], Pierluigi Lasala[1,3], Rita Mastrogiacomo[1,3], Adriana Grandolfo[1,4], Maria Luisa Cistulli[3], Livianna Carrieri[2], Rachele Castaldo[5], Angela Agostiano[1,3], Maria Lucia Curri[1,3], Elisabetta Fanizza[1,3] and Nicoletta Depalo[1]
[1]*Institute for Chemical and Physical Processes (IPCF)-CNR SS Bari, 70126, Italy*
[2]*Personalized Medicine Laboratory, National Institute of Gastroenterology "S. De Bellis", 70013, Italy*
[3]*Department of Chemistry, University of Bari, 70126, Italy*
[4]*Department of electrical and information engineering, Polytechnic of Bari, 70126, Italy*
[5]*Institute for Polymers, Composites and Biomaterials (IPCB)-CNR, 80078, Italy*
f.rizzi@ba.ipcf.cnr.it

5-Fluorouracil (5-FU) is a chemotherapeutic agent used for the first line treatment of the advanced colorectal cancer (CRC), although suffering limitations including short biological half-life and tumour cell resistance, resulting in multiple administration of high doses and severe toxicity [1]. Therefore, the development of drug delivery systems for the selective CRC targeting and treatment is required to promote the accumulation of the 5-FU to specific CRC sites and to reduce the side effects. Recently, the Frizzled 10 (FZD10) protein, a cell surface receptor belonging to the FZD protein family overexpressed in CRC cells, has been suggested as candidate for CRC targeting [2]. Dendritic mesoporous silica nanoparticles exhibit attractive properties as a novel drug delivery platforms, thanks to their unique structure including high surface area and pore volume, tuneable pore size, high therapeutic loading capacity, minimizing adverse effects and, enhancing biocompatibility and biodegradability [3]. In addition, core@shell nanostructures consisting of non-porous silica core and mesoporous silica shell allow to incorporate additional functional nanoparticles into the solid core thus providing multifunctional nanomaterials. Furthermore, the surface of these nanostructures can be easily functionalized with ligands or stimuli responsive polymers to obtain nanovectors for targeted, controlled and sustained drug delivery. Here, core@shell nanostructures with non-porous core of about 30 nm and a dendritic mesoporous shell with dahlia-like morphology and pore size ranging from 3-4 nm up to tens of nm have been synthesized (SiO_2@MSNs) and explored for the delivery of the 5-FU. In particular, pH-responsive polymer-gated and CRC targeted SiO_2@MSNs have been fabricated by grafting their surface, first with the polyacrylic acid (PAA) and then with FZD10 antibody and finally loaded with the anticancer drug. The PAA grafted SiO_2@MSNs, loaded with the 5-FU, allow the drug release only at pH>5 (as in colon environment) that is when the PAA expands, thus opening the silica pores, while preventing the delivery of the cargo at acidic pH (e.g. in gastric environment), when the polymer, coiling up, close the pores. The nanostructures have been extensively characterized in terms of size, morphology, colloidal stability, drug loading and drug release at different pH values. The effect of the nanostructures on cell viability and their targeting ability have been evaluated on different CRC cell lines, such as human colon epithelial, non-metastatic and metastatic human colorectal adenocarcinoma cells. The overall outcomes have proved the fabrication of efficient pH-responsive FZD10 antibody functionalized SiO_2@MSNs delivering the 5-FU, with final size of about 200 nm (σ%= 4%), a relevant colloidal stability in aqueous media, and a drug loading of about 15%, thus resulting promising candidates for targeted treatment of CRC.

Acknowledgement: This work was developed in the framework of the Bilateral Project CNR-RFBR Russia Joint research project (2021-2023) and TITAN-Tumor Immunotherapy by Nanotechnology, Project ID:PON ARS01_00906|(PVO-704)

[1] R. Rampado et al., Journal of Oncology 2019, 27
[2] M.P. Scavo et al., Pharmaceutics 2020, 12, 650
[3] Y. Wang et al., Nano Today 2021, 39, 101231

The effects of the interplay of substrate surface free energy and nano-geometry on the assembly of semi-crystalline polymer thin films

Roberta Ruffino[1], Giovanni Li Destri[1] and Giovanni Marletta[1].
[1]Department of Chemical Sciences, University of Catania, Viale A. Doria 6, 95125 Catania, Italy.

Conjugated semi-crystalline polymeric thin films are among the most investigated soft systems acting as active materials in light plastic electronic devices. The geometry constraints imposed by the nanometric thickness and the interfacial interactions affect the self-assembly process and, in turn, their behaviour.[1,2] The combination of geometric effects, i.e. surface nanocurvature, with surface free energy (SFE) gives the possibility to finely control the self-assembly. To this end, we have studied the influence of controlled nano-curvature and SFE on the self-assembly process of semicrystalline poly-3-hexylthiophene (P3HT).[3,4] From the morphological and structural characterization, performed via atomic force microscopy (AFM) and synchrotron radiation grazing incidence diffraction (GID) respectively, we observed that on substrates with high SFE, the polymeric lamellae completely cover the surfaces, with a reduction of the crystalline fractions as a function of the curvature. Moreover, the in-situ GID during thermal cooling shows a variation in the crystallization temperature (Tc) as a function of the geometry and SFE. Tc decreased on high-SFE nano-curved substrates with respect to the flat one, while unaltered Tc was observed at low SFE. These results highlight the interplay between geometric and energy factors, suggesting that only in the presence of an energetic gain, i.e. high SFE that counterbalance the enthalpy loss due to the formation of distorted crystals, the polymeric lamellae follow the geometry of the substrates. This correlation shed more light on how these factors influence the polymer film crystallization and could allow the determination of the crystallization enthalpy and its related loss when a nanometric strain is applied. A deeper understanding of this behaviour could pave the way for the development of the finely tailored crystalline structures via control of the substrate geometry and energy.

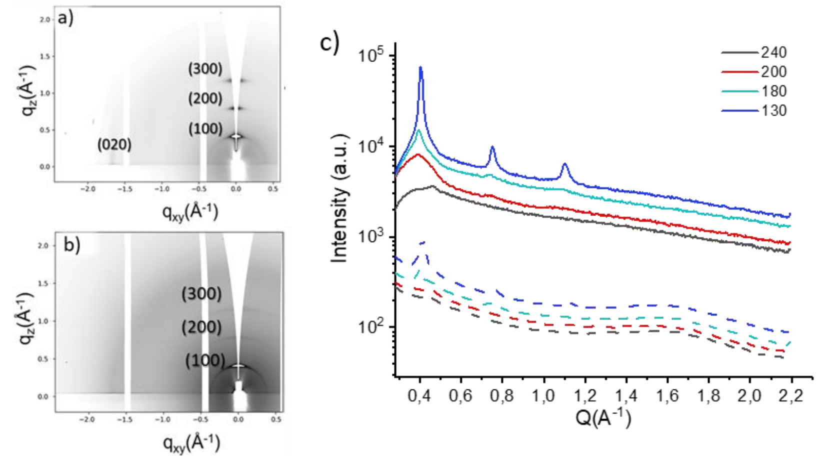


Figure 1. 2D GIXRD pattern of P3HT after thermal annealing, on flat substrates (a) and on the substrate having curvature 0.00851 nm^{-1}(b) and 1D diffraction profile (c) obtained during the cooling of thin films on of both substrates, respectively solid line and dashed line. The Bragg peak appear at a lower temperature on nano-curved substrate.

[1]. Verstraete, L., et al. *Chemical Society Reviews*, **2021**, *50*(10), 5884-5897.
[2]. Yu, C., et al. *Crystals*, **2017**, *7*(5), 147.
[3]. Ruffino, R.,et al *J. Phys. Chem. C,* ***2019***, *123*, 8967-8974.
[4]. Ruffino, R., et al. *Polymer*, **2021**, *230*, 124071.

Surviving high salt? Investigating the response of bacterial model membranes to the high salinity of the deep subsurface of Mars

Attila Tortorella[1,2], Rosario Oliva[2], Roland Winter[3], Concetta Giancola[4] and Luigi Petraccone[2].
[1]Scuola Superiore Meridionale, Via Mezzocannone 4, 80138 Napoli
[2]Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II, Via Cintia 21, 80126 Napoli
[3]Fakultät für Chemie und Chemische Biologie, TU Dortmund, Otto-Hahn-Str. 6, 44227 Dortmund
[4]Dipartimento di Farmacia, Università degli Studi di Napoli Federico II, Via Domenico Montesano, 49, 80131 Napoli
attila.tortorella@unina.it

In the recent years, the investigation of extremophiles has become increasingly important due to their ability to thrive in extreme environmental conditions. Understanding the limits of life and its related molecules from a physicochemical perspective is of great importance in biology and astrobiology [1-3]. Despite numerous examples of organisms thriving at high salt concentrations, high pressure, and extreme temperatures on Earth, little research has been done on extraterrestrial environments that may support life [2]. In this framework, considering that the membrane is necessary for the development of most forms of life, we focused our study on a bacterial model membrane within a potential Martian-like habitat to assess if there is the possibility for a microorganism to thrive in such environment. Mars is believed to contain subsurface lakes with high concentrations of salts such as magnesium perchlorate, sulphate, and chloride [2]. We investigated the impact of these salts, in combination with temperature and pressure variation, on a model membrane composed of phosphatidylethanolamine and phosphatidylglycerol, using a range of biophysical techniques including calorimetry, spectroscopy, microscopy, and small-angle X-ray scattering. Our findings revealed that despite high salt concentrations, the lipids were still able to form a lipid bilayer membrane. Moreover, we found that the chaotropic perchlorate ion stabilizes the liquid-like bilayer phase that is necessary for a living cell to function, counteracting the deteriorating effect of high pressure in the Martian subsurface. On the contrary, high Mg^{2+} salt concentrations stabilize the rigid gel phase of the membrane, rendering the ability of bacteria to survive under such environmental conditions less favorable.

[1] N. Merino et al., Front. Microbiol., 10 (2019), 780.
[2] C. S. Cockell, Blackwell Publ., Oxford, 2020.
[3] J.-M. Knop et al., Chem. Rev. 123 (2023) 73-104

Interfacial instability at liquid-liquid interphase enables high performance synthetic molecular communication

Federico Calì[1], Antonino Licciardello[1], Giovanni Li-Destri[1], Nunzio Tuccitto[1]
[1]*Dipartimento di Scienze Chimiche, Università degli Studi di Catania, v.le A. Doria n° 6 95125, Catania, Italia*

When two miscible liquids having different viscosity come in contact, interface is formed. Any interfacial instability will result in a peculiar phenomenon known as "viscous fingering". Viscous fingering is the unstable displacement of a more viscous fluid by a less viscous fluid. The fingering of an injection fluid into another flowing fluid can influence the flow behavior. Fingering occurs even in the absence of a porous medium. If a low-viscosity fluid is injected into a pipe containing a high-viscosity fluid, the low-viscosity fluid will begin to form fingers as it moves through the fluid. It will not uniformly displace the higher viscosity fluid. This physical-chemical phenomenon can be very relevant in microfluidic conditions. We have exploited this phenomenon to achieve synthetic molecular communication with high information density.[1] Synthetic molecular communication might represent a valid alternative to traditional electromagnetic wave-based communication for the development of new and sophisticated applications in any wave denied environment. We are presenting our recent findings about the exploitation of a such peculiar chemical-physical phenomenon due to the interfacial instability developing between two miscible liquids to confine chemical messengers to modulate the associated communication signal. The chemical messengers we prepare for the purpose are fluorescent nanoparticles known as Carbon Quantum Dots (CQDs). First theoretically and then experimentally, we demonstrate that using the chemical messengers' confinement a significant increase in message transmission speed can be achieved with respect to the traditional signal modulation methods already known in the Molecular Communication community.

[1] Calì, F., Fichera, L., Sfrazzetto, G. T., Nicotra, G., Sfuncia, G., Bruno, E., ... & Tuccitto, N. (2022). Fluorescent nanoparticles for reliable communication among implantable medical devices. Carbon, 190, 262-275.

Polymerization of dopamine via anoxygenic photosynthetic bacteria: bio-optoelectronics for sustainable energy production

Maria Varsalona[1,2], Rossella Labarile[1,2], Danilo Vona[1], Matteo Grattieri[1], Gianluca Maria Farinola[1], Angela Agostiano[1], Massimo Trotta[2]
[1] *University of Bari – Department of Chemistry, Via Orabona 4, 70125 Bari, Italy*
[2]*Consiglio Nazionale delle Ricerche – Istituto Processi Chimico – Fisici, Via Orabona 4, 70125 Bari, Italy*
maria.varsalona@uniba.it

Rhodobacter (*R.*) *sphaeroides* is a purple non-sulfur bacteria which performs anoxygenic photosynthesis by capturing the solar light via a specific photosynthetic antenna system and transferring it to the photochemical core (reaction center, RC). A cascade of light induced electron transfer reactions drive the metabolism that can eventually harnessed to produce photocurrents with interesting performing yield.

Dopamine (DA) is a neurotransmitter which polymerize into polydopamine (PDA), a melanin-like biocompatible material with interesting adhesive properties. Recently, PDA has been explored to enhance and improve the extracellular electron transfer from the bacterial photosynthetic apparatus of *R. sphaeroides* to an electrode. We investigated the in-situ polymerization of DA under strictly anoxygenic conditions, focusing on the possible metabolic implications.

Adaptation of photosynthetic microorganisms to increasing concentrations of DA allows to firstly investigate the effect of the monomer on the cellular activity and healthy of bacterial cells. On the other hand, the effective cellular growth in presence of DA permit to test photocurrents by adapted bacteria, with the aim of photoelectronic applications for energy production from bacteria. We demonstrate that DA is not detrimental for the bacterial growth, and also produces an increasing photocurrent that is dopamine-dependent, as the monomer concentration rises.

Adapted bacteria can represent the active layer of biodevices in bioelectronics, in which both the lifetime and electron transfer from the photosynthetic bacteria to the electrode is improved by PDA.

[1] M.L. Alfieri et al. Advances in Colloid and Interface Science (2022), 305:102689
[2] Y. Liu et al. Chem. Rev. (2014), 114(9):5057-115
[3] R.E. Blankeship et al. Kluwer Academic, The Netherlands (1995)
[4] M. Varsalona et al. IEEE (2022), 96-100
[5] G. Buscemi et al. ACS Applied Materials & Interfaces (2022), 14(23):26631–41.
[6] S.R. Liu et al. Chem. Commun. (2019), 55:10535-8
[7] F. Milano et al. MRS Advances (2020), 2:2299-307
[8] S.K. Ravi et al. Nature communications (2019) 10, 902
[9] M. Di Lauro et al. Advanced Electronic Materials (2020), 6(1) :1900888
[10] R. Labarile et al. MRS Advances (2023), DOI : 10.1557/s43580-023-00566-6 (just accepted)

Ultrasound-assisted formation of therapeutic peptide microcapsules

Mariano Venanzi[1], Gabriele Rossi[1], Erica Belforte[1], Francesca Cavalieri[1,2], Hilda Garay Peres[3]
[1] *Dept. of Chemical Science and Technologies, University of Rome Tor Vergata, 00133 Rome, Italy*
[2] *School of Science RMIT University of Melbourne, Victoria 3000, Australia*
[3] *Centre of Genetic Engineering and Biotechnology, Havana, Cuba*
venanzi@uniroma2.it

Ultrasonically synthesized core-shell microcapsules made by synthetic polymers or natural biopolymers, such as proteins and polysaccharides, have found wide applications in food science, drug delivery and cosmetics. In this contribution we describe the ultrasound-assisted preparation and characterization of peptide microcapsules formed by a therapeutic peptide (CIGB500) synthesized at the Centre of Genetic Engineering and Biotechnology (CIGB) of Havana (Cuba). CIGB is developing CIGB500, at the present time in clinical phase 2, as a therapeutic agent for the treatment of cardiovascular disease.

The aggregation properties of CIGB500 have been investigated by spectroscopic techniques, determining its critical aggregate concentration. Moreover, we show that under ultrasound-induced oil/water emulsification conditions, CIGB500 formed microcapsules, filled by soybean oil, and characterized by diameters comprised between 0.3 µm and 8 µm (Figure 1). It was found that the peptide concentration and sonication parameters play an important role in the stabilization of the microcapsules, as shown by spectroscopy and optical and electronic microscopy techniques.

We also showed that the synthesized microcapsules can be successfully used for the encapsulation of drugs without further chemical modifications. In particular, we have encapsulated a therapeutic formulation denoted as "One Primary Wound Dressing" and we have studied its release following the microcapsule breaking by temperature. Fluorescence spectroscopy and optical microscopy studies revealed that the CIGB 500 microcapsules were partially dissolved in a temperature range between 35 and 40 C°, indicating that CIGB500 could be a suitable candidate for the development of peptide drug carriers.

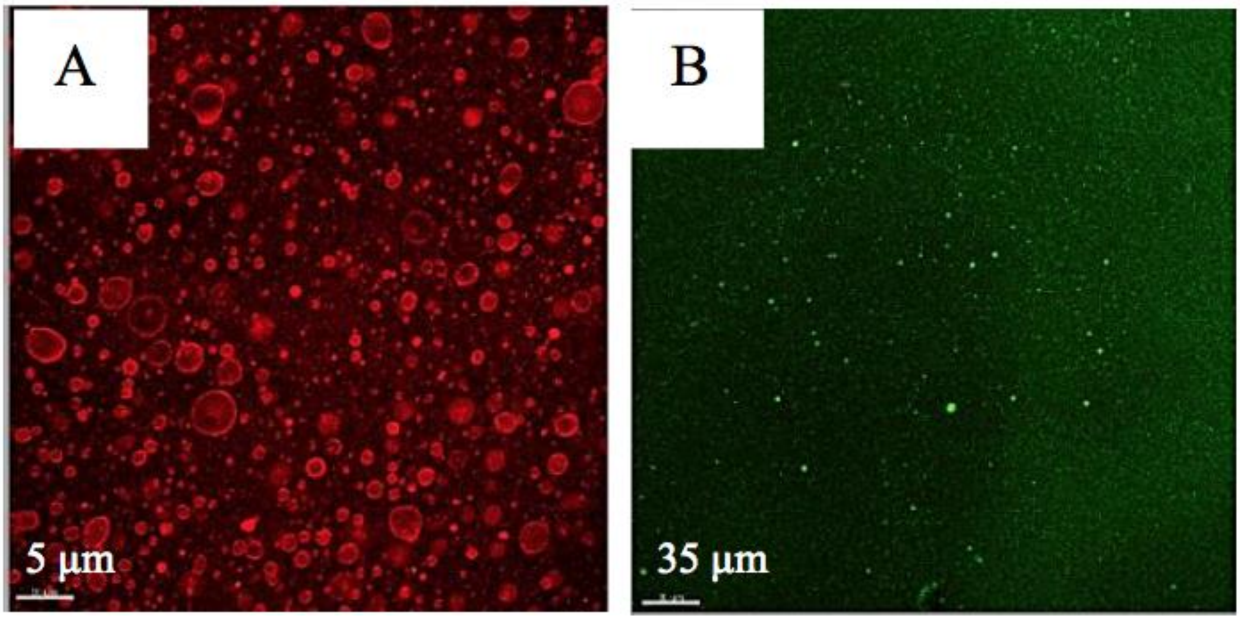


Figure 1. Confocal fluorescence microscope images of labelled CIGB500 microcapsules. A) Nile Red; B) FITC.

POSTERS

T2. PHYSICAL CHEMISTRY OF SOFT MATTER AND LIFE SCIENCE

Polysaccharide-based biodegradable films for agricultural mulching

Veronica Ciaramitaro[1], Elena Piacenza[1], Sara Paliaga[2], Giuseppe Cavallaro[3], Vito A. Laudicina[2], Delia F. Chillura Martino[1]
[1]Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF), Università degli Studi di Palermo, Viale delle Scienze – Edificio 16, 90128 Palermo (IT)
[2]Dipartimento di Scienze Agrarie, Alimentari e Forestali (SAAF), Università degli Studi di Palermo, Viale delle Scienze – Edificio 4, 90128 Palermo (IT)
[3]Dipartimento di Fisica e Chimica Emilio Segrè, Università degli Studi di Palermo, Viale delle Scienze – Edificio 17, 90128, Palermo (IT)
veronicaconcetta.ciaramitaro@unipa.it

In the last 20 years, the global population has blowout growth from 6.0 billion to 7.2 billion and will reach over 8.0 billion around 2046 [1]. Consequently, food shortage has drawn attention, and the demand for agricultural products has increased annually. To meet this need, the excessive and prolonged use of mulching films based on low-density polyethene resulted in significant environmental pollution events, leading to serious side effects on human health [2]. Due to the thickness of the plastic film and the difficulty of recovery, some mulch films were discarded in agricultural soils intentionally or unintentionally. Mulch film residue is a direct source of farmland meso- and microplastics (MMPs), which constitute a global environmental issue, as they accumulate even in the food chain [3]. MMPs' further degradation into nanoscale particles can endanger human health [4]. To provide agricultural sustainability, there is a great interest in developing biodegradable bio-based polymeric films for agriculture mulching, which can be tilled directly into the soil after use. Based on the above issues, this study aims at (i) the preparation and characterisation of biodegradable bio-based composite films and (2) their enrichment with plant nutrients, which could be efficiently released into the water to sustain their application as mulch films on the soil.

Sodium carboxymethyl cellulose (CMC), chitosan (CS) and sodium alginate (SA) were combined in the presence of glycerol as a plasticiser to produce composite films by solvent casting. Composition (i.e., concentrations and mass ratios between the precursors) and cross-linking agent ($CaCl_2$) effects on films' properties were evaluated. In the first stage, we investigated the structure of the formed films through Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy, the thermal and mechanical properties by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA), and some water-interaction properties (degree of swelling and solubility in water). This approach allowed identifying the best quality films, which were enriched with $NH_4H_2PO_4$, as N and P are generally the most deficient nutrients in the soil. Moreover, the release kinetics in the water of this salt was studied. The latter aspect is of great importance as the release of N and P helps to improve the nutrient supply to the soil, thus reducing the use of synthetic fertilisers.

[1] B. Chieng et al. J. Appl. Polym. Sci. 130 (2013) 4576-4580
[2] H. M. S . Akhtar, et al. Int. J. Biol. Macromol. 118 (2018), 469-477
[3] M.C. Rillig, M. C. Environ. Sci. Technol. 46 (2012), 6453-6454
[4] I. Ali et al. J. Clean. Prod. 313 (2021) 127863

Encapsulation of Fludioxonil in lipid-based nanocarriers for the treatment of fungal diseases in agriculture: preliminary results

Vincenzo De Leo[1], Angelo Agnusdei[2], Anna Maria Maurelli[1], Donato Gerin[2], Francesco Faretra[2], Stefania Pollastro[2], Lucia Catucci[1]
[1]*Department of Chemistry, University of Bari Aldo Moro, Via Orabona 4, 70126 Bari, Italy*
[2]*Department of Soil, Plant and Food Sciences, University of Bari Aldo Moro, Via Orabona 4, 70126 Bari, Italy*
vincenzo.deleo@uniba.it

The aim of this work was to realize lipid nanocarriers (liposomes) loaded with the phytopharmaceutical Fludioxonil (FLUD), for the containment of fungal diseases in agriculture. The application of nanostructured lipid carriers in agriculture finds its motivation in the need to overcome the problems associated with the traditional use of pesticides, such as poor bioavailability, easy degradation, and excessive dispersion in the environment. The research was conducted within the *Sos&Bio_for_One Health* project of the University of Bari.

Two methods were compared for the preparation of liposomes: the Micelle-Vesicle Transition (MVT) method and the extrusion method. Furthermore, three types of vesicles were compared that differed in composition: (I) Plain vesicles, composed of soy phosphatidylcholine and cholesterol; (II) PEG-coated vesicles, with an additional polyethylene glycol coating; and (III) Cationic vesicles, containing a cationic component capable of modifying the surface charge of liposomes (DDAB). The operating parameters, with particular regard to the total amount of lipids and the lipid/FLUD ratio, have been optimized to obtain stable, nanometric-sized vesicles with good Encapsulation Yields (EE%) and Drug Loading (DL%). In particular, through the MVT method, small unilamellar vesicles (SUVs) having a variable mean diameter in the range 80 nm – 150 nm and EE% higher than 78% were easily obtained. The extruded samples yielded mean diameter sizes between 93 nm and 150 nm, with EE% greater than 90%. With both methods the Zeta potential values measured were, in line with expectations, moderately negative for the Plain vesicles and PEG-coated samples and moderately positive for the Cationic vesicles. Subsequently, in vitro release tests of the systems loaded with FLUD were performed. A fairly slow release was verified in the early stages, to then reach higher values and remain constant in the following hours. In particular, for the Plain vesicles a plateau was reached at 96.6% after about five hours, compared to 73.4% for the PEG-Coated vesicles and 46% for the Cationic vesicles. Finally, preliminary tests of biological activity against the Botrytis cinerea fungus have been carried out. Conidial germination test, inhibition of germ-tube growth and radial growth inhibition test were conducted. In general, FLUD delivered via liposomes showed slightly better performance than free FLUD only at the lowest tested concentrations (0.1-0.3 μg/ml), while it showed similar performance to free drug at high concentrations (1 μg /ml). For intermediate concentration values, free FLUD showed better performance than the liposomal one. Further investigations are underway to evaluate the biological response of FLUD-loaded vesicles by adapting the experimental protocols to the realized systems.

[1] Sostanze naturali, microrganismi e nanocarrier bio-compatibili per lo sviluppo di azioni sostenibili con un approccio “One-Health” e la valorizzazione della biodiversità (Sos&Bio_for_One Health)

Abstract ID. T2P02

Miniaturized Stereoselective Light-Emitting Systems for chiral contaminants

Massimo Dell'Edera[1], Silvia Cauteruccio[1] , Valentina Pellicciolí[1], Sara Grecchi[1], Roberto Cirilli[2] , Emanuela Licandro[1] and Serena Arnaboldi[1]

[1]Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milan, Italy

[2]Centro Nazionale per il Controllo e la Valutazione dei Farmaci, Istituto Superiore di Sanità, Viale Regina Elena, 299, 00161 Rome, Italy
massimo.delledera@unimi.it

Nowadays the increase of human activities also related to the increment of the world population has been causing harmful consequences for the environment, in this context chiral contaminants have become critically important. [1] Chiral contaminants are a class of compounds particularly challenging to detect and analyse. These substances are present in a variety of environmental matrices, including water, soil, and air, and can include pesticides, pharmaceuticals, polychlorinated biphenyls (PCBs), and flame retardants. For this reason, it is crucial to develop methods to detect and quantify chiral contaminants in the environment.

The use of stereoselective sensors is one of the main useful approaches to analyse contaminants, to selectively recognize chiral molecules in complex mixtures [2]. In recent years, significant progress has been achieved in developing stereoselective sensors for chiral contaminants, particularly in the field of electrochemistry[3].

This study is focused on the development of a wireless miniaturized system that can qualitatively detect a chiral contaminant called 3,4-dihydroxyphenylalanine (DOPA) in micro volumes through bipolar electrochemistry, [4] demonstrating the potentialities of new and effective methods for detecting chiral contaminants in the environment.

[1] You, X., et al., Journal of Agricultural and Food Chemistry (2019) 67 (49), 13550
[2] Warning, L. A., et al., ACS Nano (2021) 15 (10), 15538
[3] Arnaboldi, S., Chemical Communications (2023) 59 (15), 2072
[4] Cauteruccio, S., et al., Chemosensors, (2023), Vol. 11

Cytosine epigenetic modifications and conformational changes in G-quadruplex DNA: an ultraviolet resonance Raman spectroscopy study

Raffaele Graziano[1], Francesco D'Amico[2], Federica D'Aria[1], Pasquale Russomanno[1], Silvia Di Fonzo[2], Jussara Amato[1], Bruno Pagano[1]
[1]*Department of Pharmacy, University of Naples Federico II, Naples, I-80131, Italy*
[2]*Elettra-Sincrotrone Trieste S. C. p. A., Science Park, Trieste, I-34149, Italy*
raffaele.graziano2@unina.it

Epigenetic modifications of DNA are known to play important regulatory roles in biological systems, especially in regulation of gene expression, and are associated with many types of human diseases, including cancer [1]. Alternative DNA secondary structures, such as G-quadruplexes, can also influence gene transcription, thus suggesting that such structures may represent a distinctive layer of epigenetic information [2]. G-quadruplex structures and DNA epigenetic modifications often go side by side, and recent evidence reveals that cytosine modifications within loops of G-quadruplexes can play a role in modulating their stability and structural polymorphism [3]. Therefore, the development and validation of experimental techniques that can easily and reliably analyze G-quadruplex structures are highly desirable [4].

In the present study, we propose to exploit the advantages of UV resonance Raman (UVRR) spectroscopy to investigate cytosine epigenetic modifications along with conformational changes in G-quadruplex-forming DNA. Our findings show that clear and specific spectral changes occur when there is a change in a G-quadruplex structure. Moreover, UVRR spectral analysis can indirectly distinguish the spectral variations occurring because of modifications in the guanine glycosidic conformations, as well as detect changes in the loops induced by H-bond formation or hydration of nitrogenous bases. The results further underscore the utility of UVRR spectroscopy for G-quadruplex structure elucidation under biologically relevant solution conditions.

Acknowledgements: This work was supported by AIRC (IG 2020 - ID 24590 to B.P.).

References

[1] S. G. Jin et al. Genomics 106 (2015) 322
[2] A. K. Mukherjee et al. Trends Genet. 35 (2019) 129
[3] Z. F. Wang et al. Nucleic Acids Res. 48 (2020) 1120
[4] S. Di Fonzo et al. Phys. Chem. Chem. Phys. 21 (2019) 2093

Spectroscopical characterization of chitin extracted from different BSF sources

Andrea Marangon[1], Geo Paul[2], Riccardo Zaghi[3], Leonardo Marchese[2], Giorgio Gatti[1]
[1] Dipartimento per lo sviluppo Sostenibile e la Transizione Ecologica, Università degli Studi del Piemonte Orientale, Piazza S. Eusebio 5-13100 Vercelli, Italia
[2] Dipartimento di scienze e innovazione Tecnologica, Università degli Studi del Piemonte Orientale, Viale Teresa Michel 11-15121 Alessandria, Italia
[3] Ticinsect SA, Via Industria 12 - CH-6710 Biasca, Svizzera

Biopolymers are finding more and more fields of use, chitin is used for medical applications, in agriculture and in the environmental field, in the food and textile industries. Chitin is a biopolymer made up of units of N-acetyl-2amino-2deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucose in pyranose form and linked to each other by 1-4 glycosidic bonds with an acetylation degree greater than 60%. [1]

Currently chitin is extracted from animal and vegetable sources of different nature such as, for example, crab shells, mushrooms, and yeasts. These sources are subject to seasonality, moderately long growth times and maintenance of specific conditions, for these reasons, over the last few years, the potential of Hermetia Illucens (Black Soldier Fly or BSF) has been investigated as this type of fly is able to grow on a variety of organic materials. Due to this characteristic, it is widely used as a means for the disposal of domestic organic waste. [2]

In the AIWTUC – EUROSTAR project: "An innovative way to use Chitin: from Organic Waste to functional fabrics", the chitin was obtained from skin and exuviae BSF larvae and was characterized by Infrared Spectroscopy, X-Ray Diffractometry, solid-state Nuclear Magnetic Resonance (^{1}H and ^{13}C ss-NMR) and thermogravimetric analysis. These characterizations were conducted to investigate the chemical physics characteristics of the chitin obtained such as the degree of crystallinity, the degree of acetylation, the presence of residual proteins or melanin and the presence of polymorphisms, fundamental characteristics for determining the fields of application.

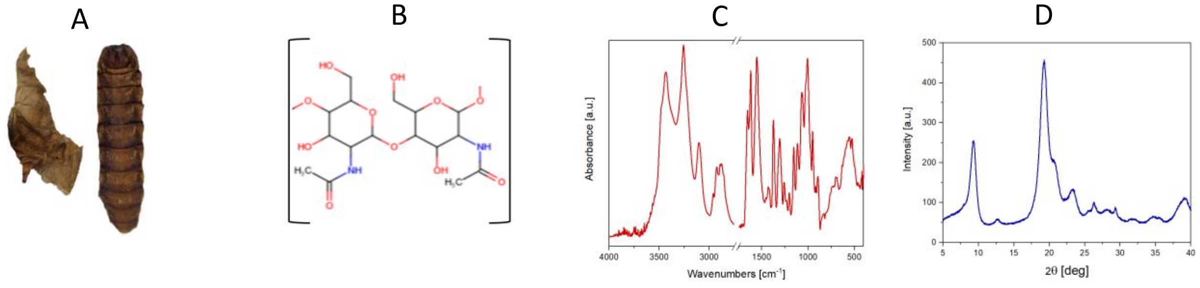


Fig.1: BSF skin and exuviae used like source of chitin (A), chitin monomers (B), FT-IR spectra (C) and XRD pattern (D) of chin extracted by BSF

[1] J. Kumirska et al. Mar. Drugs 8 (2010) 1567
[2] G.D.P. Da Silva et al. Neotrop Entomol 49 (2020) 151

Translational and reorientational dynamics of deep eutectic solvents made of choline chloride and hydrated $CaCl_2$ by ^1H NMR relaxometry

Francesca Martini[1,2], Chiara Pelosi[1], Giulio Giannessi,[1,2] Gianluca Ciancaleoni,[1] Celia Duce,[1,2] Luca Bernazzani,[1,2] Marco Geppi[1,2]
[1]*Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Giuseppe Moruzzi 13, 56123 Pisa, Italy*
[2]*CISUP, Centro per l'Integrazione della Strumentazione dell'Università di Pisa, Lungarno Pacinotti 43, I-56126, Pisa, Italy*
Presenter's e-mail address: *francesca.martini@unipi.it*

Deep eutectic solvents (DESs) are an emerging class of green solvents constituted by a hydrogen (or halogen) bond acceptor (HBA), and a hydrogen (or halogen) bond donor (HBD), which form a eutectic mixture with a melting point lower than that expected for the ideal case [1]. DESs have been proposed as a more eco-friendly, economic, and non-toxic alternative to ionic liquids (ILs), sharing with them the same general characteristics of high thermal stability, low volatility and tunable polarity combined with an easier preparation procedure. These properties make DESs promising candidates for many different applications including electrochemical applications, separation and gas capture, and biomass processing [2].

Achieving a deeper comprehension of the nanostructure of DESs and of the dynamics of the HBA and HBD components is fundamental to understand the origin of the final macroscopic behavior, and to devise systems with optimized properties for specific applications [3]. Among the characterization techniques employed to characterize DESs, NMR relaxometry has played a marginal role so far [4,5], despite this technique can potentially disclose useful information on dynamics on a wide range of motion time scale, from fast local reorientations to translational diffusion.

In this work, variable temperature ^1H NMR relaxometry has been employed to investigate the dynamic properties of type-II DESs made of choline chloride and $CaCl_2 \cdot 6H_2O$ containing different amounts of water [6]. ^1H T_2 relaxation times have been measured to obtain information on the presence of domains with different degree of mobility. Field Cycling (FC) experiments for the measurements of ^1H T_1 as a function of the ^1H Larmor Frequency allowed local reorientational motions in the MHz frequency regime and translational diffusion to be characterized in dependence of temperature and water content. In particular, from the analysis of the variable temperature data with suitable dynamic models, the activation energies of the reorientational motion and the diffusion coefficients were estimated.

[1] M.A.R. Martins et al. J. Solut. Chem. 48 (2019) 962
[2] B.B. Hansen et al. Chem. Rev. 121 (2021) 1232
[3] J. González-Rivera et al. Curr. Opin. Green Sustain. Chem. 5 (2022) 100333
[4] Y. Hinz et al. J. Chem. Phys. 156 (2022) 194506
[5] C. C. Fraenza et al. J. Phys. Chem. B 126 (2022) 890
[6] C. Pelosi et al. J. Mol. Liq. 371 (2023) 121104

Construction of Plasmonic Nanostructures for Targeting the Immune Check Point PD-L1

Marina Gobbo,[1] Isabella Caligiuri,[2] Micaela Giannetti,[3] Lucio Litti,[1] Claudia Mazzuca,[3] Flavio Rizzolio,[2,4] Antonio Palleschi,[3] and Moreno Meneghetti[1]
[1]*Department of Chemical Sciences, University of Padova, via F. Marzolo 1, 35131 Padova, Italy.*
[2]*Pathology Unit, Centro di Rif. Oncologico di Aviano (CRO) IRCCS, via F. Gallini 2, 33081 Aviano (PN), Italy*
[c]*Department of Chemical Science and Technologies, University of Rome "Tor Vergata", and CSGI unit of Rome, Via della Ricerca Scientifica, 00133 Rome, Italy*
[d]*Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, via Torino 155, 30172 Venice, Italy*
moreno.meneghetti@unipd.it

Immune check points are expressed by tumor cells and have an active role in regulating the activity of the immune system against tumors. Nanostructures can be designed as active systems that strongly bind to tumor cells and influence their interaction with the immune system.

It will be shown that plasmonic nanostructures can be engineered to target the protein PD-L1 (programmed death ligand 1). This antigen, overexpressed on tumor cells, binds to the PD-1 protein expressed on activated CD8+ T-Cells, suppressing their activity and facilitating the immune escape of tumor cells.

It will be shown that gold plasmonic nanostructures, properly functionalized with thousands of peptides identified by phage-display for targeting to PD-L1, strongly bind to MDA-MB-231 breast cancer cells overexpressing PDL-1. The SERS signals of the nanostructures will be used for quantifying the targeting activity.

The binding of the nanostructures to tumor PDL-1, inhibits the interaction with PD-1 on T-cells preserving the activity of the T-Cells.

Highly Bright Fluorescent Silk Fibroin Nanoparticles for biomedical applications

Ivana Miletto, Elia Bari, Lorella Giovannelli, Lorena Segale and Maria Luisa Torre
Department of Pharmaceutical Sciences, University of Eastern Piedmont, Largo Donegani 2/3, 28100 Novara, Italy
ivana.miletto@uniupo.it

Fluorescent silk fibroin nanoparticles have gained significant attention in recent years due to their unique properties and potential applications in nanomedicine. Silk fibroin, derived from the natural protein found in silkworm cocoons, has long been recognized for its exceptional mechanical strength, biocompatibility, and biodegradability. Furthermore, the possibility of obtaining fibroin in the form of nanoparticles through a reproducible and relatively simple desolvation method [1] has further expanded their utility, enabling efficient drug delivery of both hydrophobic and hydrophilic molecules [2]. The biomedical applications of fluorescent silk fibroin nanoparticles encompass a broad spectrum, including targeted drug delivery, bioimaging and diagnostics, biosensing, tissue engineering, and regenerative medicine. The unique properties of silk fibroin, combined with the fluorescent capabilities, offer numerous advantages in these applications. The controlled release of therapeutic agents from silk fibroin nanoparticles allows for localized and sustained drug delivery, minimizing off-target effects and improving therapeutic efficacy. Additionally, the fluorescent nature of these nanoparticles enables non-invasive imaging and tracking of biological processes at the cellular and molecular levels, facilitating disease diagnosis and monitoring treatment response.

Different approaches can be followed for the preparation of fluorescent silk fibroin nanoparticles, ranging from the genetic modification of silkworms and the feeding of silkworms with a fluorophores-containing diet [3], mainly used to produce fluorescent silk fibers or fabrics, to the chemical modification of fibroin by covalent labeling with fluorescent dyes.

In this contribution, two routes for preparing fluorescent silk fibroin nanoparticles were explored, both involving the covalent labeling of free amino groups of Lys residues of fibroin. In the first case, fibroin was labeled before the formation of nanoparticles; in the second, direct labeling of pre-formed silk fibroin nanoparticles was carried out. Two sets of green and red fluorescent silk fibroin nanoparticles were prepared using Fluorescein Isothiocyanate (FITC) and Rhodamine B (RhoB) as the fluorescent tag, respectively. The resulting fluorescent nanoparticles had a mean diameter between 130 and 150 nm, a d_{50} of about 120 nm, and a d_{90} below 250 nm, as characterized by Nanoparticle Tracking Analysis (NTA); when observed at Field Emission Scanning Electron Microscopy (FESEM), they appeared with a round-shaped morphology, while the Infrared Spectroscopy revealed the typical bands of amide I (at about 1621 cm^{-1}, C-O stretching), amide II (at about 1515 cm^{-1}, N-H bending), and amide III (at about 1230 cm^{-1}, C-N and N-H combination modes) of fibroin. UV-vis absorption, and emission spectroscopy, augmented by the measurement of fluorescence quantum yield, evidenced a good distribution of the fluorophores within the nanoparticles with the maintenance of quantum yields close to unity. The multi-technique characterization allowed highlighting the effect of synthesis parameters (functionalization route, dye loading applied) on the morphological and physico-chemical properties of the resulting fluorescent silk fibroin nanoparticles, evidencing the possibility of finely tuning the fluorescence properties by a proper synthetic approach.

[1] Bari, E. er al. Cancers 13 (2021) 1185
[2] Bari, E., Perteghella, S., Torre, M. L. (2020). Silk-based Drug Delivery Systems (1st ed.). Royal Society of Chemistry
[3] O.J. Lee et al. Frontiers in Materials 7 (2020) 50

Magnetic nanostructures: A smart platform for biomedical applications

Francesco Papatola[1*], Maria Salvador[3], Montserrat Rivas[3], Sawssen Slimani[1,2], Davide Peddis[1,2]
[1]*Università di Genova, Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31, 16146, Genova, Italy.*
[2]*CNR, Istituto di Struttrua della Materia, nM2-Lab, Monterotondo Scalo (Roma), 00015, Italy.*
[3]*Department of Physics & IUTA, University of Oviedo, Campus de Viesques, 33204.*
*francesco.papatola@edu.unige.it

Single domain magnetic nanoparticles (MNPs) have attracted significant attention in nanomedicine as a promising material for theranostic applications[1,2]. Interest in utilizing MNPs in biomedical applications originates both from the high surface/volume ratio and from their external magnetic controllability inside biological objects. The aim of the work is to analyze the potential of magnetic nanostructures and their ideal characteristics for biomedical applications (i.e., bio sensing, magnetic hyperthermia) by developping a smart platform to deliver or/and to harvest specific biomolecules (e.g., Neutravidin). This platform consists in making spinel iron oxides ($MeFe_2O_4$; Me: Fe^{2+} and Co^{2+}) nanostructures (i.e., single nanoparticles and nanoparticles aggregates) suitable for bio-applications focusing on their chemical stability at physiological pH through a proper surface modification(α-hydroxy-acids)[3]. Investigation of the morpho-structural (X-ray diffraction, Transmission electronic microscopy) and magnetic properties (Vibrating Sample Magnetometer) of MNPs have been carried out. To optimize long-term and in-use colloidal stability and to ensure biocompatibility, MNPs were coated with 2,3-dimercaptosuccinnic acid (HOOC–CH(SH)–CH(SH)–COOH, DMSA) or citric acid ($HOC(CO_2H)\ (CH_2CO_2H)_2$). The investigation of the molecular coating has been carried out through Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric analysis (TGA) and particular attention has been devoted to the particles stability in aqueous medium through Dynamic light scattering (DLS). In addition, surface modification provides new functional groups on MNPs surface that are used to provide specific sites to graft biological function through the further functionalization with proteins like Neutravidin. The success of functionalization was investigated immobilizing neutravidin in lateral flow membrane strips (LFA assay); when the sample containing the particles flows along the membrane, the biotin captures the neutravidin attached to the MNPs, which are detected by the inductive sensor.

1. Laurent, S., Dutz, S., Häfeli, U. O. & Mahmoudi, M. Magnetic fluid hyperthermia: focus on superparamagnetic iron oxide nanoparticles. *Adv. Colloid Interface Sci.* **166**, 8–23 (2011).
2. Socoliuc, V. *et al.* Magnetic nanoparticle systems for nanomedicine—a materials science perspective. *Magnetochemistry* **6**, 1–36 (2020).
3. Ruiz, A. *et al.* Magnetic nanoparticles coated with dimercaptosuccinic acid: development, characterization, and application in biomedicine. *Journal of Nanoparticle Research* (2014) doi:10.1007/s11051-014-2589-6.

Exploring the interaction of a non-canonical DNA structure with model membranes: a physicochemical study

Luigi Petraccone[1], Attila Tortorella[1,2], Concetta Giancola[3]
[1]Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II, Via Cintia 21, 80126 Napoli
[2]Scuola Superiore Meridionale, Via Mezzocannone 4, 80138 Napoli
[3]Dipartimento di Farmacia, Università degli Studi di Napoli Federico II, Via Domenico Montesano, 49, 80131 Napoli
luigi.petraccone@unina.it

The interaction between nucleic acids and membranes is widely used in medicine for gene therapy and for vaccine technology. Moreover, this type of interaction is also involved in gene replication for both prokaryotes and eucaryotes [1]. It is generally accepted that the polyanionic phosphate backbone can interact with polar headgroups of membranes with the aid of divalent cations [2]. However, previous studies have been largely focused on the interaction between canonical DNA structures and phospholipids, leaving a gap in knowledge regarding the interaction between non-canonical DNA structures and biological membranes. Among non-canonical DNA structures, G-quadruplexes are of particular interest due to their biological role and therapeutic applications [3].

In this work we explored the interaction between a G-quadruplex and two model membranes using a range of biophysical techniques including fluorescence spectroscopy, circular dichroism spectroscopy and differential scanning calorimetry. Specifically, we studied a neutral membrane composed of the zwitterionic phosphatidylcholine headgroup, and a negatively charged membrane composed of a mixture of the zwitterionic phosphatidylcholine headgroup and the negatively charged phosphatidylglycerol headgroup in a 8:2 ratio. Our preliminary results showed that even in the absence of divalent cations, the quadruplex preferentially interacts with the anionic model membrane making it slightly stiffer and without further changes in membrane properties.

[1] D. Morzy et al. J. Am. Chem. Soc. 143 (2021) 7358
[2] S. Pannwitt et al. Langmuir 35 (2019) 14704
[3] T. Tian et al. Chem 4 (2018) 1314

Rapid automatic identification and semi-quantification of common drugs of abuse using FT-IR ATR spectroscopy: presentation abstract

Francesca Sanna[1],Greta Mattiuzzo[1], Antonietta Lombardozzi[2], Morela Strano[3], Monica Andrenacci[4], Rosanna d'Angelo[3], Rosangela Santalucia[1], Marco Pazzi[1].
[1] Università degli Studi di Torino – Dipartimento di Chimica, Via Giuria 7, 10125 Torino (Italy)
[2] Ministero dell'Interno – Dipartimento di P.S. – Direzione Centrale Anticrimine della Polizia di Stato – Servizio Polizia Scientifica, Roma (Italy)
[3] Ministero dell'Interno - Dipartimento di P.S. – Direzione Centrale Anticrimine della Polizia di Stato – Servizio Polizia Scientifica, Gabinetto Interregionale di P.S. di Torino (Italy)
[4] Ministero dell'Interno - Dipartimento di P.S. – Direzione Centrale Anticrimine della Polizia di Stato – Servizio Polizia Scientifica, Gabinetto Regionale di P.S. di Genova (Italy)
francesca.sanna30@edu.unito.it

In 2022, the European Monitoring Centre for Drugs and Drug Addiction (EMCDDA) published a report revealing alarming trends of drug consumption in Europe [1]. These findings underline the necessity for law enforcement agencies to have additional tools that streamline analytical procedures and help in the fight against drug trafficking.

In recent years, Infrared Spectroscopy (IR) has proved to be a useful method in the forensic field for the analysis of drugs, explosives and polymers, as it allows to obtain information about the molecular composition and structure of a sample. Furthermore, it offers new approaches for qualitative and quantitative analysis of seized substances [2]. In particular, Attenuated Total Reflectance-Infrared Spectroscopy (ATR-FTIR) stands out for its efficiency in analyzing complex mixtures, providing rapid results with minimal sample preparation.

The aim of this project, carried out in collaboration with the forensic chemistry laboratories in Turin and Genoa, was to develop a series of ATR-FTIR libraries and a semi-automated method (workflow) capable of conducting preliminary qualitative and semi-quantitative analysis of the main narcotic substances and cutting agents. First of all, customized libraries of standards samples of narcotic substances, cutting agents, as well as binary and ternary mixtures, were developed. Subsequently, the created libraries were utilized to develop an automated procedure that can accurately and rapidly identify narcotic substances present in seized samples. Finally, the developed method was implemented, using a chemometric algorithm know as Partial Least Squares (PLS) to estimate the quantity of the active principle within these samples. To validate its applicability, the procedure was tested on a series of actual seized samples, demonstrating its effectiveness as a viable alternative to existing techniques for qualitative and semi-quantitative analysis of narcotic substances.

[1] EMCDDA, Relazione europea Tendenze e Sviluppi. 2022
[2] J. M. Chalmers, H. G. M. Edwards, and M. D. Hargreaves, Infrared and Raman Spectroscopy in Forensic Science. 2012. doi: 10.1002/9781119962328.

KEYNOTES

T3. PHYSICAL CHEMISTRY OF ENERGY PRODUCTION AND STORAGE

Computational modeling of new generation batteries: a study of parasitic chemistries and of electrolytes properties.

Enrico Bodo[1], Adriano Pierini[1], Vanessa Piacentini[1], Sergio Brutti[1]
[1]Dipartimento di Chimica, University of Rome “La Sapienza.
enrico.bodo@uniroma1.it

The current EU battery market is dominated by LIBs (Li-ion, Nickel-Cobalt-Manganese batteries) but the sourcing, refining and processing of raw materials and the LIB production are led by non-EU countries like China. At the same time, many EU countries will ban petrol-based engines in the near future with the obvious consequence of an increased demand of LIBs and of the raw materials on which they are based. In this scenario, EU seems destined to play a subordinate role. This, together with well-known shortcomings of LIBs, such as hazard, cost, charging rate and scarcity of Co and Li, is pushing the researchers toward alternative chemistries. The development of new generation batteries and new chemistries is seen as one of the possible strategies for EU to regain a leader role in the battery field.

Aprotic metal-oxygen batteries are an example of new chemistries that might replace LIBs despite being still in their research infancy. The redox chemistry of these batteries is not entirely understood, but the metal-superoxide disproportionation reaction is a crucial step for their operation in aprotic solvents. This reaction leads to peroxide and allows the battery operation, but it also spawns a complex parasitic chemistry that sees singlet molecular oxygen as the main degradation agent.

In this presentation I will summarize the results of recent computational works [1-4] where we have addressed the fundamental mechanisms of superoxide disproportionation and its thermodynamics for alkali and alkaline-earth by multiconfigurational and DFT methods. In particular, the addition of redox mediators such as I_2 and Br_2 has been recently explored and their role in selecting reactive pathways will be also discussed.

At the same time, optimization of the electrolyte composition toward its use in new generation devices has also to be pursued, possibly with the help of simulation techniques. We will present a set of simulations specifically aimed at understanding ionic transport properties in electrolytes using polarizable molecular dynamics.

[1] A. Pierini, S. Brutti and E. Bodo Superoxide Anion Disproportionation Induced by Li+ and H+: Pathways to $^1O_2$ Release in Li-O_2 Batteries, ChemPhysChem, 21, (2020) 2060–2067
[2] A. Pierini, S. Brutti and E. Bodo, Reactive pathways toward parasitic release of singlet oxygen in metal-air batteries, npj Computational Materials 7, (2021) 126
[3] A. Pierini, S. Brutti, and E. Bodo, Study of the Electronic Structure of Alkali Peroxides and Their Role in the Chemistry of Metal–Oxygen Batteries, J.Phys. Chem. A, 125, (2021) 9368–9376
[4] A. Pierini, S. Brutti, and E. Bodo, Reactions in non-aqueous alkali and alkaline-earth metal-oxygen batteries: a thermodynamic study, Phys. Chem. Chem. Phys., 23, (2021) 24487-24496

Abstract ID. T3K01

Combining shape-controlled TiO_2 nanoparticles with Mo_xC co-catalysts for efficient noble-metal free photocatalytic hydrogen evolution

Lorenzo Mino[1], Yan Wang[2], Francesco Pellegrino[1], Narcis Homs[2,3], Pilar Ramírez de la Piscina[2]
[1]Department of Chemistry and NIS Centre, University of Torino, Torino, Italy
[2]Departament de Química Inorgànica i Orgànica, Universitat de Barcelona, Barcelona, Spain
[3]Catalonia Institute for Energy Research (IREC), Barcelona, Spain
lorenzo.mino@unito.it

Hydrogen is a promising energy vector to store the power from the Sun as chemical energy. In the last years, huge research efforts have been devoted for improving the efficiency of photocatalytic water splitting and organics photoreforming processes, which allow obtaining green hydrogen. In this scenario, titanium dioxide (TiO_2) represents a key photoactive semiconductor and several studies tried to improve its performance by controlling its crystal structure, particle size, surface properties and morphology. In particular, shape-engineering has recently emerged as a power tool to optimize the NPs physicochemical properties [1, 2]. Another important aspect is the surface modification of the oxide NPs by addition of co-catalysts able to improve the charge carrier separation and to facilitate the H_2 photocatalytic production. Supported Pt, Ag, Pd or Au NPs are the most employed materials for this purpose. However, huge research efforts are devoted to developing noble-metal-free co-catalysts. Promising candidates, which are recently emerging, are transition metal carbide NPs, which exhibit catalytic properties similar to the Pt-group elements, being stable, cheaper and more abundant [3].

In this work [4] we combine shape-controlled TiO_2 NPs with molybdenum carbide (Mo_xC) as co-catalyst, using an ultrasound-assisted synthesis method, to obtain an efficient noble-metal-free photocatalyst for hydrogen production. In particular, we compared three different kind of shape-engineered anatase TiO_2 NPs with a different {101}/{001} facet ratio [1, 2], ranging from 0.25 to 9 (i.e. TiO_2(NS)-F = 0.25 , TiO_2(NS)-600 = 0.67 and TiO_2(bipy) = 9). X-ray photoelectron spectroscopy highlighted the presence of surface carbide and oxycarbide species in all cases. Moreover, in the bipyramidal anatase samples, the deposition of the carbide phase on TiO_2 likely induced a preferential reduction of the dominant {101} facets, which resulted in the presence of a Ti^{3+} signal in the Ti 2p XP spectrum.

The photoelectrochemical characterization of the materials indicated that the presence of Mo_xC onto TiO_2 NPs increases the photocurrent response and decreases the electron/hole recombination rate. These effects were higher for bipyramidal TiO_2 than for nano-sheet TiO_2. Finally, we tested the samples in the photoinduced H_2 production from ethanol aqueous solutions. The presence of the Mo_xC NPs clearly increased the reaction yields, confirming that carbide phases are promising co-catalysts to prepare efficient noble-metal-free Mo_xC/TiO_2 photocatalysts. The efficiency of the final system was correlated with the TiO_2 NPs shape and, in particular, with the amount of {101} facets present. These results, supported by the photoelectrochemical characterization, highlight that the synergistic effect of the reducibility of the anatase (101) surface and the presence of Mo_xC NPs favors the migration and localization of the photogenerated electrons at the catalyst surface and their subsequent transfer to generate H_2 [4].

[1] L. Mino et al. ACS Appl. Nano Mater. 1 (2018) 5355.
[2] F. Pellegrino et al. ACS Catal. 9 (2019) 6692.
[3] A. Pajares et al. Int. J. Hydrog. Energy 45 (2020) 20558.
[4] Y. Wang et al., Appl. Catal. B: Environ. 318 (2022) 121783.

Abstract ID. T3K02

ORALS

T3. PHYSICAL CHEMISTRY OF ENERGY PRODUCTION AND STORAGE

Electron Paramagnetic Resonance resolves different triplet states in organic mixed-valence molecular systems

Alessandro Agostini[1], Samuel Zatta[1], Eduardo Fabiano[2], Gianluca Accorsi[3], Agostina-L. Capodilupo[3], Lorenzo Franco[1]
[1] Department of Chemical Sciences, University of Padova, Via Marzolo, Padova 135131, Italy
[2] Institute for Microelectronics and Microsystems (CNR-IMM), c/o Campus Ecotekne, Via Monteroni, Lecce 73100, Italy
[3] Institute of Nanotechnology (CNR-NANOTEC), c/o Campus Ecotekne, Via Monteroni, Lecce 73100, Italy
alessandro.agostini.1@unipd.it

Mixed-valence molecular systems have steadily raised in interest in recent years in virtue of their applications in organic and hybrid electronic devices such as organic photovoltaic, organic light-emitting diodes, and organic field-effect transistors. Their performances stem from their complex photophysics, of which several distinct triplet states are an integral part. However, despite triplet states are pivotal in determining their excited state dynamics, with important consequences to the properties of their luminescence and in their photostability, they are commonly overlooked [1].
Time-resolved Electron Paramagnetic Resonance (TR-EPR) is of pivotal relevance in the investigation of excited triplet states, and with the support of DFT calculations, it is possible to draw a more precise picture of the electron densities of these paramagnetic states and a better understanding of their photophysics [2], [3]. We applied this joint spectroscopic approach to a series of molecules with double arylamine moieties linked by conjugated bridges of variable structure [4], [5] in order to investigate the role of the coupling between the two groups in the overall photophysical properties.

[1] A. J. Gillett et al. Chem. Mater. 34 (2022) 7095
[2] B. H. Drummond et al. Nat. Commun. 12 (2021) 4532
[3] E. W. Evans et al. J. Phys. Chem. Lett. 9 (2018) 4053
[4] A.-L. Capodilupo et al. J. Phys. Chem. A 125 (2021) 7840
[5] A.-L. Capodilupo et al. Dye. Pigment. 177 (2020) 108325

Hydrogen production through thermal degradation of Ammonia Borane-high boiling aromatic amine mixture: thermodynamic and kinetic study

Mattia Bartoli[1,2] , Sergio Bocchini [1,3] and Candido Fabrizio Pirri[1,3]
[1] *Center for Sustainable Future, Italian Institute of Technology, Via Livorno 60, 10144 Italy*
[2] *Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, Florence, Italy*
[3] *Department of applied science and technology, Polytechnic of Turin, C.so Duca Abruzzi 24, 10129-Turin, Italy*
email: mattia.bartoli@iit.it

The development of highly efficient materials for chemical hydrogen storage is one of the great challenges for driving the hydrogen economy to a major breakthrough. The safety of hydrogen tanks and the energy required for compression to high pressure have drastically slowed down the spread of the hydrogen-based mobility. Several alternatives have been proposed to overcome these problems using inorganic or organic carriers. Among all the available species, ammonia borane (AB) is one of the most interesting compounds with a theoretical gravimetric hydrogen storage capacity of up to 19.6 wt %. The most challenging and attractive AB dehydrogenation route is the solid-state thermal-induced dehydrogenation. Nevertheless, this reaction is complex, involves several pathways and mechanisms that could be promoted or suppressed by the presence of additives. The solid-state dehydrogenation kinetic of AB under thermal stimuli is widely investigated by directly mixing AB with dehydrogenation catalysts[2] or by confinement into a porous matrix[3].

Nevertheless, an interesting process is the preparation on a unstable AB with a tuned the degradative pathways by adding a chemical species.

In our work, we proposed a new route to modify the thermochemical behaviour of AB by solid state mixing with high boiling point aromatic amine to reduce the volatility of intermediates promoting the dehydrogenation reactions upon the others. We diffusely studied these systems using TGA-IR, DSC and IR spectroscopy several mixture producing a solid interpretation based on kinetic and thermodynamic parameters of the chemical pathways.

[1] Smythe, N. C., & Gordon, J. C. (2010). Ammonia borane as a hydrogen carrier: dehydrogenation and regeneration. *European Journal of Inorganic Chemistry*, *2010*(4), 509-521.

[2] Alpaydın, C. Y., Gülbay, S. K., & Colpan, C. O. (2020). A review on the catalysts used for hydrogen production from ammonia borane. *International Journal of Hydrogen Energy*, *45*(5), 3414-3434.

[3] Bartoli, M., Pirri, C. F., & Bocchini, S. (2022). Unraveling the Effect of Carbon Nanotube Oxidation on Solid-State Decomposition of Ammonia Borane/Carbon Nanotube Composites. *The Journal of Physical Chemistry C*, *126*(39), 16587-16594.

Addressing key challenges in the development “beyond Li-ion” chemistries

Giuseppe Antonio Elia, Claudio Gerbaldi…
GAME Laboratory, Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 24, Torino 10129, Italy
National Reference Center for Electrochemical Energy Storage (GISEL) - INSTM, Via G. Giusti 9, Firenze 50121, Italy
Presenter’s e-mail address: giuseppe.elia@polito.it

Renewable energy production is characterized by intermittent power output and requires large-scale applications to improve energy storage capability (currently, less than 1% of the electrical energy production can be stored). Developing low-cost and environmentally friendly electrochemical storage systems characterized by high performance is of fundamental importance for a sustainable energy economy. The currently most mature battery technology is the lithium-ion battery, considered one of the most appealing candidates as a power source for electric vehicle applications. However, the large-scale application of lithium-ion batteries is currently under discussion due to the limited lithium and certain transition metals such as Co and Ni resources. Several other metallic anodic materials such as sodium, potassium, calcium, magnesium and aluminium [1-3], characterized by a higher abundance of lithium, have been considered suitable candidates for electrochemical storage devices in replacing lithium systems. Notably, significant efforts are being devoted to understanding and addressing key challenges in developing these so-called “beyond Li-ion” chemistries, and substantial insights into their storage and failure mechanisms have been obtained over the past few years thanks to advanced characterization and computation/modelling techniques. An overview of our activity in “beyond Li-ion” batteries field and an evaluation of the capability of this technology will be presented. [4–9]

[1] G. A. Elia, K. Marquardt, K. Hoeppner, S. Fantini, R. Lin, E. Knipping, W. Peters, J.-F. Drillet, S. Passerini, R. Hahn, Adv. Mater. 2016, 28, 7564.
[2] G. A. Elia, K. V Kravchyk, M. V Kovalenko, J. Chacón, A. Holland, R. G. A. Wills, J. Power Sources 2021, 481, 228870.
[3] G. G. Eshetu, G. A. Elia, M. Armand, M. Forsyth, S. Komaba, T. Rojo, S. Passerini, Adv. Energy Mater. 2020, 10, DOI 10.1002/aenm.202000093.
[4] G. A. Elia, I. Hasa, G. Greco, T. Diemant, K. Marquardt, K. Hoeppner, R. J. Behm, A. Hoell, S. Passerini, R. Hahn, J. Mater. Chem. A 2017, 5, 9682.
[5] G. A. Elia, G. Greco, P. H. Kamm, F. García-Moreno, S. Raoux, R. Hahn, Adv. Funct. Mater. 2020, 30, 2003913.
[6] X. Liu, G. A. Elia, S. Passerini, J. Power Sources Adv. 2020, 2, 100008.
[7] X. Liu, H. Euchner, M. Zarrabeitia, X. Gao, G. A. Elia, A. Groß, S. Passerini, ACS Energy Lett. 2020, DOI 10.1021/acsenergylett.0c01767.
[8] X. Liu, G. A. Elia, B. Qin, H. Zhang, P. Ruschhaupt, S. Fang, A. Varzi, S. Passerini, ACS Energy Lett. 2019, DOI 10.1021/acsenergylett.9b01675.
[9] S. Porporato, M. Bartoli, A. Piovano, N. Pianta, A. Tagliaferro, G. A. Elia, R. Ruffo, C. Gerbaldi, Batteries 2022, 8, 183.

High-rate CO_2 and CO electroreduction to formate and acetate

Ivan Grigioni[1], Maria Vittoria Dozzi[1], Laura Vigni[1], Roham Dorakhan[2], Byoung-Hoon Lee[2], Edward Sargent[2], Elena Selli[1]
[1]Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy
[2]Department of Electrical and Computer Engineering, University of Toronto, Ontario, Canada

Electrochemical CO_2 and CO reduction reactions (CO_2RR and CORR) enable the recycling of CO_2 waste and storing of renewable electricity into energy-rich chemicals conventionally produced from fossil resources [1]. Liquid hydrocarbons produced via CO_2RR and CORR are widely employed commodity chemicals (e.g. formate, ethanol, acetate, and propanol), they have high energy density and offer straightforward storage and transportability. Therefore, we sought to develop electrocatalysts with high selectivity to formate and acetate at reaction rates (current densities) of industrial interest. Inspired by the high selectivity to formate of indium-based catalysts and the high activities of nanostructured catalysts, we integrated colloidal quantum dots (CQDs) made of indium phosphide and capped with indium ligands into gas diffusion electrodes for CO_2RR. These cathodes generate formate with selectivity, measured as Faradaic efficiency (FE), above 90% within a wide current density range (400-1000 mA cm^{-2}, see Figure 1). Operando Raman and electrochemical characterizations, together with ex-situ XPS analyses, suggest that the active catalyst presents the coexistence of metal indium and surface sulphur, which cooperatively allow the high selectivity and activity of this catalyst [2]. Upgrade of CO to hydrocarbons favours high selectivity toward long hydrocarbon (C_{2+}) products. Additionally, the low solubility of CO in aqueous electrolytes results in increased energy efficiencies when CO_2RR-to-CO is followed by CORR-to-hydrocarbons. To exploit these advantages, we developed Cu-oxide-derived electrocatalysts that enhance the FE to C_{2+} liquid products, mainly acetate, at industrially relevant current densities [3]. Lastly, we targeted high carbon dioxide utilization in CO_2RR and developed copper-based electrocatalysts for acidic conditions to avoid losses of CO_2 due to carbonate formation.

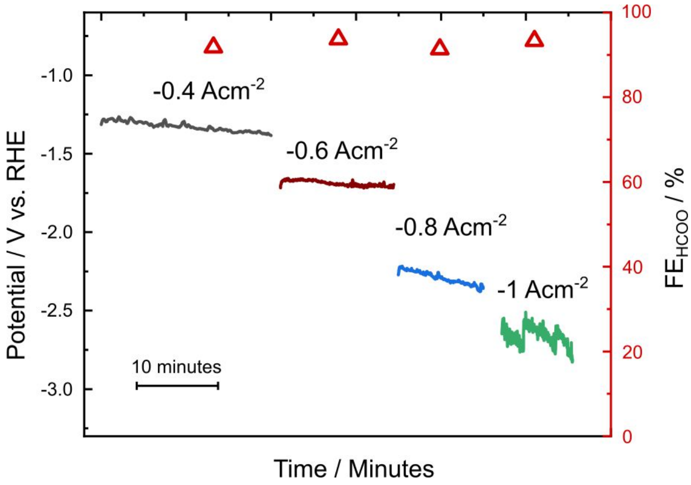


Figure 1: stepped chronopotentiometry from 400 to 1000 mA cm^{-2} with an InP CQDs-based cathode. In 3 M KOH, applied voltage (left axis) and Faradaic Efficiency (right axis) to formate.

[1] D. T. Whipple et. Al., JPCL 24 (2010) 3451
[2] I. Grigioni et al., ACS Energy Lett. 6 (2021) 79
[3] R. Dorakhan et al., Nature Synt. 3 (2023) 1307

Abstract ID. T3O04

Photosynthetic bacteria in coffee-based photoelectrochemical system

Rossella Labarile[1], Paolo Stufano[2], Matteo Grattieri[1,3], Maria Varsalona[1,3], Giacomo Mandriota[1],
Massimo Trotta[1]

[1] *Consiglio Nazionale delle Ricerche, Istituto per i Processi Chimico Fisici (CNR-IPCF),* via Orabona 4, Bari, Italy
[2] *Consiglio Nazionale delle Ricerche, Istituto di Nanotecnologia (CNR-NANOTEC),* via Orabona 4, Bari, Italy
[3]*Università degli Studi di Bari "Aldo Moro", Dipartimento di Chimica,* via Orabona 4, Bari, Italy
Presenter's e-mail address: r.labarile@ba.ipcf.cnr.it

Technological interventions are required for the sustainable valorization of the huge amount of waste produced by agricultural systems. Photosynthetic bacteria-based technology [1] can meet the urgent need to design and develop eco-friendly, cost-effective, and socially acceptable agri-waste management technologies.

Photosynthetic purple non sulfur bacteria are anoxygenic microorganisms with versatile metabolism, as they use sunlight to oxidize a broad variety of organic compounds in addition to heterotrophic and photoautotrophic alternative metabolisms. [2] Representative strains of two *Rhodobacter* (*R.*) species, *R. capsulatus* and *R. sphaeroides*, were selected for their ability to rapidly adapt to several growth media. [3]

Based on the promising evidences of their photo-metabolism on coffee and coffee-waste based media, we explored the possibility of developing bio-hybrid photoelectrochemical systems. We showed that *R. capsulatus* and *R. sphaeroides* are able to generate a measurable photocurrent at bio-hybrid interfaces by using green coffee extracts, and more specifically chlorogenic acids, as effective mediators for Extracelluar Electron Transfer (EET). Moreover, the preliminary results obtained by coupling such system with bio-based carbon composite electrodes recently developed [3], pose the foundation for a new class of circular and coffee-based bio-hybrid photoelectrochemical systems.

Funding: This work was funded by the Fonds National Suisse de la Recherche Scientifique, project *Phosbury - Photosynthetic bacteria in Self-assembled Biocompatible coatings for the transduction of energy* - (Project Nr CRSII5_205925/1).

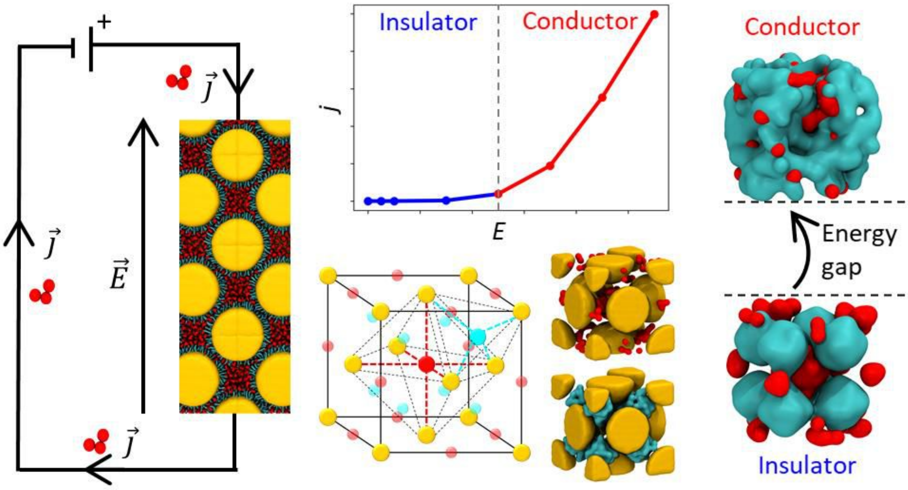
[1] J. Chen et al. Environment International, 137 (2020) 105417
[2] D.M. George et al. Biotechnology Reports, 28 (2020) e00563
[3] Labarile et al. MRS Advances (2023) https://doi.org/10.1557/s43580-023-00566-6
[4] G. Buscemi et al. ACS Applied Materials & Interfaces, 14(23), (2022) 26631–26641

Supramolecular Semiconductivity through Emerging Ionic Gates in Ion−Nanoparticle Superlattices

Chiara Lionello[1], Claudio Perego[2], Andrea Gardin[1], Rafal Klajn[3], Giovanni M. Pavan[1,2]
[1]*Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy*
[2]*Department of Innovative Technologies, University of Applied Sciences and Arts of Southern Switzerland, Polo Universitario Lugano, Via la Santa 1, 6962 LuganoViganello, Switzerland*
[3]*Department of Organic Chemistry, Weizmann Institute of Science, Herzl St 234, Rehovot 76100, Israel*
chiara.lionello@polito.it

The self-assembly of nanoparticles (NPs) driven by small molecules or ions may produce colloidal superlattices with properties evocative of those of metals or semiconductors. Recent studies demonstrated that in multicomponent colloids the NPs composing the crystal structure behave as atom equivalents, while the smaller species, which are responsible for the assembles structure, act as superelectron equivalents.[1,2,3]

However, how much the properties of such supramolecular crystals actually resemble those of atomic materials often remains unclear. Herein, coarse-grained molecular simulations demonstrate how a behavior evocative of that of electronic semiconductors may arise even on a higher scale in a colloidal superlattice.[4] In particular, we focus on gold nanoparticles functionalized with positively charged groups that self-assemble into FCC crystals through the mediation of citrate counterions.[5] *In silico* ohmic experiments show to what extent the dynamically diverse behavior of the counterions in different superlattice domains permits the opening of conductive ionic gates above certain levels of applied electric fields. The observed binary conductive/non-conductive behavior is reminiscent of that of conventional semiconductors, while, at a supramolecular level, crossing the “band gap” requires a sufficient electrostatic stimulus to break the electrostatic interactions and make ions diffuse throughout the superlattice's cavities



[1] M. Girard et al. Science 346 (2019) 201-224
[2] S. Wang et al. Nat. Mat. 21 (2022) 580-587
[3] X. Zhao et al. Nat. Electron. 13 (2021) 109-115
[4] C. Lionello et al. ACS Nano 17 (2023) 275-287
[5] T. Bian et al. Nat. Chem. 13 (2021) 940-949

Solar energy conversion via photothermocatalytic hydrogen production

Livolsi Simone, *Elena Selli and Gian Luca Chiarello*
Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20132 Milano, Italy
simone.livolsi@unimi.it

Photocatalytic processes are usually considered to be temperature independent, however the surface reaction mechanisms can be greatly influenced by this parameter. It this work we have explored the effect of temperature on the photo-steam reforming of methanol ($CH_3OH + H_2O \rightarrow CO_2 + 3\ H_2$) over one-step flame made TiO_2, Pt/TiO_2 and $Pt/CeO_2/TiO_2$ photocatalysts [1]. The reaction has been investigated under both dark and light conditions in the 40-350 °C temperature range, and its effect on the reaction mechanism was studied by operando Modulated Excitation DRIFT (Diffuse Reflectance Infrared Fourier Transform) analysis. This was performed by alternating light and dark conditions at different temperatures, by in-situ monitoring the dynamics of reactive surface species, including H_2O, CO_2, and $HCOO^-$ adsorbed on the TiO_2 surface and CO on Pt. (Fig.1a-c) [2-4]. The presence of Pt nanoparticles (0.75% wt.) led to an impressive increase in hydrogen production rate (r_{H2}), up to ca. 420 mmol $h^{-1}\ g_{cat}^{-1}$ at 350°C, together with a strong activity also in the dark at temperatures higher than 190°C (Fig. 1). However, in these conditions, the high r_{H2} is obtained together with a high selectivity to CO as the main methanol oxidation product, limiting the production of H_2. The selectivity to CO_2 (s_{CO2}) has been increased from 5% to 55% at 190°C, together with a higher r_{H2}, upon CeO_2 addition in catalyst formulation (from 5 to 50% wt.), exploiting the Water Gas Shift (WGS) reaction ($CO + H_2O \rightarrow CO_2 + H_2$) promoted by this metal oxide (Fig.1d). This work demonstrated that both r_{H2} and selectivity to each methanol oxidation product are affected by the operating temperature. Moreover, r_{H2} and s_{CO2} can be further increased by the addition of CeO_2. The use of photoreactors combined with solar concentrators may allow the exploitation of powerful synergistic effects between photocatalytic and thermal reactions.

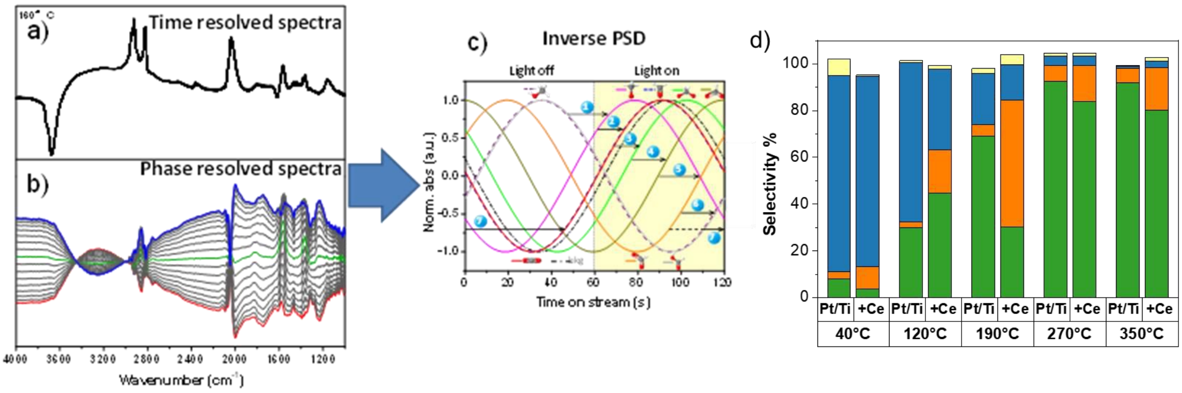


Fig.1 - In-situ Modulated Excitation DRIFT results at 160°C: a) time resolved spectra; b) phase resolved spectra; c) time on stream variation of the identified species obtained by inverse PSD; d) Selectivity to methanol oxidation products (yellow HCOOH, blue HCHO, orange CO_2 and green CO) over Pt/TiO_2 (Pt/Ti) and $Pt/CeO_2/TiO_2$ at different temperatures.

[1] G.L. Chiarello, M.V. Dozzi, J.D. Grunwaldt and E. Selli, Appl. Catal. B, 160 (2014) 144
[2] G.L. Chiarello and D. Ferri, Phys. Chem. Chem. Phys. 17 (2015) 10579-10591
[3] G.L. Chiarello, M. Bernareggi, E. Selli, ACS Catal., 12 (2022) 12879
[4] A. Urakawa, T. Bürgi, A. Baiker, Chem. Eng. Sci., 63 (2008) 4902

Photo-electrocatalytic approach for simultaneous hydrogen production and pollutant abatement

Enrica Maria Malannata, Alessandro Auditore, Nunzio Tuccitto, Antonino Licciardello
Dipartimento di Scienze Chimiche, Università degli Studi di Catania, v. A. Doria 6, 95125 Catania (Italy)
enrica.malannata@phd.unict.it

The demand for better environmental quality and the need to create a non-fossil fuel economy are among the major hot topics in our society. In this context, water pollution is an increasingly serious and urgent problem to be solved. More and more contaminants are present in water, such as pesticides, pharmaceuticals, microplastics, organic dyes and microplastics, organic dyes, and so on (emerging pollutants - EPs). EPs can cause many adverse effects on the environment and human health, so their removal is necessary. At the same time, energy production must be done through sustainable processes and without the use of fossil fuels, using energy carriers such as H_2.

One potential solution that combines these two environmental challenges is the use of EPs as feedstock for H_2 generation. Several processes have recently been proposed for this purpose, such as photocatalysis, electrocatalysis, and, only recently, combined photo-electrocatalysis [1].

In this context, TiO_2 is the most widely used material, but it has several problems, including a band gap around 3.0-3.2 eV that does not allow absorption of visible light.

With appropriate surface modifications, such as the presence of phosphate anions, it is possible to increase the generated photocurrent [2] to improve the performance of the material.

For this purpose, in this work, the surface of TiO_2-based nanostructured films was engineered by chemical surface modification to improve their photo-electrocatalytic performance, with the goal of obtaining hydrogen from the target pollutant through a multi-catalytic approach.

Specifically, the mesoporous TiO_2 film was engineered using zirconium phosphate (ZP) modification [3] to improve the sunlight sensitivity, electrical properties, and thermal stability of the material and to obtain an ideal platform to anchor co-catalysts (such as Ru-based systems).

The functionalization of the surface of the samples was verified using TOF-SIMS, which allows for spatially resolved 3D chemical information. This provides the necessary information for the efficient engineering of the material in order to obtain the best performances for the required function.

The morphology, structure and optical properties of the modified samples were investigated by different techniques, such as SEM, XRD and UV-DRS. Hydrogen detection was investigated by GC measurements. Finally, a comparison of materials used in the photo-electrocatalytic approach was made in order to define the best performing material for simultaneous water purification and H_2 evolution.

[1] R. Dewil, et al. J. Environ. Manage. 195, 93 (2017).
[2] L. Jing et al. Energy Environ. Sci. 5, 6552 (2012).
[3] S. Vitale et al. J.Vac. Sci. Technol. B, Nanotechnol. Microelectron. Mater. Process. Meas. Phenom. 34, 03H110 (2016).

This work has been partially funded by European Union (NextGeneration EU), through the MUR-PNRR project SAMOTHRACE (ECS00000022)

Design challenges for efficient molecular solar-thermal systems

Marco Marazzi[1,2], Martina Nucci[1], Cecilia Merino-Robledillo[1], Marta Delgado-Gómez[1], Luis M. Frutos[1,2]
[1]Universidad de Alcalá, Physical Chemistry Unit, Alcalá de Henares, Madrid, Spain
[2]Universidad de Alcalá, Chemical Research Institute ''Andrés M. del Río'' (IQAR), Alcalá de Henares, Madrid, Spain
marco.marazzi@uah.es

Molecular solar-thermal systems (MOSTs) [1] could in principle constitute an efficient solution for storing and releasing solar energy, through the design and technological implementation of specific molecular photoswitches: solar irradiation can convert a low-energy isomer into a high-energy isomer, thus storing energy that could be released at demand (see Figure a,b). Although attractive, the design of an efficient MOST is far from a trivial task, since several criteria need to be fulfilled at the same time:

- The low-energy isomer has to be activated by solar light, possibly covering a wide spectral window, while the high-energy isomer has to be photochemically inactive.
- Energy storage is possible only if the high-energy isomer is chemically stable, but at the same time the activation energy required to release such energy needs to be lowered by the addition of a proper catalyst.
- The storage density (defined as the ratio between storage enthalpy and molecular weight) needs to be maximized, hence requiring a small-size molecule capable of the highest possible raise in photoinduced enthalpy.
- The overall MOST system (i.e., both isomers) is expected to be in a liquid phase, to facilitate its technological use (see Figure c).

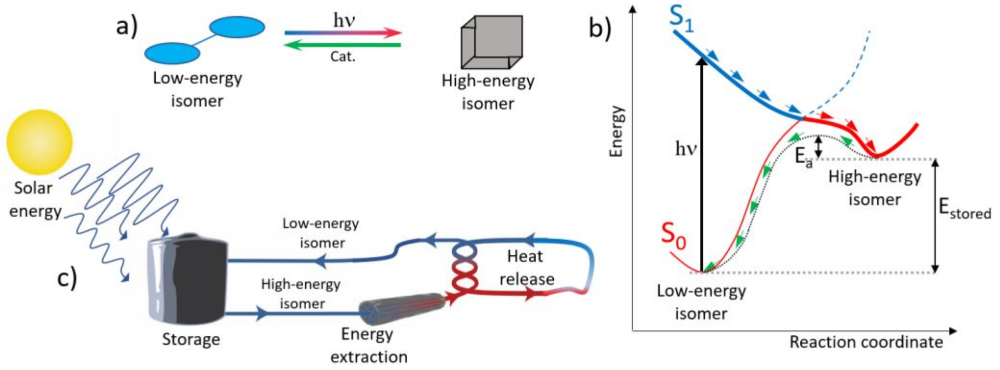


Figure. Functioning scheme of a MOST in terms of chemical reaction (a) and potential energy surfaces (b). A sketch of the technological desired outcome is also shown (c).

Here, we show the results obtained by our group in the last 5 years, including the optimization of existing MOSTs (norbornadiene/quadricyclane [2] and *E*/*Z* azobenzene [3]) by mechanochemically suggested substitution patterns, as well as the proposal of completely new systems, based on cubane, cubadiene [4] and the photo-formation of oxetane species [5]. Pros and cons of the different systems will be highlighted, concerning reaction mechanisms, electronic absorption properties, the eventual design of multi-chromophoric units, and the feasibility of their use as MOSTs.

This work was funded by Comunidad de Madrid and Universidad de Alcalá through the project "SolFuel" (Ref.: CM/JIN/2021-022).

[1] X. Xu et al. Small 18 (2022) 2107473.
[2] M. Nucci et al. ACS Sustainable Chem. Eng. 7 (2019) 19496.
[3] M. Nucci et al. Adv. Sustainable Syst. 6 (2022) 2200097.
[4] C. Merino-Robledillo et al. Front. Chem. 11 (2023) 1171848.
[5] M. Delgado-Gómez et al. In preparation.

Structural investigation and kinetic features of CO_2 conversion processes induced by photochemical and mechanochemical activation

Gabriele Mulas[1], A.Taras[1], M.D.Simula[1], L.Cappai[1], S.Enzo[1], F.Murgia[1], S.Garroni[1]

[1]Department of Chemical, Physical, Mathematical and Natural Sciences, University of Sassari, Sassari, Italy
mulas@uniss.it

The development of new chemical systems and sustainable approaches to mitigate the ever-increasing CO_2 concentration in the atmosphere, is nowadays a compelling challenge for the scientific community. To this regard, Carbon Capture Utilization and Storage, CCUS, sums up the set of scientific and technological efforts related to the strategies and potential solutions which look towards on large-scale application. Several issues, including technological, economical, regulatory ones, are still open. In particular, there is the need for endeavouring CO_2 transformations driven by renewable energy sources and over widely available and cheap chemical systems. CO_2 conversion by carbon mineralization processes, a strategy present in CCUS, include chemical transformations occurring in nature, although requiring specific conditions and featuring sluggish kinetics. In this work we focus on this class of processes paying attention the reactivity of minerals and waste materials, arising from industrial slags, based on silicates, and acting as solid substrates for CO_2 transformation induced by photochemical and mechanochemical activation. The CO_2 conversion has been investigated under batch and flow conditions, highlighting kinetic features and the efficiency of the processes. Structural, morphological, and electronic properties of the solid materials have been evaluated by several instrumental techniques providing insights into the different reaction mechanisms and local specific properties.

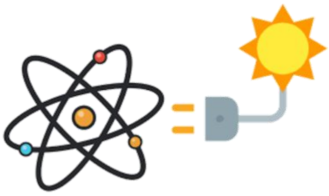
Abstract ID. T3O10

First principles assessment of electronic and charge transfer properties at functional interfaces for emerging photovoltaics

Ana B. Muñoz-García[1], Francesca Fasulo[2], Adriana Pecoraro[1], Michele Pavone[2]
[1]Department of Physics “Ettore Pancini”, University of Naples Federico II, Via Cintia 21, 80126, Naples, Italy
[2]Department of Chemical Sciences, University of Naples Federico II, Via Cintia 21, 80126, Naples, Italy
anabelen.munozgarcia@unina.it

Solar energy conversion is a fundamental pillar within the ongoing ecological transition towards a sustainable economy and society. Emerging photovoltaic (PV) technologies such as dye-sensitized solar cells (DSCs) [1] and perovskite solar cells (PSCs) [2] inspire a vast scientific community due to their intrinsic advantages with respect to entrenched Si-based PVs: lower materials cost, easier manufacturing, flexible and light modules, and less energy/mass requirements resulting in a lighter environmental footprint. In these systems, the conversion of light into electricity involves charge transport (CT) across several materials, difficult to understand holistically solely from experimental outcomes due to the inherent complexity of the functional interfaces involved. For this reason, computational modeling tools based on atomistic and first-principles approaches are at the forefront of the current revolution of material design and optimization for PV technologies.

This contribution will discuss how DFT-based approaches are able to assess the CT features across several interfaces between optically active materials and charge-collector layers in different electrochemical environments, which are the core events for PV functioning. In particular, we will discuss promising Cu-based molecular redox-couples in DSC photo-anodes [3] and heterogenous interfaces between lead halide perovskites and inorganic and organic hole transport materials [4, 5], from the analysis of electronic structures to the determination of CT dynamics and rates [6].



[1] A. B. Muñoz-García, I. Benesperi , G. Boschloo, J. J. Concepcion, J. H. Delcamp, E. A. Gibson, G.J. Meyer, M. Pavone, H. Pettersson, A. Hagfeldt, M. Freitag. Chem. Soc. Rev. 50 (2021) 12450-12550
[2] J. Young Kim, J-W. Lee, H. Suk Jung, H. Shin, N-G. Park. Chem. Rev. 120 (2020) 7867–7918
[3] I. Benesperi, H. Michaels, T. Edvinsson, M. Pavone, M.R. Probert, P. Waddel, A. B. Muñoz-García, M. Freitag . Chem 8 (2022) 439-449
[4] A. Pecoraro, A. De Maria, P. Delli Veneri, M. Pavone, A. B. Muñoz-García. Phys. Chem. Chem. Phys. 22 (2020) 28401-28413
[5] P. Mäkinen, F. Fasulo, M. Liu, G. K. Grandhi, D. Conelli, B. Al-Anesi, H. Ali-Löytty, K. Lahtonen, S. Toikkonen, G. P. Suranna, A. B. Muñoz-García, M. Pavone, R. Grisorio, P. Vivo. Chem. Mater 35 (2023) 2975-2987
[6] A. Pecoraro, F. Fasulo, M. Pavone, A.B. Muñoz-García. Chem. Commun. 59 (2023) 5055-5058

Metastable $NaCB_{11}H_{12}$ polymorph prepared by mechanical milling as new superionic conductor for post-Li solid-state batteries

Fabrizio Murgia,[1,2] Matteo Brighi,[2] Laura Piveteau,[3] Claudia E. Avalos,[3] Valerio Gulino,[4] Laura Caggiu,[2] Peter Ngene,[4] Petra de Jongh[4], Sebastiano Garroni[1], Gabriele Mulas[1] and Radovan Černý[2]
[1]Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy
[1]Laboratory of Crystallography, Department of Quantum Matter Physics, University of Geneva, Quai Ernest-Ansermet 24, CH-1211 Geneva, Switzerland
[3]Institute of Chemical Sciences and Engineering, NMR Platform, Ecole Polytechnique Fédérale de Lausanne, Station 6, CH-1015 Lausanne, Switzerland
[4]Materials Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, 3584 CG Utrecht, The Netherlands
fmurgia@uniss.it

In the search for safer and more efficient electrochemical energy storage systems, Na-based all-solid-state batteries (Na-ASSBs) represent a viable evolution from the current Li-ion technology. Na-ASSBs combine the advantages of availability and low cost of Na precursors, with both intrinsic enhanced safety and extended temperature operating range offered by the non-flammable solid electrolyte (SE) when compared to lithium-ion batteries.[1,2] The challenge for Na-ASSBs has been mainly the development of room temperature (*rt*) SE that withstand elevated current densities, *i.e.* providing both (electro)chemical robustness and favourable mechanical properties. Sodium salts of large-cage hydridoborates $[B_xH_x]^{2-}$ ($x = 10,12$), and their C-derivatives $[CB_{x-1}H_x]^-$ have proven to be promising Na-based SE. Indeed, they show an excellent electrochemical stability, arising from the strong electron delocalization on the anion cluster, as well as low area resistance, low density and soft mechanical properties.[3] Fast cationic motion generally occurs after a polymorphic transition towards higher-symmetry phases. This *order-disorder* phase transition provides structures with more free sites for the cations, as well as an increased rotational energy of the anion cages, which enhances the cation motion (*e.g.* paddle-wheel effect).[4] However, such phase change occurs far above *rt*, thus hampering practical applications. Lowering (or suppressing) the phase transition has been made possible by chemical tuning (anion substitution) or physical treatments implying either the formation of composites, nanoconfined materials or by mixing anionic (or neutral) hydridoborate clusters.[5,6] In contrast to these strategies, here we present the effect of mechanical milling in stabilizing at *rt* the superionic conductive phase of a single-anion material, $NaCB_{11}H_{12}$. The high-energy ball milling quenches the metastable, body-centred cubic (*bcc*) polymorph, which exhibits a larger number of available Na^+ sites. Macroscopically, this results in a conductivity of 4 mS cm^{-1} at 20°C (Fig. 1), without altering the electrochemical stability.[7] Preliminary electrochemical tests show that *bcc*-$NaCB_{11}H_{12}$ withstand a critical current density of 0.12 mA cm^{-2}. Finally, the rich polymorphism of $NaCB_{11}H_{12}$ has been thoroughly elucidated by temperature-dependent synchrotron X-ray diffraction.

[1] S. Ferrari *et al.*, *Adv. Energy Mater.*, 2021, **2100785**, 2100785.
[2] C. Vaalma *et al.*, *Nat. Mater. Rev.*, 2018, **3**, 18013.
[3] R. Černý, M. Brighi and F. Murgia, *Chemistry (Easton).*, 2020, **2**, 805–826.
[4] T. J. Udovic *et al.*, *Chem. Commun.*, 2014, **50**, 3750.
[5] M. Brighi *et al.*, *J. Power Sources*, 2018, **404**, 7–12.
[6] L. Duchêne *et al.*, *Chem. Commun.*, 2017, **53**, 4195–4198.
[7] F. Murgia *et al.*, *ACS Appl. Mater. Interfaces*, 2021, **13**, 61346–61356.

Exploring the chemical physical properties of Phase Transition - MOlecular Solar Thermal materials under a computational lens

Mattia Perrone[1], Massimo Delle Piane[1], Giovanni M. Pavan[1,2]
[1]*Department of Applied Science and Technology, Politecnico di Torino,*
Corso Duca degli Abruzzi 24, I-10129 Torino, Italy
[2]*Department of Innovative Technologies, University of Applied*
Sciences and Arts of Southern Switzerland, Polo Universitario Lugano,
Campus Est, Via la Santa 1, CH-6962 Lugano-Viganello,
Switzerland
mattia.perrone@polito.it

Molecular Solar Thermal (MOST) energy storage compounds, which undergo light-induced reversible isomerization, have garnered significant interest for their potential in optically controlled thermal energy storage and release. These compounds are especially promising for use as solar energy collectors, where they can absorb solar radiation during the day and release thermal energy subsequently on demand. A recent advancement in this field involves the design of phase transition MOST (PT-MOST) compounds, which transition from a solid to a liquid state upon light irradiation, allowing for the storage of additional energy in the form of latent heat.

A recent study by G. Han and coworkers [1] explored various PT-MOST compound candidates based on the photo-isomerization of azo-containing molecules. These specially designed compounds display exceptional properties, such as large penetration depths of light, near 100% conversion through extremely facile photoswitching, and high energy density storage (>300 J/g). However, the underlying mechanism behind the observed crystal-to-liquid phase transition upon photo-isomerization remains elusive, and it is unclear why some compounds exhibit photomelting while others do not.

In this oral presentation, we will delve into the behavior of different systems examined through atomistic molecular dynamics simulations, supplemented by enhanced sampling techniques. Through these means, we are able to analyze at atomistic detail the complex interplay between molecular structure, dynamics, and photo-excitation. This in turn provides crucial insights into the photomelting phenomenon and potential avenues for the design and optimization of future PT-MOST materials for efficient energy storage applications.

[1} J. Am. Chem. Soc. 2022, 144, 42, 19430–19436

Screening of electrolytes for novel batteries through polarizable molecular dynamics

Vanessa Piacentini[1], Adriano Pierini[1], Enrico Bodo[1]
[1]*Chemistry Department, University of Rome La Sapienza, Rome, Italy*
adriano.pierini@uniroma1.it

The ongoing electrification of many industrial and societal compartments is demanding for radical upgrades in current battery technology. Going beyond state-of-art Li-ion batteries requires the design of novel battery materials, and the research on electrolytes is a key factor for improving the electrochemical performance of batteries, as well as their stability and safety. Computational screening is a powerful resource for investigating structure-property relations of electrolytes from a molecular point of view. Among computational techniques, molecular dynamics with classical force fields is a prominent tool for the study of condensed-phase ionic systems, but an accurate description of electrostatics becomes challenging especially when the electronic charge density of large solvent molecules or anions gets strongly polarized by small monoatomic cations [1,2]. In such cases, the inclusion of polarization effects beyond the fixed-charge electrostatics can be crucial for obtaining accurate and predictive simulations of electrolytes [3,4].
We extended the AMOEBA polarizable force field to cover a range of electrolytes, thus allowing to exploit the predictive power of large-scale molecular dynamics simulation in order to screening the properties of novel electrolyte formulations. These include different organic solvents, ranging from glymes to sulfoxides and sulfones, as well as the lithium salts. The parametrization was first tested to reproduce ab-initio calculations of ionic-pair potentials and solvation energies, then the calculations were validated against experimental measurements of temperature-density relationships and transport properties. Special attention is given to the prediction of quantitatively correct diffusion coefficients of the ionic species, whose contribution to the transport numbers has a key impact on battery capacities. We attempt to relate diffusion coefficients to the local structural properties and solvation dynamics of the solvated cations, aiming at characterizing the contribution of different transport modes to the global ionic mobility.

[1] T. Liyana-Arachichi et al. J. Phys. Chem. B 122 (2018) 8548
[2] O. Starovoytov et al. J. Phys. Chem. B 125 (2021) 11242
[3] D. Bedrov et al. Chem. Rev. 119 (2019) 7940
[4] K. Goloviznina et al. J. Chem. Theory Comput. 17 (2021) 1606

Multiple effects induced by molybdenum doping in highly performing $BiVO_4$ photoanodes: surface vs bulk properties

Annalisa Polo[1], Maria Vittoria Dozzi[1], Ivan Grigioni[1], Kevin Sivula[2], and Elena Selli[1]
[1]Dipartimento di Chimica, Università degli Studi di Milano, Milano, Italy
[2]Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland
annalisa.polo@unimi.it

Among the most promising photocatalysts for solar energy conversion into hydrogen as a clean fuel via photoelectrochemical water splitting, $BiVO_4$ has emerged as a leading candidate as photoanode for water oxidation. So far, the doping with hexavalent metal ions such as Mo^{6+} or W^{6+} has been largely employed to increase the conductivity of the material by supplying additional free electrons [1,2]. In this work, the underlying mechanism for the Mo^{6+} doping induced increase in the photoelectrochemical performance of $BiVO_4$ is elucidated through a complementary structural, morphological, and photoelectrochemical investigation revealing not only the impact of the dopant onto the material bulk charge transport, but also its crucial role on the surface properties of $BiVO_4$. Photoelectrodes of pure and Mo^{6+} doped $BiVO_4$ with different doping degree and high optical transparency were prepared as multilayer films via spin coating deposition of aqueous-based precursor solutions onto conductive glass-substrates, followed by annealing. Transient absorption spectroscopy in the nano- to microsecond time scale reveals, for the first time, an elongation of the lifetime of photoproduced holes in the doped films, as a result of the far improved electron transport within the material bulk compared to the pristine electrode. Moreover, photoelectrochemical impedance spectroscopy points out a decrease in charge accumulation at the electrode/electrolyte interface under irradiation, detected through the build-up of the interfacial surface state capacitance in pristine $BiVO_4$, which acts as primary factor governing the performance increase observed with Mo^{6+} doped $BiVO_4$ photoanodes.

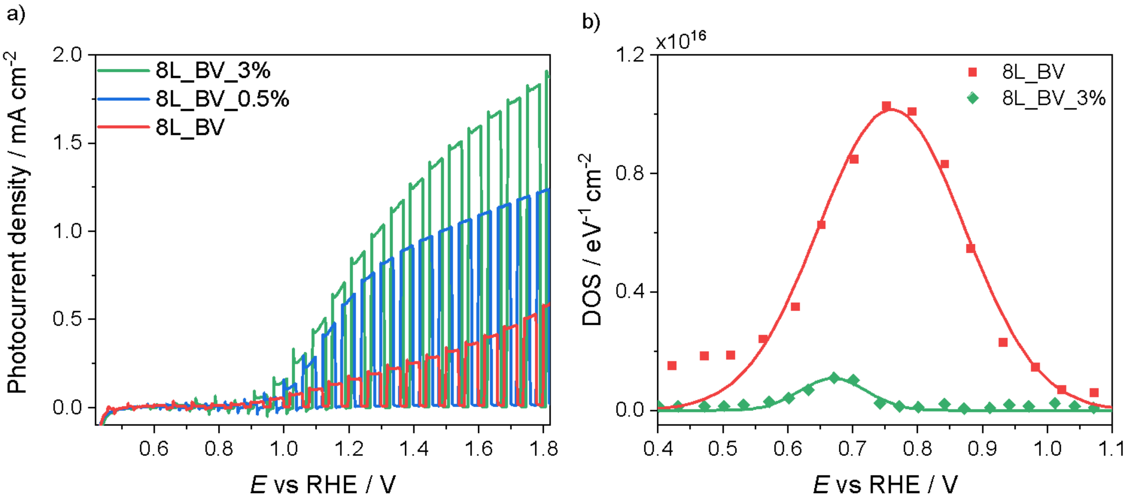


Fig. 1 a) Linear sweep voltammetry of the different investigated Mo^{6+} doped materials vs pristine $BiVO_4$ in 0.5 M Na_2SO_4 under AM 1.5 G front-side illumination and b) energy distribution of density of surface states (DOS) for the highest doped material and $BiVO_4$, fitted with a Gaussian function.

[1] Y. Park et al. Chem. Soc. Rev. 42 (2013) 2321
[2] A. Polo et al. Appl. Surf. Sci. 556 (2021) 149759

Thermodynamic study of chalcogenide perovskites and its precursors for photovoltaic applications

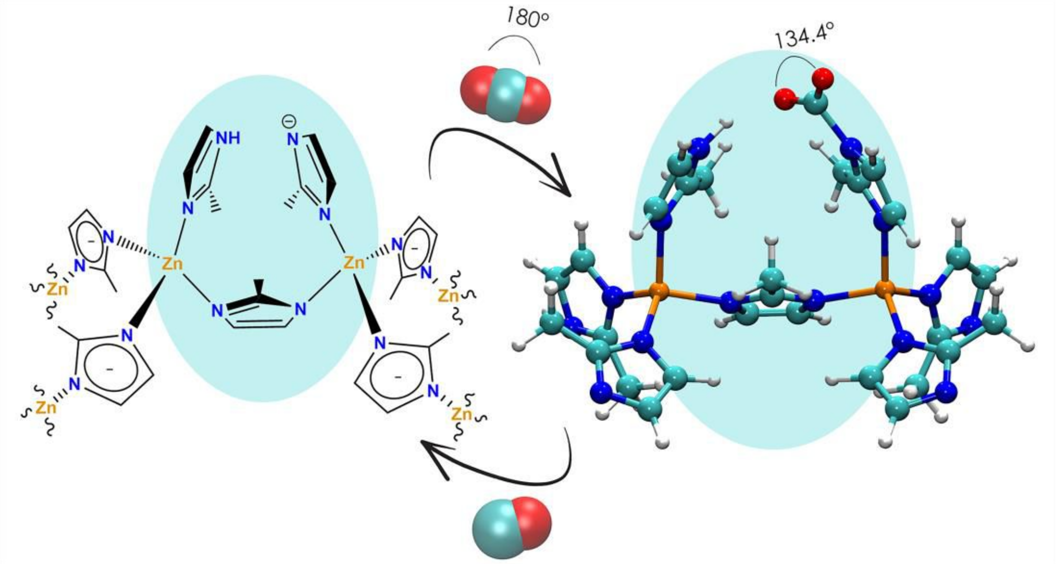
Lorenza Romagnoli[1], Alessandro Latini[1], Andrea Ciccioli[1], Hasan Arif Yetkin[2], Phillip J. Dale[2]
[1]*Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy*
[2] *Department of Physics and Materials Science, University of Luxembourg, 41, rue du Brill,*
L-4422 Belvaux, Luxembourg
lorenza.romagnoli@uniroma1.it

Among the profusion of new semiconductors currently investigated, halide perovskites have gained in the last years a prominent role, thanks to their optimal optoelectronic properties, combined with an inexpensive and easy synthesis; unfortunately, they suffer from severe instability issues, owing to their high reactivity towards environmental agents, which presently hinders their applications in real devices. However, much less work has been done by now on chalcogenide perovskites, even though interesting photovoltaic properties have been reported for the prototypical compound $BaZrS_3$ [1]; moreover, they have shown remarkably higher stability in ambient air and at high temperatures, compared to their halide counterparts. Unlike the mild conditions used for hybrid perovskites synthesis, strategies for attainment of bulk chalcogenide perovskites typically require 1000 K and long reaction times, often with flowing CS_2 or H_2S (both flammable and very toxic) on oxide precursors, while thin films are usually prepared by physical vapor deposition techniques, also involving temperatures of at least 450 °C [2]. Despite chalcogenide perovskites having witnessed a growing interest in the last years, a great deal of information about their thermodynamics is still missing, which is also the case for their precursors and for related binary sulfides. Several DFT calculations on these perovskites have been performed indeed [3], but their limitations lie in both neglecting entropy contributions and in focusing only on the stability of the ternary compounds with respect to precursors or competing phases. The lack of fundamental information about these intriguing systems led our research group to undertake an experimental investigation of $BaZrS_3$ and related sulfide perovskites, with the primary aim of studying their thermal behavior; this study appears particularly important in view of the preparation and characterization of thin films to be embedded in photovoltaic devices. Furthermore, by studying the decomposition thermodynamics at high temperature, it is in principle possible to derive the enthalpies of formation, both from solid precursors and from elements, which can be used to assess chemical stability at the operating and synthesis temperatures. $BaTiS_3$, $BaZrS_3$ and $BaHfS_3$ were therefore synthesized from BaS, elemental S and the corresponding metal in an evacuated and sealed glass tube at 500 °C for 6 days; under the same conditions, the binary trisulfides BaS_3 and ZrS_3 were prepared, starting from BaS and ZrS_2, respectively, and elemental S. In addition, an analogous synthesis of mixed $BaM_xM'_{1-x}S_3$ perovskites is currently underway. All the samples are characterized by powder XRD, Raman and UV-vis DRS, while thermal characterization involves TG-DTA, both in air and, for the binary trisulfides, in inert atmosphere, together with Knudsen effusion mass spectrometry on the perovskites and also on the binary compounds. The latter technique, in particular, allows to determine the identity and partial pressures of the released gas species, and to derive the thermodynamic properties therefrom. The routes to preparing phase pure chalcogenide perovskites and their stability will be discussed.

[1] X. Wei et al. Nano Energy 68 (2020) 104317
[2] K. V. Sopiha et al. Adv. Optical Mater. 10 (2021) 2101704
[3] S. A. Filippone et al. MRS Advances 3 (2018) 3249

Synergic effect of Carbon Nanotubes on Zeolitic Organic Framework catalyst for CO_2 electroreduction

Daniele Sassone[1]
[1]Istituto Italiano di Tecnologia, Via Livorno 60, Torino, Italy
daniele.sassone@iit.it



The electrochemical reduction of carbon dioxide (CO_2RR) into more energetic molecules, as chemicals and fuels, is becoming in the recent years an actual and promising technology that will have an important role to achieve a future zero-impact society.

In the last decade, a tremendous growth has characterize the CO_2RR technology, nevertheless the industrialization scale up is still a far goal to achieve, due to low performances and overall high costs. An often-underestimated aspect is the prize of materials employed, especially the metals typically used for the cathode and anode fabrication. If the electro-catalysis of carbon dioxide is dominated by metal/metal oxide species, a proper investigation and optimization of these metals atom should be encouraged. Confining metal atoms in an ordered and accessible porous structure, as in the metal organic framework (MOF), is considered an advanced strategy that enhances the atom efficiency and selectivity. A brand new sonochemical-synthesis of a zeolitic imidazole framework (ZIF-8), a subclass of MOF, grown on and inside of multi-walled carbon nanotubes (MWCNTs) were studied as catalyst for the CO_2RR. The strong π-π interaction between MWCNTs and the imidazole ligand prevent crystal growth during the synthesis assisted by the strong acoustic waves, leading to the formation of stable nano-particles. A deep electrochemical study of the material towards the CO_2 reduction reaction (CO_2RR) was performed in different concentrations of $KHCO_3$ aqueous solutions. The highest faradaic efficiency for CO_2RR products achieves 70.4% at -1.2 V vs the reversible hydrogen electrode (RHE) in 0.5 M $KHCO_3$ electrolyte, with a stable production rate of 0.08 mmol h^{-1} cm^{-2} in 16 hour of test, while the highest turnover frequency number (TOF) reaches a value of 453.9 s^{-1} at the same potential in 1.0 M $KHCO_3$ solution. Such approach highlight a different strategy to use metal atoms with a new and sustainable approach without losing the specific activity of their typical metal/metal oxide form.

POSTERS

T3. PHYSICAL CHEMISTRY OF ENERGY PRODUCTION AND STORAGE

Unraveling the Effect of Carbon Nanotube Oxidation on Solid-State Decomposition of Ammonia Borane/Carbon Nanotube Composites

Mattia Bartoli[1,2] , Sergio Bocchini [1,3] and Candido Fabrizio Pirri[1,3]
[1] Center for Sustainable Future, Italian Institute of Technology, Via Livorno 60, 10144 Italy
[2] Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, Florence, Italy
[3] Department of applied science and technology, Polytechnic of Turin, C.so Duca Abruzzi 24, 10129-Turin, Italy
email: mattia.bartoli@iit.it

Among the routes to perform hydrogen release from ammonia in solid state, the nanoconfinement into a carbonaceous matrix or the use of carbon-supported catalysts for the thermal degradation of ammonia borane is the most interesting one[1]. Oxidized carbon nanotubes (CNTs) represent a suitable choice for preparing ammonia borane mixtures or for anchoring catalysts for dehydrogenation. Nevertheless, literature lacks detailed study about the influence of CNTs oxidation degree on the AB degradation/hydrogen release.

In our study[2], study, we first described in a comprehensive way that the thermal degradation of AB mixed with CNTs by varying the CNT oxidation degree enlightens the degradative routes mainly active in each case as summarized in figure 1. Using highly oxidized CNTs, we observed a decrement of activation energy of the degradative process up to around 53% and the activation/suppression of different pathways based on the amount of oxygen functionalities present in the mixtures.

Furthermore, the presence of oxidized CNTs modulated the solid-state reactivity of AB reducing the release of nitrogen/boron species together with hydrogen. These findings lead the way for the design of new hydrogen storage materials.

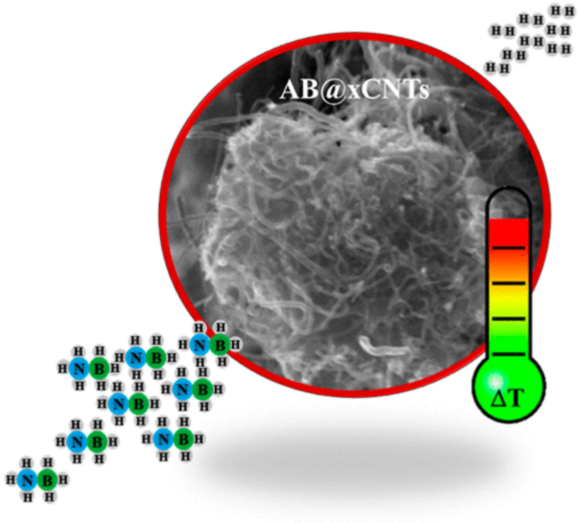


Figure 1: Schematic representation of AB@CNTs for hydrogen release

[1] Alpaydın, C. Y., Gülbay, S. K., & Colpan, C. O. (2020). A review on the catalysts used for hydrogen production from ammonia borane. *International Journal of Hydrogen Energy*, *45*(5), 3414-3434.

[2] Bartoli, M., Pirri, C. F., & Bocchini, S. (2022). Unraveling the Effect of Carbon Nanotube Oxidation on Solid-State Decomposition of Ammonia Borane/Carbon Nanotube Composites. *The Journal of Physical Chemistry C*, *126*(39), 16587-16594.

Realtime analysis of electrochemical reactions in batteries: the OpMetBat project

Sergio Brutti[1], Leonardo Suraniti[1], Maria Assunta Navarra[1], Marco Agostini[2]
[1]Dipartimento di Chimica, University of Rome La Sapienza, P.le Aldo Moro 5 00185 Roma (IT)
[2]Dipartimento di Chimica e Tecnologie del Farmaco, University of Rome La Sapienza, P.le Aldo Moro 5 00185 Roma (IT)
Sergio.brutti@uniroma1.it

The development of new battery materials is key to improving the performance, lifetime, safety and cost of energy storage technologies like Li-ion batteries for electric vehicles. However, innovation is hampered by the inability of industry to reliably characterize their structure and chemistry in an operating environment.

The OpMetBat project will build a metrological framework supporting traceable operando characterization of state-of-the-art battery materials under dynamic charge / discharge conditions. This includes advancement and validation of ex situ methods, establishing new protocols, cells and a best practice guide for operando approaches and developing new instrumentation enabling hybrid, multiparameter measurement to inform new materials development.

The project aims to develop operando techniques and hybrid (multi-modal) instrumentation, supported by quantitative and validated ex situ analysis and electrochemical measurements methods, to enable beyond state-of-the-art materials characterization for high-capacity energy storage technologies.

The good practice guide developed within this project will benefit the scientific community by improving reliability, repeatability/reproducibility and fidelity of operando measurements. The project will pioneer operando metrology for battery research at several European synchrotron radiation facilities and the transfer into laboratories to support industry and researchers.

The 21GRD01 OpMetBat project has received funding from the European Partmership on Metrology Participating States and from the European Union’s Horizon 2020 research and innovation programme.

Innovative chemistry in batteries aprotic electrolytes

Andrea Cioffi[1,2], Sergio Brutti[2], Giovanni Battista Appetecchi[1]

[1]ENEA, Materials and Physicochemical Processes Technical Unit (SSPT-PROMAS-MATPRO)Via Anguillarese 301, 00123,Roma, Italy
[2]La Sapienza University of Rome, Department of Chemistry, Piazzale Aldo Moro 5, 00185, Rome, Italy
AndreaCioffi13081999@gmail.com

The global energy production is mostly derived by fossil fuels combustion, which are non-renewable resources and have a deep environmental impact. These issues led to large investments towards the development of renewable energies. However, these sources are usually restricted by their intermittence and poor storage efficiency. Electrochemical energy storage (in particular Li/Na batteries) provides a feasible approach to store electric energy from these sources [1,2]. This work aims to investigate silica-gel based mesoporous electrode substrates, for being addressed to metal sodium batteries where the Na° anode is initially absent (i.e., “sodium-less” devices), in ionic liquid (IL)-based electrolytes. ILs, salts molten at room temperature, are non-flammable fluids with negligible vapor pressure and are proposed as alternative solvents to volatile and hazardous alkyl carbonates, commonly used in electrochemical energy storage devices. The electrode substrate’s structure is a threefold-made component: active material (Sodium silica-gel), electronic conductor (carbon) and a polymer (binder). The polymers used are PolyEthilene Oxide (PEO) and PolyVinylidenediFluoride (PVdF). As far as concerns the electrolyte, trimethyl-butyl-ammonium bis(fluorosulfonyl)imide (N_{1114}FSI) was selected as the ionic liquid [3] in combination with the NaTFSI and NaFSI salts. XRD, Raman and SEM (SEM-EDX) analysis were carried on the electrode substrates for investigating their chemical structure whereas galvanostatic cycling tests were run to examine the electrochemical behaviour. The results show a coulomb efficiency of 100% (after an appropriate activation procedure) already from the 1st cycle for more than 500 cycles in conjunction with very low cell voltage (3-30 mV), highlighting for efficient and reversible Na° stripping/plating process. These results are likely ascribable to the optimal electrode/electrolyte interphase due to the FSI film-forming ability. SEM-EDX analysis, carried out after prolonged cycling tests (> 500 cycles), evidence a stronger degradation for the FSI anion with respect to the TFSI one and a thicker passive film in the PVdF-containing electrode substrates. The N_{1114}FSI ionic liquid shows very good compatibility with the substrates and the Na° electrodes. The best performances were found in NaFSI-based electrolyte. To summarize, this work demonstrated the feasibility of ionic-liquid electrolytes as innovative components in “sodium-less” batteries, enhancing at the same time the safety/reliability and the performances (as compared with organic electrolytes).

References:
[1] K. Kubota, M. Dahbi, T. Hosaka, S. Kumakura, S. Komaba, Towards K-Ion and Na-Ion Batteries as “Beyond Li-Ion”. Chem. Rec. 18 (2018) 459–479.
[2] M.Á. Muñoz-Márquez, D. Saurel, J.L. Gómez-Cámer, M. Casas-Cabanas, E. Castillo-Martínez, T. Rojo, Na-Ion Batteries for Large Scale Applications: A Review on Anode Materials and Solid Electrolyte Interphase Formation. Adv. Energy Mater. 7 (2017) 1700463.
[3] G. Maresca, P. Casu, E. Simonetti, S. Brutti, G.B. Appetecchi, Sodium-conducting ionic liquid electrolytes: Electrochemical stability investigation, Applied Science 12 (2022) 4174.

STRUCTURAL AND DYNAMIC CHARACTERIZATION OF MIXED MATRIX MEMBRANES BASED ON FLUORINATED METAL-ORGANIC FRAMEWORKS BY SOLID STATE NUCLEAR MAGNETIC RESONANCE

Elisa Della Latta,[1] Francesca Nardelli,[2] Francesca Martini,[1,3], Marco Geppi,[1,3] Francesca Nerli,[1] Marco Taddei, [1,3] Carmen Rizzuto,[4] Elena Tocci,[4] Alessio Fuoco,[4] Virginia Guiotto,[5] Valentina Crocellà,[5] Matteo Signorile,[5] Diletta Morelli Venturi,[6] Ferdinando Costantino,[6] Lucia Calucci [2,3]

[1]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Giuseppe Moruzzi 13, 56124 Pisa, Italy
[2]Istituto di Chimica dei Composti Organo Metallici, Consiglio Nazionale delle Ricerche, Via Giuseppe Moruzzi 1, 56124 Pisa, Italy
[3]Centro per l'Integrazione della Strumentazione Scientifica dell'Università di Pisa (CISUP), Pisa, Italy
[4]Istituto per la Tecnologia delle Membrane, Consiglio Nazionale delle Ricerche, via P. Bucci 17/C, 87036 Rende (CS), Italy
[5]Dipartimento di Chimica, Centro di Riferimento NIS e INSTM, Università di Torino, Via G. Quarello 15, I-10135 and Via P. Giuria 7, I-10125 Torino, Italy
[6]Dipartimento di Chimica, Biologia e Biotecnologie, Unità di Ricerca INSTM, Università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy
elisa.dellalatta@phd.unipi.it

Mixed matrix membranes (MMMs) are emerging as a promising technology for gas separation. These materials are composites made from a polymer blended with a porous filler with exceptional adsorption properties, such as a covalent organic framework or a metal-organic framework (MOF). Thanks to their composition, they are considered next-generation membranes, since they combine the benefits derived from the processability of the polymer with the enhanced separation properties of the filler [1]. The physico-chemical properties of both the filler and the polymer as well as their interactions in the composite play a key role in obtaining MMMs with enhanced separation performances. It is thus important to unravel these properties at the molecular level to understand the structure-property relationship and to guide the design of optimized materials.

Solid State Nuclear Magnetic Resonance (SSNMR) has established itself as one of the most powerful techniques for investigating structural and dynamic properties of MOFs and composite materials at the atomic scale, as well as for gaining insight into the interaction with adsorbents [2,3]. In fact, high-resolution SSNMR spectra provide information on local structure and spatial proximity between nuclei. Moreover, other nuclear observables (e.g. nuclear relaxation times and anisotropic line shapes) give unique possibilities for the study of molecular dynamics.

In this work, multinuclear SSNMR is applied to investigate structural and dynamic properties of perfluorinated MOFs with high affinity towards CO_2 [4,5], gas separation membranes obtained from commercial polymers and the corresponding MMMs. In particular, ^{13}C, ^{19}F and ^{1}H high-resolution SSNMR experiments based on magic angle spinning (MAS) are carried out to study the structural properties of each material, while ^{1}H and ^{19}F spin lattice relaxation times (T_1) are exploited to gain information on the dynamics of polymer and MOF moieties. MAS and static ^{13}C SSNMR experiments are also applied to unravel the interaction of CO_2 with MOFs and membranes on selected samples.

[1] J. Dechnik, et al. Angew. Chem. Int Ed. 56 (2017) 9292
[2] B. E. G. Lucier, et al. Accounts of Chemical Research 51 (2018) 319
[3] B. Reif, et al. Nat Rev Methods Primers (2021) 1, 2.
[4] R. D'Amato, et al. ACS Sustainable Chem. Eng. 7 (2019) 394
[5] M. Cavallo, et al. J. Mater Chem. A. 11 (2023) 5568

Theoretical computational characterization of calcium electrolytes through Molecular Dynamics simulations

Marcello Della Sala[1], Matteo Busato[1], Enrico Bodo[1], and Paola D'Angelo[1]
[1] *Department of Chemistry, Sapienza University,*
Piazzale Aldo Moro 5, Rome, Italy
marcello.dellasala@uniroma1.it

In recent years, the demand for energy storage devices with excellent performance, eco-compatibility, safety, and scalability has grown owing to the general political push for reducing carbon emissions. The need for a rapid development of these devices is a key point for reaching eco-sustainability and preserving the environment's health. One of the main storage devices used nowadays are lithium ion-based intercalation batteries (LIBs). However, the low crustal abundance of lithium (and of cobalt, a crucial secondary ingredient of LIBs) makes it necessary to develop new battery paradigms based on the intercalation of other ions. There are different other ions with the potential to be used for the construction of next generation batteries and that could open the way for the use of new chemistries and ensure better safety, improved performance and lower costs associated with the raw materials. A possibility is represented by polyvalent ions, such as calcium, magnesium, zinc and aluminium, but only few solutions have been proposed so far [1]. In this work we employ molecular dynamics simulations to study the performance of calcium salts - amides electrolytes, shown in Fig. 1, as the electrolyte component of next generation batteries. The simulations were performed for different electrolyte solutions varying the temperature, the molecular weight of amides solvents, and the counterions of calcium.

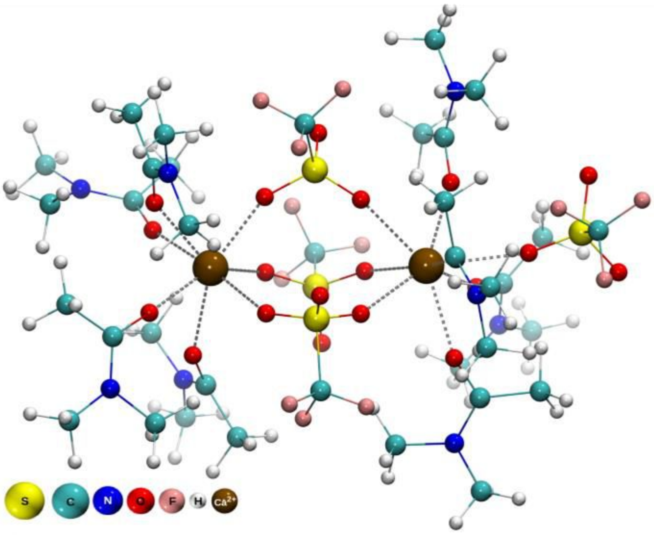


Figure 1: Representative snapshot from the molecular dynamics simulations of $Ca(TfO)_2$ 0.1 M solution in dimethylacetamide.

[1] L. Stievano et al. Journal of Power Sources Vol. 482, p. 228875 (2021).

Development of UiO-66-based metal-organic frameworks as single-ion conducting solid-state electrolytes

Valentino G. Martello[1, 2, 3], Barbara Centrella[2], Matteo Bonomo[2, 4], Alessandro Piovano[3,4], Claudio Gerbaldi[3, 4], Silvia Bordiga[2]
[1]University School for Advanced Studies IUSS, 27100, Pavia
[2] Department of Chemistry, NIS and INSTM Reference Centre, University of Torino, Via P.Giuria 7 I-10125 and Via G. Quarello 15/A I-10135, Torino
[3]GAME Lab, Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Torino
[4] National Reference Center for Electrochemical Energy Storage (GISEL) - INSTM, Via G. Giusti 9, 50121, Firenze
Email: valentino.martello@iusspavia.it

In the last decades, many research efforts have been devoted to the development of solid-state electrolytes (SSE), in order to eliminate the flammability issues related to liquid electrolytes and allow the manufacturing of compact, more durable and with higher energy density secondary batteries. In this context, we recently started a new research study focused on the synthesis of novel SSE based on metal-organic frameworks (MOFs) with single-ion conducting features. This is obtained by anchoring anionic pendants to the MOF structure, leaving only the cations (e.g. Li^+, Na^+, Mg^{2+}, Al^{3+}) free to flow.[1] This strategy was first proposed in the seminal work of Yang et al.,[2] who reported the synthesis of UiO-66-Br and its post-synthetic modification via insertion of a pendant group consisting of lithium 4-vinylbenzenesulfonate (UiO-66-LiSS, as shown in Figure 1). Aiming to evaluate the effect of defects on the ionic conductivity of the material, we here compare the electrochemical behavior of the UiO-66-LiSS material synthesized using the standard 2-bromoterephthalic acid linker (**1**) with different materials obtained by employing the linkers 1,3,5-tri- (**2**) and 1,2,4,5-tetra-carboxylic acid (**3**). Furthermore, due to their additional polar groups, the use of **2** and **3** also allows to synthetize the MOFs employing water as solvent, fostering the sustainability of the process. All the synthesized materials are fully characterized on the structural and spectroscopic viewpoints, prior to testing their performance in lab-scale electrochemical cells.

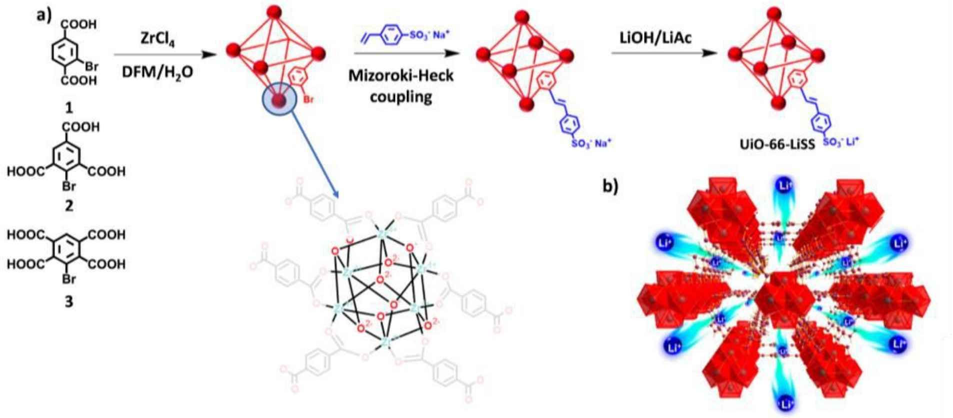


Figure 1 (a) Synthetic route and the schematic UiO-66-LiSS structure; (b) envisioned Li^+ ion transport mechanism in UiO-66-LiSS. The linkers 2 and 3 will be used as alternative to terephthalic acid. Adapted with permission from Yang et al. [2]

[1] H. Yang, B. Liu, J. Bright, S. Kasani, J. Yang, X. Zhang, N. Wu. ACS Appl. Energy Mater. 2020, 3, 4007–4013
[2] R. A. Kharod, J. L. Andrewsm, M. Dincă. Annu. Rev. Mater. Res. 2022, 52, 103–28

Combined Effects of Mo^{6+}-doping and TiO_2-coupling on $BiVO_4$ Photoanodes

Stefano Pezzoli, Laura Vigni[a], Annalisa Polo[a], Maria Vittoria Dozzi[a], Elena Selli[a,*]
[a]Department of Chemistry, University of Milan, via Golgi 19, I-20133, Milan, Italy
e-mail: stefano.pezzoli1@studenti.unimi.it

In artificial photosynthesis, sunlight is converted into chemical energy using a photoelectrochemical (PEC) cell, where water is split into hydrogen and oxygen. Thus, artificial photosynthesis has the potential to revolutionize the energy industry driving the development of a hydrogen economy. PEC water splitting involves the use of a semiconductor material which can generate electrons and holes under solar irradiation. Bismuth vanadate ($BiVO_4$), an extensively studied n-type semiconductor, is a cornerstone in photocatalysis research. Its capability to absorb a large portion of sunlight, *i.e.*, the visible radiation, combined to the favorable energy levels alignment makes it a promising material to successfully achieve the water splitting process. However, its most relevant drawbacks concern the extensive electron-hole recombination and the poor electron conductivity, which, in addition to the sluggish water oxidation kinetics, limit its overall PEC performance.

In our work, doping with Mo^{6+} ions and coupling with TiO_2, another quintessential photocatalyst, were carried out to evaluate their effects on the activity and stability of $BiVO_4$ photoanodes. The introduction of Mo^{6+} ions in the $BiVO_4$ crystal lattice ($Mo:BiVO_4$) has produced a dramatic photoactivity increase with respect to the pristine material (Figure 1), as widely observed [1]. Regarding the composite materials, instead, despite the unfavorable type I band alignment predicted at the $TiO_2/BiVO_4$ interface, a hot electrons injection mechanism from pure $BiVO_4$ to TiO_2 active only at $\lambda \leq 490$ nm, *i.e.*, for photons with an excess energy to reach sufficiently high energy levels in $BiVO_4$ CB, has already been demonstrated [2]. We verified that, while the coupled system outperforms only with respect to the TiO_2 component, the optimized $TiO_2/Mo:BiVO_4$ heterojunction shows an increased photoactivity with respect to both the undoped $TiO_2/BiVO_4$ composite material and each of the two single components. Interestingly, the $TiO_2/Mo:BiVO_4$ composite exhibits also greatly higher photocurrent stability over 4 h – long irradiation under constant applied potential, with respect to the single $Mo:BiVO_4$ material (Figure 2).

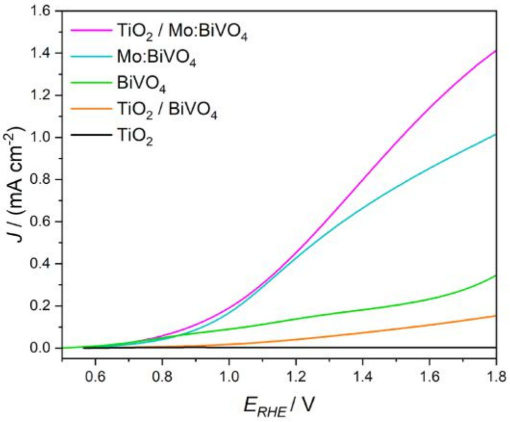


Fig. 1 LSV in a 0.5 M Na_2SO_4 electrolyte solution under visible light irradiation.

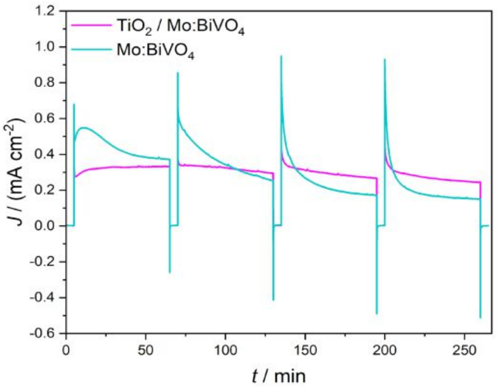


Fig. 2 Chronoamperometry in a 0.5 M Na_2SO_4 electrolyte solution under visible light irradiation and under a constant potential of 1.23 V_{RHE}.

Thus, we successfully synthetized well performing and highly stable $BiVO_4$-based photoanodes through two simple material modification techniques, *i.e.*, by doping with Mo^{6+} and by coupling doped $BiVO_4$ with TiO_2 in a heterojunction.

[1] K. P. S. Parmar et al. ChemSusChem 5 (2012) 1926.
[2] A. Polo et al. Catal. Today 340 (2020) 19.

Zero-dimensional model for a planar Solid Oxide Electrolyser Cell (SOEC) at different working temperatures

I. Polloni[1], D. Grilli[1], M. Pani[1,2], C. Artini[1,3], M. Viviani[4], S. Presto[4], A. M. Asensio[5], A. Barbucci[5], P. Costamagna[1]*
[1]DCCI, University of Genova, Via Dodecaneso 31, 16146 Genova Italy; [2]CNR-SPIN, Corso Perrone 24, 16152 Genova, Italy; [3]CNR-ICMATE, Via De Marini 6, 16149 Genova, Italy; [4] CNR-ICMATE, c/o DICCA-UNIGE, Via all'Opera Pia 15, 16145 Genova, Italy; [5] DICCA, University of Genoa, Via All'Opera Pia 5, I-16145, Genova, Italy
**irepolloni@gmail.com*

The demand for sustainable and environmentally friendly processes of producing syngas has led to the development of high-temperature co-electrolysis of carbon dioxide and steam. In an electrolyser, molecular hydrogen and oxygen are produced by water, respectively at the cathodic and anodic side, thanks to an external electrical power supply. In the same way, CO_2 can be converted into CO and oxygen in a reaction named carbon dioxide electrolysis. CO_2 and H_2O electrolysis can be paired together (co-electrolysis) to obtain H_2 and CO, which is known as syngas, a widely used intermediate gas mixture in synthesis processes. Performing the process at high rather than low temperatures has the advantage of requiring less electrical energy. This is explained by the decrease of the ΔG of the reactions with increasing temperature[1]. Therefore, solid oxide electrolyser cells (SOECs) are currently at the cutting edge of research. Since the output syngas ratio is a key factor, it is crucial to understand the effects related to the functioning of the electrolyser. These can be estimated through a model, aiming at evaluating the current-voltage (*j*-*V*) SOEC curves and the composition of the syngas produced in different operating conditions. In this framework, a zero-dimensional model is developed. The chemical part of the model includes the calculation of the outlet cathode gas composition, considering that the water gas shift reaction occurs and reaches thermodynamic equilibrium:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \tag{1}$$

The electrochemical part of the model is based on the calculation of the Nernst reversible voltage U_N. Then, the operating voltage U is obtained by subtracting all the voltage losses, which include ohmic, concentration and activation losses:

$$U = U_N + \eta_{ohm} + \eta_{conc} + \eta_{act} \tag{2}$$

The theoretical equations have been implemented in Matlab. The simulation results show that the CO_2:H_2O ratio in the cathode inlet gas strongly influences the slope of the *j*-*V* curves.

This work is developed with the fundings of the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No. 1561 of 11.10.2022 of Ministero dell'Università e della Ricerca (MUR); funded by the European Union – NextGenerationEU- : Project code PE0000021, Concession Decree No. 1561 of 11.10.2022 adopted by Ministero dell'Università e della Ricerca (MUR), CUP - D33C22001330002, Project title "Network 4 Energy Sustainable Transition – NEST".

1. Ebbesen, S. D., Jensen, S. H., Hauch, A. & Mogensen, M. B. High Temperature Electrolysis in Alkaline Cells, Solid Proton Conducting Cells, and Solid Oxide Cells. *Chem. Rev.* **114**, 10697–10734 (2014).

Corrosion of Al alloys tanks in bio ethanol blended gasoline fuel

Filippo Antonio Vernile[1], Federico Scaglione[1], Giancarlo Marchiaro[2], Claudio Errigo[2], Guido Viscardi[1], Marcello Baricco[1]
[1]*Dipartimento di Chimica e NIS - INSTM, Università di Torino, Via Pietro Giuria 7, 10125 Torino, Italia.*
[2]*CRF - Materials Engineering Methods & Tools Surface Treatment & Anticorrosion, C.so Settembrini 40, Torino, Italia.*
e-mail: filippoantonio.vernile@unito.it

Biofuels are suggested as substitutes for fossil fuels in transport applications to reduce greenhouse gas emissions. In vehicles using aluminium alloy tanks, contact with this type of fuel can lead to corrosion phenomena, resulting in reduced vehicle durability and safety [1]. This work aims to investigate the evidence of corrosion, close to the welded joints, on an Al alloy (AA1050) tanks in contact with E27 biofuel (i.e. 27% v/v ethanol) under operating conditions (incubation for 1000 hours at 60 ˚C).The fuel was analysed, by means of FT-IR analysis and mass spectrometry, before and after interaction with the material, checking for the presence chemical compounds that can affect the stability of the passivating layer of the alloy, such as alcohols, acetic acid and water. The tank alloy was analysed using SEM and EDS, before and after corrosion. Using the grazing angle XRD technique, the presence of oxides on the surface of the samples was investigated. Using free corrosion experiments and electrochemical analysis, the corrosive phenomenon was analysed on a laboratory scale. A significant water content (about 0.025 %) was observed in the freshly produced fuel, which did not generate the corrosion, whereas the fuel used under operating conditions showed a content up to ten times lower. FT-IR analyses of the fuel excluded the formation of alcoholates. Similarly, the presence of acetate ion, and thus acetic acid, was not observed, which allowed the oxidation of ethanol to acetic acid to be ruled out as a cause of corrosion. No significant differences were observed in the Open Circuit Voltage curves between samples with and without the welded zone. The welded specimen showed a corrosion potential of E_{corr}=-0.27 V when in contact with fresh production fuel, suggesting greater corrosion resistance with respect to the unwelded specimen, which showed a corrosion potential of E_{corr}=-0.36 V. The water content within the fuel appears to play a key role in the corrosion phenomena of the aluminium alloy under investigation. Different quantities of water were added to the fuel (0.4%, 0.6%, 0.8%) in order to investigate a possible raising of corrosion rate of the samples. Freshly produced fuel containing a sufficient amount of water favours passivation of the alloy rather than its corrosion. In fact, the presence of water led to the formation of protective oxides on the surface layer of the tank [2]. This layer, which also formed during the free corrosion experiments, blocked the corrosion phenomenon, as the surface was ennobled.

[1] Yoo, Y. H., Park, I. J., Kim, J. G., Kwak, D. H., & Ji, W. S. (2011). Corrosion characteristics of aluminum alloy in bio-ethanol blended gasoline fuel: Part 1. the corrosion properties of aluminum alloy in high temperature fuels. *Fuel*, *90*(3), 1208–1214. https://doi.org/10.1016/j.fuel.2010.10.058

[2] Park, I. J., Yoo, Y. H., Kim, J. G., Kwak, D. H., & Ji, W. S. (2011). Corrosion characteristics of aluminum alloy in bio-ethanol blended gasoline fuel: Part 2. the effects of dissolved oxygen in the fuel. *Fuel*, *90*(2), 633–639. https://doi.org/10.1016/j.fuel.2010.09.049

KEYNOTES

T4. THEORETICAL AND COMPUTATIONAL CHEMISTRY

Multiscale Multilevel Methods for Complex Systems

Tommaso Giovannini[1], Henrik Koch,[1,2] Chiara Cappelli[1]
[1]*Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy*
[2]*Department of Chemistry, Norwegian University of Science and Technology, Trondheim 7491, Norway*
tommaso.giovannini@sns.it

The theoretical description of large molecular systems in the condensed phase at a high level of accuracy is particularly challenging, due to the large number of degrees of freedom (both electronic and nuclear) that need to be treated. However, for molecular systems embedded in an external environment, such complexity can be drastically reduced by partitioning the total system into smaller, interacting subsystems, with a special focus on a specific portion [1-3]. The theoretical approaches developed within this framework belong to the family of focused models [1-3], and are indeed valuable tools used to bridge the gap between theory and experiment.

In this contribution, we present the recent developments in the framework of multilevel quantum-embedding approaches, defined in the framework of both Hartree-Fock (HF) and Density Functional Theory (DFT) [4-6], specifically designed to describe large molecular systems interacting with an external environment. The methods are defined in the molecular orbital (MO) basis of the target system (the active fragment) only [4-6], for which specific localization procedures are also proposed [7-8]. This aspect automatically allows for a saving in the computational cost, because the inactive density matrix is kept frozen, and thus the inactive MOs are not involved in the self-consistent field (SCF) procedure. Such a feature is also exploited in the extension of the methods to the calculation of molecular properties. Here, we discuss the accuracy of the methods for selected test cases by also comparing the numerical results with available experimental data [6,7,9,10].

[1] J. Tomasi et al. Chem. Rev. 105 (2005) 2999
[2] H. M. Senn et al. Angew. Chem., Int. Ed. 48 (2009) 1198
[3] T. Giovannini et al. Chem. Soc. Rev. 49 (2020) 49 5664
[4] S. Saether et al. J. Chem. Theory Comput. 13 (2017) 5282
[5] G. Marrazzini et al. J. Chem. Theory Comput. 17 (2021) 791
[6] T. Giovannini et al. J. Chem. Theory Comput. 19 (2023) 1446
[7] T. Giovannini et al. J. Chem. Theory Comput. 17 (2021) 139
[8] T. Giovannini et al. J. Chem. Theory Comput. 18 (2022) 4806
[9] L. Goletto et al. Phys. Chem. Chem. Phys. 23 (2021) 4413
[10] L. Goletto et al. Phys. Chem. Chem. Phys. 24 (2022) 27866

This work has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No. 818064).

Abstract ID. T4K01

Computational chemistry as the missing piece in the characterization puzzle of biological mineralization

Frederik Tielens
General Chemistry (ALGC), Materials Modelling Group, Vrije Universiteit Brussel (VUB), Pleinlaan 2, 1050 Brussel, Belgium.
Frederik.tielens@vub.be

The body of your abstract begins here. The abstract should be a concise summary of your work. It Solids of biological origin such as hydroxyapatite or calcium oxalates are directly involved in chemistry of “life”: Hydroxyapatite as the main compound of human bones and calcium oxalate as main compound of kidney stones. In this broad study around chemistry of life, materials chemistry and computational chemistry we focus here on Calcium Oxalate and Hydroxyapatite.

We have performed DFT studies on different interfaces and investigated the interaction with a series of bio-organic molecules, and characterized them by calculating vibration frequencies and chemical shifts, which were compared to experimental data.

From the bulk crystal structures of calcium oxalate polymorphs obtained through DFT methods[1, 2, 3] the low index surfaces were build. Since the thermodynamic stability depends on the medium in which the surface is introduced, the calculation of the interaction of the calcium oxalate surface with water, urea, and other small molecules gives us the possibility to understand the change in crystal morphology of the final oxalate crystal in its natural medium. The final aim is the prediction of the shape of the kidney stone in its natural medium.

Another biological mineral that we have studied is hydroxyapatite, being the major mineral component of tooth enamel, dentin and bone in which it is currently associated to biomolecules and various biopolymers. Organic nanosized particles are described as comprising a core surrounded by a crystalline hydrated amorphous layer. In this study the characterization of the surface of hydroxyapatite nanoparticles is essential to better understand their formation, and dissolution mechanisms and interactions existing at the interface between the crystalline and amorphous phases. The purpose of this study is to model a surface(s) of hydroxyapatite and analyze the physicochemical properties using the methods of quantum chemistry (periodic DFT).

[1] H. Colas, L. Bonhomme-Coury, C. Coelho, F. Tielens, F. Babonneau, C. Gervais, D. Bazin, D. Laurencin, M.E. Smith, J.V. Hanna, M. Daudon, and C. Bonhomme, Cryst. Eng. Comm. 15, (2013), 8840.
[2] T. Debroise, T. Sedzik, J. Vekeman, Y. Su, C. Bonhomme and F. Tielens, Cryst. Growth & Design 20, (2020), 3807.
[3] I. Petit, G.D. Belletti, T. Debroise, M. Llansola, I.T. Lucas, C. Leroy, C. Bonhomme, L. Bonhomme-Coury, D. Bazin, M. Daudon, E. Letavernier, J.P. Haymann, V. Frochot, F. Babonneau, P. Quaino and, F. Tielens, Chemistry Select, 3 (2018) 8801.
[4] T. Debroise, E. Colombo, G. Belletti, J. Vekeman, Y. Su, R. Papoular, N.S. Hwang, D. Bazin, M. Daudon, P. Quaino, and F. Tielens, Crystal Growth & Design, 20, (2020), 2553.

ORALS

T4. THEORETICAL AND COMPUTATIONAL CHEMISTRY

Quantum Chemical Study of Nickelocene: From Magnetic Molecules to Materials

Maristella Alessio[1,2] and Anna I. Krylov[1]
[1]*Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482, USA*
[2]*Present address: Department of Chemistry, KU Leuven, 3001 Leuven, Belgium*
maristella.alessio@kuleuven.be

A reliable *ab initio* description of molecular magnetic behavior is key to developing novel molecule-based quantum devices, with the potential to be more efficient and easily tunable. However, quantum chemical calculations of such magnetic materials are limited to density functional theory (DFT) or DFT+U (Hubbard correction to DFT). We employ our recently developed protocol based on the equation-of-motion coupled-cluster (EOM-CC) framework to investigate electronic structure and magnetic behavior of nickelocene ($NiCp_2$, Cp=cyclopentadienyl) molecular magnet. The protocol is implemented within the *ezMagnet* software. Our EOM-CC calculations on isolated $NiCp_2$ agree well with experimentally derived magnetic anisotropy and susceptibility values. The calculations also show that magnetic anisotropy in $NiCp_2$ originates from the spin-orbit coupling between the triplet ground state and the third singlet state, instead of the closest-lying singlet state. Upon benchmarking spin-flip (SF)-DFT against EOM-CC, SF-DFT is applied on a large enough finite model of the $NiCp_2$/MgO(001) absorption complex. The analysis of the resulting spinless transition density matrices and their natural transition orbitals explains how spin states and magnetic properties of $NiCp_2$ are retained upon adsorption on MgO, making $NiCp_2$ attractive as a spin sensor. The adopted computational protocol is general and has the potential to be combined with density embedding techniques, allowing us to investigate systems as large and complex as magnetic atoms and/or molecules on metal surfaces and their self-assemblies.

[1] M. Alessio, A. I. Krylov J. Chem. Theory Comput. 17 (2021) 4225.
[2] M. Alessio, S. Kotaru, G. Giudetti, A. I. Krylov J. Chem. Phys. C 7 (2023) 3647.

Tracking High-Dimensional Fluctuations in Complex Molecular Systems *via* Time-Variations of Local Environments

C. Caruso[1], A. Cardellini[2], M. Crippa[1] , D. Rapetti[1], and G. M. Pavan[1,2]
[1] *Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy*
[2] *Department of Innovative Technologies, University of Applied Sciences and Arts of Southern Switzerland, Via la Santa 1, 6962*
cristina.caruso@polito.it

Many molecular systems and physical phenomena are controlled by local fluctuations and microscopic dynamical rearrangements of the constitutive interacting units that are often difficult to detect. This is the case, for example, of phase transitions, phase equilibria, nucleation events, and defect propagation, to mention a few. A detailed comprehension of local atomic environments and of their dynamic rearrangements is essential to understand such phenomena, and also to draw structure-property relationships useful to unveil how to control complex molecular systems.

Considerable progresses in the development of advanced structural descriptors (*e.g.*, Smooth Overlap of Atomic Position (SOAP)[1], etc.) have certainly enhanced the representation of atomic-scale simulations data. However, despite such efforts, local dynamic environment rearrangements remain still difficult to elucidate. Here, exploiting the structurally rich description of atomic environments of SOAP and building on the concept of time-dependent local variations, we propose a SOAP-based descriptor, *Time*SOAP (τSOAP)[2], which essentially tracks the time variations in the local SOAP environments surrounding each molecule (*i.e.*, each SOAP center) along ensemble trajectories. We demonstrate how the τSOAP time-series allow to robustly and efficiently identify domains with different structural and dynamical behaviors in a variety of systems with diverse intrinsic dynamics. Ranging from supramolecular assemblies to metals traditionally considered as hard matter, we prove the potentiality of such an approach to detect structural transitions, phase transitions, and the coexistence of phases. Noteworthy, the first time derivative of τSOAP also provides sharp signals which give further insights on predicting how environments reconstruct or evolve in time.

We expect that our simple and general approach will help to shed light on a variety of complex dynamical phenomena, by improving the Molecular Dynamics data investigation for pattern recognition with temporal information and more dynamics understanding.

[1] A. P. Bartòk, R. Kondor, and G. Csànyi, “On representing chemical environments”, Physical Review B **87**, 184115 (2013).
[2] C. Caruso, A. Cardellini, M. Crippa, D. Rapetti, and G. M. Pavan* , “*Time*SOAP: Tracking high-dimensional fluctuations in complex molecular systems via time-variations of SOAP spectra”, ArXiv 2023, DOI:10.48550/arXiv.2302.09673.

Design and characterization of oligopeptides capable of interacting with the programmed death ligand 1 receptor for future theragnostic applications

Micaela Giannetti,[1] Marina Gobbo,[2] Isabella Caligiuri,[3] Lucio Litti,[2] Claudia Mazzuca,[1] Flavio Rizzolio,[3,4] Moreno Meneghetti,[2] and Antonio Palleschi[1]
[1]Department of Chemical Science and Technologies, University of Rome "Tor Vergata", and CSGI unit of Rome, Via della Ricerca Scientifica, 00133 Rome, Italy
[2]Department of Chemical Sciences, University of Padova, via F. Marzolo 1, 35131 Padova, Italy.
[3]Pathology Unit, Centro di Rif. Oncologico di Aviano (CRO) IRCCS, via F. Gallini 2, 33081 Aviano (PN), Italy
[4]Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, via Torino 155, 30172 Venice, Italy
micaela.giannetti@uniroma2.it

The programmed death-1 protein (PD-1) present on the membrane of T lymphocytes performs its function only if activated by interactions on its extracellular portion with suitable ligands. PD-L1 (programmed death ligand-1) is a protein placed on the surface of some (regulatory) cells that, by binding to the PD-1 receptor, forms the PD-1/PD-L1 complex and suppresses the immune response against antigens[1].

The interaction is exploited by tumor cells as a strategy to escape the immune system. Indeed, many particularly aggressive tumors, such as melanoma, overexpress PD-L1 on their cells; thus, they manage to deactivate the T lymphocytes, inhibiting the response of the immune system.

In this work, the design and characterization of a new generation of oligopeptides showing a high affinity with the target PD-L1 region able to interact to PD-1 will be presented. Molecular dynamics simulations, supported by experimental data, in solution and on gold surface, suggest that such peptides can compete with the current immunoglobulin and peptide inhibitors[2]. Given the promising results, future studies will consider the appropriate functionalization of gold nanoparticles with these peptides to evaluate their efficacy and selectivity on cancer cells.

[1] Y. Iwai et al. J. Biomed. Sci. 24 (1) (2017) 26
[2] M. Gobbo et al., SERS nanostructures with engineered peptides for targeting the PD-L1 immune checkpoint of tumor cells, submitted.

Fluorescence Enhancement of Chromophores near Plasmonic Nanoparticles: Atomistic vs. Continuum Models

Pablo Grobas Illobre[1], Piero Lafiosca[1], Teresa Guidone[1], Tommaso Giovannini[1], Chiara Cappelli[1]
[1] *Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy.*
pablo.grobasillobre@sns.it

Plasmonic materials are a cornerstone in the state-of-the-art engineering of novel fluorescence-based biosensors. Noble metal nanoparticles (NPs) have been shown to enhance/quench the fluorescence signal of target biomolecules. Indeed, such an effect has been experimentally proved to be strongly dependent on the NPs-molecule distance [1,2]. Moreover, the optical response of plasmonic NPs is highly influenced by their shape and dimension [3-5]. In this context, accurate simulations of the fluorescence process play a relevant role for the *in-silico* design of selective NPs-molecule biosensors. Successful approaches treat the molecule at the quantum-mechanical (QM) level while the NP is studied from the perspective of classical electrodynamics. Several studies relying on a continuum description of the NP with the Boundary Element Method (BEM) have been proposed [6-8]. However, an atomistic description of the plasmonic substrate for this purpose is still lacking. On this basis, we have recently developed an atomistic yet classical approach called ωFluctuating Charges Fluctuating Dipole (ωFQFμ). ωFQFμ combines the Drude model, classical electrostatics, quantum tunneling, and an additional atomic polarizability to accurately describe the optical response of complex-shaped NPs. [9,10] ωFQFμ has shown a perfect agreement with *ab initio* methods, being able to replicate usual size-related phenomena in quantum physics. This includes the degree and direction of the plasmon shift, the atomistic description of the plasmon-induced electron density, and the non-local response of the NP, among others. Furthermore, the classical nature of the model permits to treat systems formed by thousands of atoms [10,11], which are intractable by typical *ab initio* calculations. ωFQFμ can be coupled to a QM Hamiltonian [12]. The resulting QM/ωFQFμ extended to the Time-Dependent Density Functional Theory (TDDFT) formalism and is here challenged to compute the fluorescence enhancement or quenching of selected molecular systems. Results are compared with QM/BEM values, thus highlighting the importance of an atomistic description of the NP.

[1] J. Xu et al. J. Pharm. Anal. 12 (2022) 808
[2] L. Jiang et al. Microchem. J. 148 (2019) 285
[3] L. J. Sherry et al. Nano lett. 5 (2005) 2034
[4] K. Lee et al. J. Phys. Chem. B 110 (2006) 19220
[5] V. Giannini et al. Chem. Rev. 111 (2011) 3888
[6] V. N. Pustovit et al. J. Chem. Phys. 136 (2012) 204701
[7] S. Vukovic et al. J. Phys. Chem. C 113 (2009) 121
[8] S. Corni et al. J. Chem. Phys. 117 (2002) 7266
[9] T. Giovannini et al. Nanoscale 11 (2019) 6004
[10] T. Giovannini et al. ACS Photonics 9 (2022) 3025
[11] P. Lafiosca et al. J. Phys. Chem. C. 125 (2021) 23848
[12] P. Lafiosca et al. submitted

ELECTRONIC PROPERTIES OF NEUROTRANSMITTERS IN A HYBRID SYSTEM WITH ZEOLITE L

Cristiano invernizzi[1], L. Grimm[2], F. Biedermann[2], G. Tabacchi[1], E. fois[1]
[1]*Department of Science and High Technology, University of Insubria, Como, Italy*
[2]*Karlsruhe Institut of Technology (KIT), Eggenstein-Leopoldshafen, Germany*
Presenter's e-mail address: *cinvernizzi@uninsubria.it*

The hybrid compound Zeolite L + 2,7-dimethyldiazapyrenium (MDAP, photosensitive dye, charged + 2) is an artificial receptor with high affinity for small neurotransmitter molecules. The efficacy of this system as nanosensor has been shown in the literature by the significant change of its optical spectra after titration with Serotonin (having a +1 charge in water) [1]. More specifically, the association of the neurotransmitter with the dye causes the onset of a long-wavelength signal in the UV-vis absorption spectrum, which was absent in the spectrum of the Zeolite L + MDAP receptor. We analyzed by ab initio methods the electronic excitations of the following model systems: a) Zeolite L + H_2O + MDAP; b) Zeolite L + H_2O + MDAP + Serotonin. Our goal was to identify the nature of the long-wavelength signal in the experimental spectrum, and to understand the molecular-level factors that influence the position and intensity of this band. To this purpose, electronic excitations were calculated at the CAM-B3LYP/6-311++G(df,pd) level on different configurations of the MDAP + Serotonin aggregate. These configurations were sampled from an ab initio molecular dynamics trajectory, conducted at 298 K on the Zeolite L + H_2O + MDAP + Serotonin system. The simulated absorption spectrum of the aggregate, averaged over the considered configurations, shows a similar trend to that found in the experimental one. Furthermore, comparison with the spectrum similarly calculated for the Zeolite L + H_2O + MDAP system indicates that the association of the neurotransmitter with MDAP causes a reduction in the intensity of the MDAP-related peaks - in agreement with experimental observations, [1] and the appearance of a new signal, assigned to a charge-transfer transition from Serotonin to MDAP. The overall data analysis shows that the charge-transfer transition, regardless from the Serotonin conformation, exhibits higher wavelength and oscillator strength in configurations having the π-systems of Serotonin and MDAP perpendicular to each other, a not excessively distorted MDAP geometry and a smaller Serotonin-MDAP distance. The latter depends on both the number and the position of water molecules around the aggregate: these can be located between MDAP and Serotonin, preventing them from coming any closer, or in positions that allow a closer contact between MDAP and Serotonin. Finally, this insight, which is not accessible experimentally, represents a fundamental basis for the improvement of artificial zeolite-based sensors for diagnostics and other biomedical applications.

[1] Laura M. Grimm et al, Fluorescent Nanozeolite Receptors for the Highly Selective and Sensitive Detection of Neurotransmitters in Water and Biofluids, Advanced Materials, 2021, 2104614, pp. 1-12.

From Ferrite Nanostructures to Sintered Bulk Permanent Magnets

P. Maltoni[1], G. Barucca[2], B. Rutkowski[3], N. Yacoub[4], J.A. De Toro[5], G. Varvaro[6], D. Peddis[6,7], R. Mathieu[1]
[1]*Department of Materials Science and Engineering, Uppsala University, 751 03 Uppsala, Sweden*
[2]*Dipartimento di Scienze e Ingegneria della Materia dell'Ambiente ed Urbanistica, Università Politecnica delle Marche, 60131 Ancona, Italy*
[3]*Faculty of Metals Engineering and Industrial Computer Science, AGH University of Science and Technology, 30-059 Kraków, Poland*
[4]*Institut des Molécules et Mateŕiaux du Mans, CNRS UMR-6283, Université du Maine, F-72085 Le Mans, France*
[5]*Instituto Regional de Investigacion Cientıfica Aplicada (IRICA) and Departamento de Fısica Aplicada, Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain*
[6]*Consiglio Nazionale delle Ricerche, Istituto di Strttura della Materia, nM2-lab, Monterotondo Scalo (RM), 00015 Italy*
[7]*Dipartimento di Chimica e Chimica Industriale, Università di Genova, 1-16146 Genova, Italy*
pierfrancesco.maltoni@angstrom.uu.se

Among the relevant strategies to design Rare-Earth-free permanent magnets (PM), combining two or more prototypical magnetic phases at the nanoscale have become a well-established route to maximize the energy product of permanent magnets [1]. Within this context, achieving an optimal exchange-coupling at the interface between the phases has resulted significantly demanding [2]. The next critical step is to consolidate the nano-powders into a dense bulk magnet, while avoiding excessive growth of crystallites, lack of magnetic alignment and secondary impurities.

In this work, we have investigated the role of magnetic interactions in multiphase $SrFe_{12}O_{19}/CoFe_2O_4$ composites obtained by a simple low-cost sol-gel self-combution method [3]. The unique combination of first order reversal curves (FORCs) analysis and relaxation measurements in a reverse field could define the limits to achieve ferromagnetic coupling between particles with different magnetic anisotropy. The achieved local texture at the interface observed by electron microcopy was a critical parameter to obtain overall good magnetic properties and avoid further deteriorations. Next, a set of samples was selected for the subsequent compaction step to produce dense bulk permanent magnets, performed by spark plasma sintering (SPS) as illustrated by [4]. There are two essential steps to guarantee an optimal permanent magnetic performance: (i) control the nanocrystallites size and (ii) obtain a magnetic orientation. During the compaction of the nanopowders, the controlled thermal treatment permitted the self-alignment of the particles without the application of a magnetic field along the c-axis of the $SrFe_{12}O_{19}$ phase, and thus the corresponding high-density bulk magnets showed square loops with an enhancement of the energy product, $(BH)_{MAX}$.

[1] J. Cui, M. Kramer, L. Zhou, F. Liu, A. Gabay, G. Hadjipanayis, B. Balasubramanian, and D. Sellmyer, Acta Mater. 158 (2018) 118
[2] H. Zeng, J. Li, J.P. Liu, Z.L. Wang, and S. Sun, Nature, 420 (2002) 395
[3] P. Maltoni, T. Sarkar, G. Barucca, G. Varvaro, F. Locardi, D. Peddis, and R. Mathieu J. Phys. Chem. C 125 (2021) 5927
[4] M. Saura-Múzquiz, C. Granados-Miralles, H. L. Andersen, M. Stingaciu, M. Avdeev, and M. Christensen, ACS Appl. Nano Mater. 1 (2018) 6938

Fully Atomistic QM/Classical Models for Surface Enhanced Raman Scattering

Luca Nicoli[1], Piero Lafiosca[1], Tommaso Giovannini[1], Chiara Cappelli[1]
[1]*Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy*
luca.nicoli@sns.it

Surface enhanced Raman scattering (SERS) arises from the enhancement of the Raman signal of a target molecule adsorbed on a nanostructured plasmonic substrate [1]. This can allow for single molecule detection thanks to enhancement factors as high as 10^{14} [1]. In this contribution, we present a novel theoretical approach to treat SERS, in which the plasmonic structure is described by means of fully atomistic, classical, electromagnetic models, which have recently been developed by the present authors [2-5], while the adsorbed molecular system is treated at the quantum mechanical (QM) level. Our atomistic, yet classical, approach is able to predict the plasmonic properties of complex nanostructures such as metal nanoparticles [2,3,5] and graphene-based nanoaggregates [4,7]. Comparison with experimental spectra demonstrate the reliability of the developed method for the prediction of SERS signals [8].

[1] J. Langer et al. ACS Nano 14 (2019) 28
[2] T. Giovannini et al. Nanoscale 11 (2019) 6004
[3] L. Bonatti et al. Front. Chem. 8 (2020) 340
[4] T. Giovannini et al. J. Phys. Chem. Lett. 11 (2020) 7595
[5] T. Giovannini et al. ACS Photonics 9 (2022) 3025
[6] L. Bonatti et al. Nanoscale Adv. 4 (2022) 2294
[7] S. Zanotto et al. ACS Photonics 10 (2023) 394
[8] P. Lafiosca et al. under revision

This work has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No. 818064).

Challenges in modeling Singlet Oxygen release from Li-air battery cathode: periodic DFT versus embedded cluster CASPT2

Michele Pavone[1], Francesca Fasulo[1], Arianna Massaro[1], Ana B. Muñoz-García[2]
[1]Department of Chemical Sciences, University of Naples Federico II, Via Cintia 21, 80126, Naples, Italy
[2]Department of Physics "Ettore Pancini", University of Naples Federico II, Via Cintia 21, 80126, Naples, Italy

michele.pavone@unina.it

Li-air batteries are a promising energy storage technology for large-scale applications [1], but the release of highly reactive singlet oxygen ($^1O_2$) during battery operation represents a main concern that sensibly limits their effective deployment [2]. An in-depth understanding of the reaction mechanisms underlying the $^1O_2$ formation is crucial to prevent its detrimental reactions with the electrolyte species. However, describing the elusive chemistry of highly correlated species such as singlet oxygen represents a challenging task for state-of-the-art theoretical tools based on Density Functional Theory (DFT). Thus, here we discuss the results of an embedded cluster approach, based on CASPT2 and effective point charges, to address the evolution of $^1O_2$ at the Li_2O_2 surface during oxidation, i.e. the battery charging process [3]. Based on recent hypothesis, we depict a feasible $O_2^{2-}/O_2^{-}/O_2$ mechanisms occurring from the $(11\underline{2}0)$-Li_2O_2 surface termination. Our highly accurate calculations allow for the identification of a stable superoxide as local minimum along the potential energy surface (PES) for $^1O_2$ release, which is not detected by periodic DFT. We find that $^1O_2$ release proceeds *via* a superoxide intermediate in a two-step one-electron process or another still accessible pathway featuring a one-step two-electron mechanisms. In both cases it represents a feasible product of Li_2O_2 oxidation upon battery charging. Thus, tuning the relative stability of the intermediate superoxide species can enable key strategies aiming at controlling the detrimental development of $^1O_2$ for new and highly performing Li-air batteries.

[1] S. Ferrari, M. Falco, A.B. Muñoz-García, M. Bonomo, S. Brutti, M. Pavone, C. Gerbaldi, Advanced Energy Materials 11 (2021) 2100785.
[2] L. Johnson, C. Li, Z. Liu, Y. Chen, S.A. Freunberger, P.C. Ashok, B.B. Praveen, K. Dholakia, J.-M. Tarascon, P.G. Bruce, Nat. Chem. 6 (2014) 1091-1099.
[3] F. Fasulo, A. Massaro, A. B. Muñoz-García, M. Pavone, manuscript submitted

Molecular Dynamics Simulations of the Ceria-Silica Chemical Mechanical Polishing Process

Luca Brugnoli,[a] Katsuaki Miyatani, [b] Masatoshi Akaji,c Shingo Urata,[b] and Alfonso Pedone [a*]
[a)]Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, via G. Campi 103, 41125, Modena, Italia
[b)]Innovative Technology Laboratories, AGC Inc., Yokohama, Kanagawa 230-0045, Japan
[c)] Electronics Company, AGC Inc., Yokohama, Kanagawa 230-0045, Japan

Chemical Mechanical Polishing (or Planarization) of silica-based glasses is a key enabling technology of fundamental importance for the production of defect free ultra-smooth glass surfaces for a wide range of applications, including display panels, flat glass for window panes, optical glass, precision glass lenses, liquid crystal displays, glass magnetic memory disks, silicon wafers etc. [1].

In this communication, I will present some Molecular Dynamics Simulations carried out by using Reactive Force-Fields developed in our group to study the mechanism of interaction and removal of silicate units from silica glass with ceria nanoparticles at the atomic level.

We have investigated 1) the effect of the morphology of the glass surface and the gel layer formed by hydroxylation of the surface; 2) in which form silica is extracted (isolated SiO_4 units dimers or chains) and the number of Ce-O-Si bonds and anchoring sites required to extract them; 3) which is the effect of the ceria surface morphology (111 vs 100), the degree of hydroxylation and hydration in relation to the pH of the slurry on the CMP efficacy; 4) How the atomic level mechanism changes with the application of loading pressure as well as the effect of the temperature. 5) How the simulated CMP process vary when a ceria nanoparticle is used as abrasive instead of a regular crystalline surface.

References

[1] R. Sabia, H. J. Stevens Machining Science and Technology 4(2) (2000) 235–251.

Hybrid Born-Oppenheimer Ab initio Molecular Dynamics for Condensed Matter Simulations Made Possible: Microcanonical and Canonical Post-Processing Properties

Chiara Ribaldone[1] and Silvia Casassa[1]
[1] Department of Theoretical Chemistry, University of Torino, Italy

Ab initio Molecular Dynamics (AIMD), based on Hartree-Fock (HF) or Density Functional Theory (DFT), has become established since its early days as an important tool for simulations of an increasingly wider range of problems in geology, condensed matter physics, chemistry and biology.[1,2] This method combines the quantum-mechanical static description given by ab initio theories such as HF and DFT with a classical evolution of the nuclear coordinates in the phase space, thus allowing a dynamic characterization of structural and electronic properties of a condensed matter system. In the Born-Oppenheimer method, the nuclear positions are propagated by forces that are calculated, through the Hellmann-Feynman theorem,[3] at the self-consistent electronic ground state for each instantaneous arrangement of the nuclei.

In this work, the implementation of an original Born-Oppenheimer molecular dynamics module is presented, which is able to perform structural optimization based on AIMD concepts,[4] together with simulations of large-scale and complex condensed-phase systems for sufficiently long time scales at the level of hybrid DFT, in the microcanonical and canonical ensembles. The algorithm is fully integrated in the CRYSTAL code, a program for quantum-mechanical simulations of materials whose peculiarity stems from the use of atom-centered basis functions within a linear combination of atomic orbitals to describe the wavefunction. The corresponding efficiency in the evaluation of the exact Fock exchange series has driven to the implementation of a rich variety of hybrid density functional approximations at a low computational cost, thus leading to the possibility to perform efficient AIMD simulations with hybrid functionals . The information contained in the trajectory of the dynamics is extracted through a series of post-processing algorithms, that provide the radial pair distribution function, as well as the diffusion coefficient and the vibrational frequencies density of states. A brief description of the theoretical methods and of the algorithmic implementation, followed by a critical evaluation of the accuracy and parallel performance of this approach, will be given. Taking the periodic liquid water $(H_2O)_{32}$ as a reference system, the post-processing analysis of microcanonical and canonical AIMD trajectories leads to a detailed analysis and discussion of the structural and dynamical properties of this system at different temperatures, which is capable of giving insights and shedding lights on atomic-scale features of the liquid water that have been debated for a long time in literature.[5,6]

[1] M. E. Tuckerman, J. Phys. Condens. Matter 14 (2002) R1297
[2] T. D. Kühne, Wiley Interdiscip. Rev. Comput. Mol. Sci. 4 (2014) 391
[3] R. P. Feynman, Phys. Rev. 56 (1939) 340
[4] C. Ribaldone and S. Casassa, AIP Advances 12 (2022) 015323
[5] J. VandeVondele et al., J. Chem. Phys. 122 (2005) 014515
[6] S. Y. Willow et al., Sci. Rep. 5 (2015) 14358

Molecular Modelling of a per-fluorinated Ce^{IV}-based metal-organic framework for CO_2 capture

Carmen Rizzuto[1], Alessio Fuoco[1], Elisa Esposito[1], Lucia Calucci[2,3], Francesca Nardelli[2], Marco Taddei[3,4], Marco Lessi[4], Diletta Morelli Venturi[5], Ferdinando Costantino[5], Virginia Guiotto[6], Matteo Signorile[6], Valentina Crocellà[6], Alessio Caravella[7], Piergiuseppe Fiore[7], Agostino Lauria[8], Elena Tocci[1]

[1]Institute on Membrane Technology, CNR-ITM, Via P. Bucci 17/c, 87036 Rende (CS), Italy
[2]Institute of Chemistry of Organometallic Compounds, CNR-ICCOM, Via G. Moruzzi 1, 56124 Pisa, Italy
[3]Centro per l'Integrazione della Strumentazione Scientifica dell'Università di Pisa (CISUP), Pisa, Italy University of Pisa, Pisa, Italy
[4]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Giuseppe Moruzzi 13, 56124 Pisa, Italy
[5]Dipartimento di Chimica, Biologia e Biotecnologie, Unità di Ricerca INSTM, Università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy
[6]Dipartimento di Chimica, Centro di Riferimento NIS e INSTM, Università di Torino, Via G. Quarello 15, I-10135 and Via P. Giuria 7, I-10125 Torino, Italy
[7]Department of Computer Engineering, Modelling, Electronics and Systems Engineering, University of Calabria, Via P. Bucci, Cubo 42C, Rende (CS) 87036, Italy
[8]Department of Engineering for Innovation, University of Salento (UNISALENTO), Corpo Z, Campus Ecotekne, SP.6 per Monteroni, Lecce (LE), Italy

c.rizzuto@itm.cnr.it

CO_2 is the main Greenhouse Gas (GHG) emitted through anthropogenic activities. Global warming and climate changes directly result from high CO_2 emission levels in the atmosphere due to energy consumption. Membrane technology for gas separation is a growing field with a focus on developing advanced membranes to capture CO_2. The efficiency of the separation processes can be achieved by exploiting the innovative combination of a polymeric matrix with crystalline porous filler to develop membranes able to overcome the Robeson upper bound limit, which is the empirical upper bound relationship between the permeability of the fast gas of a gas pair and their separation factor [1,2]. These next-generation membranes can be used to capture CO_2 because they combine the transport properties of inorganic fillers, such as metal-organic frameworks (MOFs), with the permselectivity characteristics of the classic polymeric matrices. In this work, computational tools are used as a powerful insight into the field of MOFs, providing molecular-level information suitable for gas separation experiments. We will use molecular modeling to investigate the potentiality of a novel per-fluorinated Ce(IV)-based MOF with MIL-140A topology for CO_2 capture [3]. MD simulations will be carried out to analyze CO_2 adsorption mechanism, also in the presence of water, in order to confirm the available experiment data. A detailed characterization of the anisotropy, the connectivity and the tortuosity of three-dimensional porous structures will be indicated [4].

[1] L.M. Robeson, J. Memb. Sci. 320 (2008) 390
[2] L.M. Robeson, et al., J. Memb. Sci. 476 (2015) 421
[3] M. Cavallo, et al. J. Mater. Chem. A 11 (2023) 5568
[4] A. Caravella, et al. Chem. Eng. Sci. 268 (2023) 118386

Abstract ID. T4O12

Energy Transfer Mechanism in Magnetic Nanoparticle Hyperthermia

Gloria Tabacchi[1], Ilaria Armenia[2], Giovanni Bernardini[3], Norberto Masciocchi[1], Antonietta Guagliardi[4], Ettore Fois[1]
[1]*Dipartimento di Scienze e Alta Tecnologia,University of Insubria, and INSTM, via Valleggio 11, I-22100 Como, Italy*
[2]*Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Zaragoza 50009, Spain.*
[3]*Dipartimento di Biotecnologie e Scienze della Vita, University of Insubria, via Dunant 3, I-21100 Varese, Italy.*
[4]*Istituto di Cristallografia - To.Sca.Lab and INSTM, CNR. Via Valleggio 11, I-22100 Como, Italy.*

gloria.tabacchi@uninsubria.it

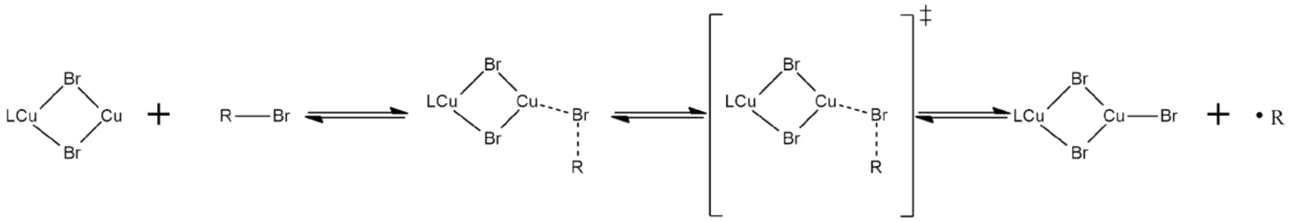
Iron oxide nanoparticles (IONP) attract growing interest in biotechnology for their potential uses in medical imaging, drug release, or innovative cancer treatments. In these applications, thermophilic enzymes – which optimally function at temperatures in the 80-100 °C range - are linked to the IONP, and then remotely heated and activated via alternate magnetic fields [1]. This phenomenon - known as Magnetic Nanoparticle Hyperthermia (MNH) - involves the energy transfer (as heat) from the IONP to the surrounding molecules. Experiments showed that magnetically induced heating is local - being limited to a few nanometers range from the nanoparticles - and does not affect the overall temperature of the medium [1,2]. However, experimental evidences could not be rationalized on the basis of standard heat-transport theories, as the temperature measured by moving apart from the IONP decays faster than what predicted by the diffusive Fourier law [2].
This study explores whether microscopic-level mechanisms different from the standard (diffusional) heat transport theories may be at the origin of MNH-effects. Using first-principles molecular dynamics and a linear response approach, we reveal that at low wavenumbers in the infrared region the vibrational spectra of the magnetic Fe cations of the IONP overlap with the vibrational spectra of the atoms surrounding the magnetic nanoparticle. This finding suggests that the heat flow from the IONPs to the atoms in the proximity of the surface may be governed by a resonance mechanism which, typically, operates at the nanometer scale [3].

[1] I. Armenia et al. J. Colloid Interface Sci. 537 (2019) 615
[2] A. Riedinger et al. Nano Lett. 13 (2013) 2399
[3] G. Tabacchi et al, ACS Applied Nano Materials (2023), in press

Bromine transfer to a Cu complex to activate an ARGET ATRP reaction

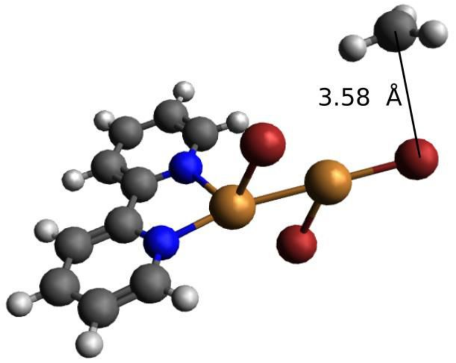
Stefano Vaghi[1,2], Massimo Mella[1], Hélène Gérard[2]
[1]*Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, 22100 Como, Italy*
[2]*Sorbonne Université, CNRS, LCT, UMR 7616, 4 Place Jussieu, 75005 Paris, France*
svaghi@uninsubria.it

Atom Transfer Radical Polymerization (ATRP) is a versatile polymerization technique. However, the catalytic mechanism is yet to be determined. To investigate this mechanism we considered the reaction model reported in Equation 1



Equation 1

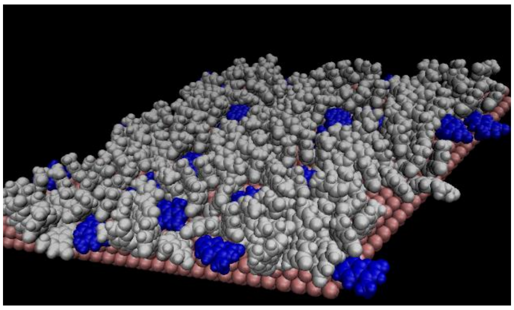
where L = BPY, BPY$_2$, Me$_6$TREN and R=CH3Br, ethyl bromoacetate (EBAc), ethyl α-bromoisobutyrate (EBIB). While we know that the global reaction is endothermic, we still do not have the transition barriers for all the cases involved. In fact it can be easily noted there is a change in the spin state between reactant (singlets) and products (doublet), thus an uncertainty on the spin state of the transition state we encounter (singlet or triplet). Our first lead in this investigation has been the work from Fang et al. [1], where the authors proposed an inner sphere electron transfer transition state for a similar, albeit smaller system. Therefore we employed the 6-31++G(d,p) basis set at B3LYP level of theory to optimize products, reactants and singlet and triplet intermediates. From there we performed PES scans along the C-Br bond, searching for a transition state. Eventually, through a subsequent broken symmetry approach, we were able to locate some of them in an open shell singlet state. However the structures we found (Figure 1) are deeply different from the ones previously known, in fact our geometries suggest a dissociative mechanism to form the radical, due to the distance measured between carbon and bromine (greater than 3.5 Å). This variation can aid to investigate on the ATRP mechanism from an other point view, possibly enhancing our comprehension of the mechanism of this reaction. Indeed our plan is now to start from the kinetic constants we are obtaining for the open shell singlet to simulate the evolution of the reaction through Kinetic Monte Carlo method.



[1] *J. Am. Chem. Soc.* 2019, 141, 18, 7486–7497 Fang, C. Fantin, M. Pan, X. de Fiebre, K. Coote, M. L. Matyjaszewski, K. Liu, P.

Thermodynamics of Self Assembled Monolayers formation: a computational investigation.

A. Zoccante[1], D. Marchi[1], M. Cossi[1]
[1]*Dipartimento di Scienze e Innovazione Tecnologica (DISIT), Università del Piemonte Orientale,*
via T. Michelle 11, I-15121, Alessandria, Italy
alberto.zoccante@uniupo.it



While the general chemical-physical mechanism behind "self-assembled monolayers" (SAMs) formation on metal surfaces has been widely clarified, it is not always clear whether the monolayer is formed through a process of physisorption or chemisorption and which are the reasons for the differences observed[1,2].

We investigated monolayer formation of several types of SAMs (7-mercapto-4-methylcoumarin, 3-mercapto-propanoic acid, methanethiol) on a flat gold surface, formed through either a physisorption or a chemisorption process, at various densities.

This allowed us to obtain two separate sets of results, of theoretical and practical relevance:

- from the comparison of the free energies for different absorption processes, we could determine the most likely way of formation of the monolayer
- we were also able to predict the maximum achievable monolayer density (which could be of use for technological applications)

In our approach, previously validated against experimental results[3], we used Bennet Acceptance Ratio method on Molecular Dynamics data to compute chemical potentials for chemisorbed and physisorbed molecules at different monolayer densities.

The results of our analyses clearly point towards monolayers formed by chemisorbed molecules in all cases at high densities. However, this does not hold true for lower densities where the preference for absorption mechanism appears to be dependent on the molecule. Our results seem to point towards smaller chains having a preference for physisorption at lower densities.

We speculate that this might be due to a higher ratio of compound-metal/compound-compound interactions in smaller molecules compared to larger ones and we hope to further our research in the subject in the future.

[1] F. Schreiber Progress in Surface Science 65 (2000) 151
[2] C. Vericat et al. Chem. Soc. Rev. 39 (2010) 1805
[3] D. Marchi et al. Phys. Chem. Chem. Phys. 70 (2022) 22083

Abstract ID. T4O16

POSTERS

T4. THEORETICAL AND COMPUTATIONAL CHEMISTRY

First insights on the prebiotic polymerization of HCN on interstellar silicates surfaces

Niccolò Bancone[1,2], Stefano Pantaleone[2], Piero Ugliengo[2], Albert Rimola[1], Marta Corno[2]
[1]*Universitat Autònoma de Barcelona, Departament de Química, E-08193, Bellaterra – SPAIN*
[2]*Università degli Studi di Torino, Dipartimento di Chimica, I-10125, Torino – ITALY*
niccolo.bancone@uab.cat

Hydrogen cyanide (HCN) has been receiving an increasing attention as a possible precursor of life since when J. Orò synthesized adenine from a solution of HCN and ammonia.[1] Since HCN molecules are widespread in the interstellar medium and the products of its polymerization (including purines) have been detected on meteoritic fragments,[2] the scientific community is now investigating the possible pathways for the oligomerization of HCN in cosmic environments to form molecules of prebiotic interest. In this sense, the gas phase oligomerization of HCN is hindered by high energetic barriers which cannot be overcome at the conditions of a molecular cloud.[3] In the condensed phase, instead, more promising results were obtained, thanks to a more feasible acid-base chemistry.[4]

For these reasons, the surfaces of interstellar dust grains, as well as other materials such as carbonaceous chondrites and cometary nuclei, may play a fundamental role in this type of chemistry. Moreover, it has been recently demonstrated that the surfaces of silicates, among the primary components of dust grains cores, are able to catalyze the oligomerization of HCN to adenine.[5]

In this work we investigated the dimerization of two HCN molecules adsorbed on crystalline Mg_2SiO_4 (forsterite) surfaces with the formation of iminoacetonitrile ($H_2C_2N_2$). By modelling five dimerization cases on three different surfaces, we observed that, thanks to their acid-base properties,[6] forsterite surfaces are able to deprotonate one adsorbed HCN molecule, triggering the reaction, and to stabilize the transition states of iminoacetonitrile formation. Most cases show favorable energetic barriers and, according to a kinetic analysis, the reaction is likely to take place at the conditions proper of proto-planetary disks and planetesimals formation, while it results to be hindered in molecular clouds.

[1] J. Orò Nature 191 (1961) 1193-1194
[2] Z. Martins et al. Orig. Life Evol. Biosph. 39 (2009) 214
[3] I. W. M. Smith et al. Astron. Astrophys. 369 (2001) 611-615
[4] O. Kikuchi et al. J. Mol. Struct. THEOCHEM 507 (2000) 53-62
[5] R. Santalucia et al. Phys. Chem. Chem. Phys. 24 (2022) 7224-7230
[6] M. Signorile et al. ACS Earth Space Chem. 4,3 (2020) 345-354

Computed Binding Energies and Frequencies Distribution of Relevant S-Bearing Species at Interstellar Icy Grains

V. Bariosco[1], S. Pantaleone[1], C. Ceccarelli[2], A. Rimola[3], M. Corno[1] and P. Ugliengo[1]
[1]University of Turin, Department of Chemistry, Via Pietro Giuria 7, Turin – ITALY
[2] Université Grenoble Alpes, IPAG, 414 Rue de la Piscine, Grenoble – FRANCE
[3]Universitat Autònoma de Barcelona, Departament de Química, 08193, Bellaterra - SPAIN
e-mail: vittorio.bariosco@unito.it

Binding energies (BEs) are crucial parameters to understand the evolution of molecular species in dense clouds, determining whether a species is frozen onto the grain surfaces or free in the gas phase. Nowadays, BEs are usually provided as single point values, however the predominant amorphousness of icy grains gives rise to a distribution of BE sites and values. Until now, several grain models have appeared in literature, however, lacking a comprehensive physical and systematical description. Recently, ACO-FROST, an automatic procedure to simulate realistic icy grains has been released.[1] This code allows to build up models of amorphous ice up to 1000 molecules and to simulate a large variety of BE sites, see Figure 1 left panel.

In the present work, the aforementioned procedure was applied to compute BE distribution of S-bearing species, i.e., H_2S, OCS, CH_3SH. S-species were selected in order to contribute to a long-standing issue in the field: the Sulphur depletion problem. [2] BEs were computed at DFT level (B97-3c) and then refined with one of the highest level of theory available (DLPNO-CCSD(T)). The previous reported BE values are overestimated with respect to our new BE distribution, [3] see Figure 1 central panel. Besides, frequencies distribution was calculated for OCS molecule and compared to the James Webb Space Telescope (JWST) observations [4] as reported in Figure 1 right panel. The computed distribution outstandingly reproduces JWST data indicating the robustness of the model studied and thus defining a novel computational tool to predict icy species vibrational features.

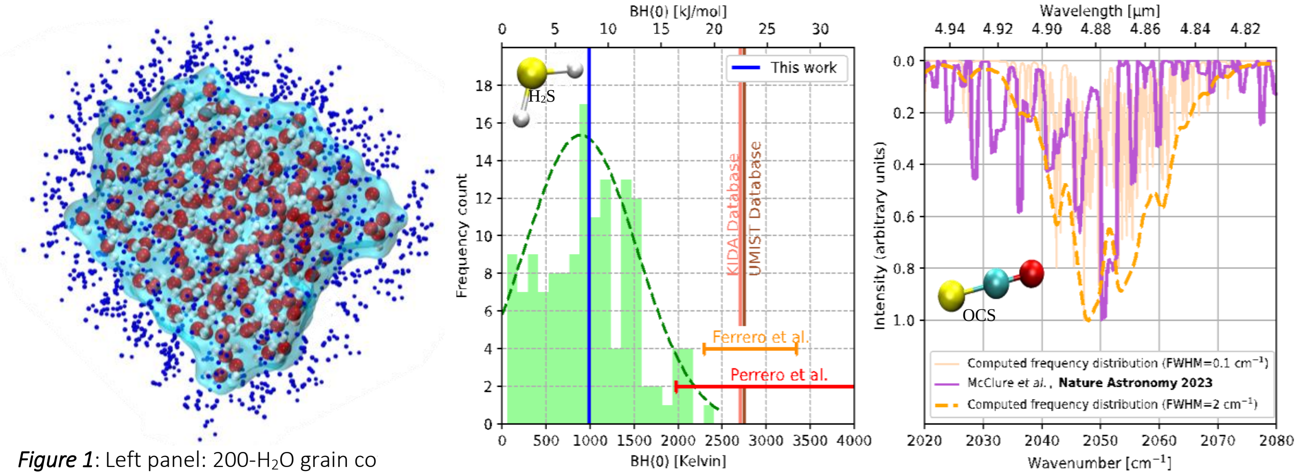


Figure 1: Left panel: 200-H_2O grain co
previous results. Right panel: Computed frequencies distribution for OCS molecule compared with JWST observations

[1]. A. Germain, L. Tinacci, S. Pantaleone, et al., ACS Earth Space Chem. 2022, 6, 1286-1298

[2]. R. Martin-Domenech, I. Jimenez-Serra, G. M. M. Caro, et al., Astron. Astrophys. 2016, 585, 1-9

[3]. S. Ferrero, L. Zamirri, C. Ceccarelli, et al., ApJ 2020, 904, 1-20

[4]. M. K. McClure, W. R. M. Rocha, K. M. Pontoppidan, et al., Nature Astronomy 2023, 1-13

Diffusion Coefficient of Lithium in Cathode Materials for Lithium Ion Batteries From DFT, Metadynamics and Post-HF

Laura Bonometti[1], Loredana E. Daga[1], Riccardo Rocca[1], Naiara L. Marana[1], Maddalena D'Amore[1], Fabrizio Silveri[2], Denis Usvyat[3], Mauro Sgroi[1], Anna M. Ferrari[1], Lorenzo Maschio[1]
[1] Department of Chemistry, University of Turin, Via P. Giuria 5, 10125, Turin, Italy
[2]Gemmate Technologies SRL, Via Reano 31, 10090 Buttigliera Alta, Italy
[3]Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, D-12489 Berlin, Germany
laura.bonometti@unito.it

In the roadmap towards designing new and improved materials for lithium ion batteries (LIBs), the ability to estimate the diffusion coefficient of Li ions in electrodes is key. Since it is exceptionally difficult to estimate it both computationally and experimentally, we attempted to devise a computational protocol for the determination of the Li-migration energy barrier and diffusion coefficient, focusing on a common cathode material as $LiNiO_2$, that can be ported to the study of more complex and less investigated systems.[1]

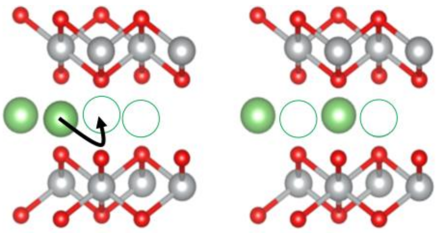


Figure 1: Schematic representation of Li migration path in $LiNiO_2$.

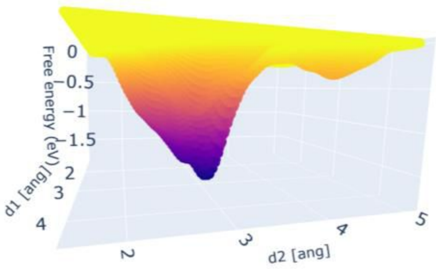


Figure 2: Computed free energy surface of $LiNiO_2$.

We tested three different methodologies: i) sampling of the theoretical path defined by hand; ii) *ab initio* molecular dynamics (AIMD) and iii) metadynamics. We also exploited two different programs, namely CRYSTAL [2] for performing path sampling and CP2K [3] for AIMD and metadynamics simulations. From the results of our work, metadynamics emerged to be the most suitable methodology for the designation of Li migration path, which then needs to be sampled to overcome the intrinsic limitations of metadynamics and find more reliable value of the energy barrier.

We intend also to perform sampling of the identified path with post-HF methods as CCSD(T), using CRYSCOR code[4], to benchmark different DFT functionals and individuate the best performing ones for the investigation of the energy barrier of Li intercalation compounds.

Moreover, we proposed a smart and easy way to approximately calculate the effective frequency ν*, by fitting the minimum correspondent to the initial equilibrium state of the system with a parabola and exploiting the monodimensional harmonic oscillator approximation.

[1] L. Bonometti et al. In Preparation
[2] A. Erba et al. J. Chem. Theory Comput, In Press (2022)
[3] T. D. Kühne et al. J. Chem. Phys. 152 (2020) 194103
[4] C. Pisani et al. Phys. Chem. Chem. Phys. 14 (2012) 7615

Development of a specifically tailored Reactive Force Field to model electrode coatings in solid-state Lithium Anode batteries with superionic conductors: the Multiscale Simulation Paradigm at work.

Maddalena D’Amore[1], Moon Y. Yang [2], Minho Kim[2], Anna M. Ferrari [1], Mauro F. Sgroi[1], Alessandro Fortunelli[3], William A. Goddard III [2]
[1]*Department of Chemistry, University of Turin, Italy*
[2] *Materials and Process Simulation Center, California Institute of Technology, Pasadena, USA*
[3]*CNR-ICCOM, Pisa, Italy*
maddalena.damore@unito.it

In order to improve battery performance, it is important to switch from current generation Lithium ion batteries (LIB) to next generation Li metal anodes (LMA). This requires new electrolytes stable against a LMA or else a protective layer to stabilize the solid-electrolyte interface (SEI). In the field of ionically conductive solids, significant progress has been made recently with the discovery of numerous “sulphide-based” compounds particularly Argyrodites Li_6PS_5X with X= (Cl, Br, I) [1,2] that represent a class of crystalline Li-rich solids with an unusual high Li^+ mobility. Unfortunately, these promising superionic conductors can react with Li anodes. Therefore, we are investigating how to stabilize solid electrolytes at the interface with the Li electrodes. In particular, we are looking at coatings that decrease degradation with the electrolyte while maintaining high Li^+ conductivity. In the present study, we considered Li_2S as possible coating in Argyrodite/Lithium interfaces. The modelling of chemical and transport phenomena in these systems requires molecular dynamics to be run for $t \geq 1n$ nanoseconds on realistic models with > 100,000 atoms, which is far too large for quantum mechanics (QM) calculations. Instead, we use the ReaxFF reactive force field, [3] for which reactive molecular dynamics on > 100,000 atoms for $t > 10$ nanoseconds is practical. To optimize the ReaxFF parameters for a Li_2S coating on the Li anode we used Density Functional Theory (DFT) at PBE0/TZVP and M062X/TZVP level for model systems. We will report the ReaxFF predictions for multiscale reactive simulations on the interfaces.

[1] H-J Deiseroth et al., Ang. Chem. Int. Ed. 47 (2008), 755.
[2] M. D’Amore et al. Phys. Chem. Chem. Phys. 24 (2022), 22978.
[3] Adri C. T. van Duin et al. J. Phys. Chem. A 105 (2001), 9396.

Unveiling the complexity of host-guest interactions and defects formation in Metal-Organic Framework from first principle lattice dynamics

Lorenzo Donà[1], Barbara E. Souza[2], Tao Xiong[2], Annika F. Möslein[2], Jin-Chong Tan[2] and Bartolomeo Civalleri[1]
[1] *Dipartimento di Chimica, Università di Torino, Torino 10125, Italy*
[2] *Multifunctional Materials and Composites Laboratory, Department of Engineering Science, University of Oxford, Oxford OX1 3PJ, U.K*
Presenter's e-mail address: *lorenzo.dona@unito.it*

Due to their chemical versatility and their modular nature, thousands of Metal-Organic Frameworks (MOF) [1] of different size and topology have been either synthesized or built by design. In addition, framework modifications, host-guest interactions, defects and lattice interpenetration can occur thus further complicating the structure. Despite this, all these features make them unique materials for several important applications [2], from gas adsorption and separation, sensing, drug delivery, catalysis and photocatalysis, defect engineering.

Apparently, the structural and chemical complexity of MOFs can pose a limit to the applicability of quantum mechanical methodologies. To cope with this, low cost, yet accurate ab initio methods are needed. Recently, a new class of cost-effective ab initio methods for solid-state calculations have been developed and implemented by some of us in the CRYSTAL code [3] with the main target to predict accurate structural, vibrational and energetical properties. These composite methods, dubbed as *sol-3c* [4], rely on a HF/DFT hybrid functionals (e.g., PBEsol0 and HSEsol) evaluated in a double-zeta quality basis set tuned for solids and augmented with two semi-classical corrections to take into account dispersive interactions (D3[5a]) and the basis set incompleteness error (gCP[5b]). The excellent trade-off between cost and accuracy shown by *sol-3c* composite methods allows running costly calculations such as vibrational frequencies and lattice dynamics even on small scale computing resources.

In this work, we adopted the *sol-3c* composite methods to unveil the detailed dynamics of vibrational motions that occur in host-guest interactions and defects formation of MOFs, to this end, our first-principle simulations have been exploited to corroborate the experimental ATR-FTR data, pinpointing the complex vibrational processes that take place at the atomic scale. More in detail, thanks to a synergy between experiments and modeling we investigated three different applications for which MOFs can be considered as promising candidates, these encompass the field of drug delivery and encapsulation of anticancer drug (5-fluorouracil) in HKUST-1[6], nano-confinement of luminescent dyes in ZIF-8 for solid-state LED devices[7] and defect engineering of Zeolitic Imidazolate Frameworks[8].

[1] H. C. Zhou, J. R. Long, O. M. Yaghi, Chem. Rev. 112 (2012)
[2] (a) D.J. Tranchemontagne et al., Chem. Soc. Rev. 38 (2009); (b) Zhou et al., Chem. Soc. Rev. 43 (2014); (c) Kirchon et al., Chem. Soc. Rev. 47 (2018)
[3] R. Dovesi, A. Erba, R. Orlando, C. M. Zicovich-Wilson, B. Civalleri, et al., WIREs Comput. Mol. Sci. 1360 (2018)
[4] L. Donà, J. G. Brandenburg, and B. Civalleri, J. Chem. Phys. 151 (2019)
[5] (a) S. Grimme et al., J. Chem. Phys. 132 (2010); (b) H. Kruse et al., J. Chem. Phys. 136 (2012)
[6] B. E. Souza, L. Donà, K. Titov, P. Bruzzese, Z. Zeng, Y. Zhang, A. S. Babal, A. F. Möslein, M. D. Frogley, M. Wolna, G. Cinque, B. Civalleri, and J.-C. Tan, ACS Appl. Mater. Interfaces 12 (2020)
[7] T. Xiong, Y. Zhang, L. Donà, M. Gutiérrez, A. F. Möslein, A. S. Babal, N. Amin, B. Civalleri, and J.-C. Tan, ACS Appl. Nano Mater. 4 (2021)
[8] A. F. Möslein, L. Donà, B. Civalleri, and J.-C. Tan, ACS Applied Nano Mater. 5 (2022)

A QM-MM study of di-imidazolium ionic liquids.

M. Farina [1,2], E. Bodo[1], I. Daidone[2], M. Aschi[2]
[1] *Dipartimento di Chimica, Università di Roma "La Sapienza", Piazzale Aldo Moro 5, Roma, RM*:
[2] *Università degli Studi dell'Aquila, Via Vetoio 48, Coppito, AQ*
matteo.farina@uniroma1.it

We present a computational study of geminal di-imidazolium bis(trifluoromethylsulfonyl)imide ionic liquids also known as ($[C_n(mim)_2](TFSI)_2$), where *n* represents the length of the alkyl chain. In particular, our work aimed at finding a reliable, but cheap computational strategy to provide accurate spectroscopic observables such as Raman spectra.

As already underlined in previous works,[1,2] the complexity of these systems lies in the large conformational mobility of the cation, hence in the need of considering many possible conformations to simulate a realistic vibrational spectrum.

Using a refined version of CL&P Force field[3,4,5] we have performed MD simulations of bulk phase of ($[C_3(mim)_2](TFSI)_2$) and ($[C_4(mim)_2](TFSI)_2$) with GROMACS software. From the trajectory, using in-house codes, we have extracted the most representative cluster structures, mapping different configurations of the system and using free energy as a selection criterion. These structures have been used as starting points for the simulation of vibrational spectra (Raman and IR) with DFT methods using standard software.

While this procedure cannot account completely for the bulk effect, it is sensitive to the conformational variability of the system, and able to correctly sample the state of the liquid phase, thus providing a realistic simulation of the vibrational spectra with a very small computational effort.

[1] E. Bodo, M. Chiricotto, R. Caminiti, 2011, J. Phys. Chem. B, 115, 14341–14347
[2] A. Serva, P. D'Angelo et al., 2016, Phys. Chem. Chem. Phys., 18, 16544-16554
[3] J.N. Canongia Lopes, J. Deschamps, A.A.H. Padua J Phys Chem B, 2004, 108, 2038-2047
[4] J.N. Canongia Lopes, J. Deschamps, A.A.H. Padua J Phys Chem B, 2004, 108, 11250-11250.
[5] J. N. Canongia Lopes, I. M. Marruchoab, C. E. S. Bernardes et al., Phys. Chem. Chem. Phys., 2017,19, 29617-29624.

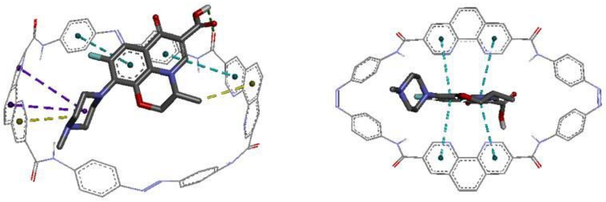
Designing photocages for encapsulation of biomedically relevant molecules

Cristina García-Iriepa[1,2], Luis Miguel Gutiérrez[1], Jesús Moreno[1]
[1]*Universidad de Alcalá, Departamento de Química Analítica, Química Física e Ingeniería Química, Grupo de Reactividad y Estructura Molecular (RESMOL), Alcalá de Henares, Madrid, Spain*
[2] *Universidad de Alcalá, Instituto de Investigación Química ''Andrés M. del Río'' (IQAR), Alcalá de Henares, Madrid, Spain*
cristina.garciai@uah.es

Photocages are efficient systems for encapsulation and selective delivery of relevant molecules [1]. In this study, we propose their use for the selective encapsulation/delivery through non-covalent interactions of two families of compounds: antibiotics and G-quadruplex (G4) ligands. On one hand, elimination of antibiotics (fluoroquinolones) from the wastewater, considered as emerging contaminants, can be performed through their encapsulation. Wastewater, applied for further domestic use or irrigation, has a significant antibiotic content and a direct impact on human's health (antibiotic's resistance). On the other hand, G4s are formed both *in vitro* and *in vivo* and are involved in relevant biological processes (replication, transcription, mRNA splicing, translation) and implicated in human pathogenesis such as cancer. Ligands for G4 stabilization have been already proposed for cancer therapeutics and so, we aim their selective delivery by irradiation of the photocage.

The followed approach can be summarized in six steps:

1) Design of cages with a molecular photoswitch (azobenzene), responsible for the structural change upon irradiation [2], aromatic parts and hydrogen-bond acceptor/donor groups, according to the nature of the selected ligands to be encapsulated.
2) Optimization in the ground state at the DFT level of the designed cages of both, the *cis* and *trans* isomers. Two key points are evaluated: *i)* the 3D structure of at least one of the cage isomers to be able to encapsulate the molecule and *ii)* a large structural difference between the *cis* and *trans* isomers of the photocages ensuring one state for encapsulation and the other for delivery.
3) Simulation of their absorption spectra at the TD-DFT level. The overlap of the two isomers and ligands absorption spectra, undesired, is checked.
4) Molecular docking to retrieve cage-ligand complexes, avoiding biased structures driven by chemical intuition. The interactions of the most favorable complexes are analyzed in detail (Figure 1).
5) Evaluation of the energetics (Gibbs free energy) of the cage-ligand association process, using the complexes retrieved form docking.
6) For the most promising cages, the stability of the cage-ligand complexes along time is modeled through molecular dynamics simulations.



Trans isomer *Cis* isomer

Figure 1. Cage-antibiotic (ofloxacin) complex (*cis* and *trans* isomers) retrieved from docking. The most relevant interactions are shown.

1. A. Díaz-Moscoso, P. Ballester, *Chem. Commun.* 53 (2017) 4635.
2. C. García-Iriepa, M. Marazzi, L. M. Frutos, D. Sampedro, *RSC Adv.* 3 (2013) 6241–6266.

Theoretical Study of the solid-state electrolyte Li_3PS_4, the interfaces formed with Li_2S and Li-anode, and the Li migration

Naiara L Marana[1], Mauro Sgroi,[1] Silvia Casassa,[1] Riccardo Rocca,[2] Fabrizio Silveri,[3] Lorenzo Maschio,[1] and Anna Maria Ferrari[1]
[1]Chemistry Department, Torino University, Torino, Italy
[2]Centro Ricerche FIAT S.C.p.A, Orbassano, Italy
[3]Gemmate Technologies s.r.l. Buttigliera Alta, Italy
naiaraleticia.marana@unito.it

Over the last few decades, Li-ion batteries have become the most used in different technological devices. However, with the advent of ever more powerful technologies, the need to develop more efficient and longer-lasting batteries has increased. In particular, with the eminent restriction of combustion engines for cars and their replacement by electric motors, the search for more efficient batteries has also become a matter of environmental necessity. In this scenario, MODALIS^{2}, a transnational European research program, was created to investigate new materials for next-generation Li-ion batteries for electric vehicles. One of these materials is the lithium thiophosphate, Li_3PS_4, which belongs to a class of solid electrolytes that has been gaining prominence due to their high ionic conductivity, good thermal and mechanical stability, and good electrochemical window. In particular, β-Li_3PS_4 has an ionic conductivity of about 3.0×10^{-2} S cm-1 at 573 K, the higher obtained for the Li_3PS_4 structures [1]. However, one of the problems that arise when it comes to ASSLBs is that of interfaces formed between the solid-electrolytes and the anode/cathode, and their defects, in particular the Li dendrites, which can compromise the correct functioning of the battery and the Li-ion migration. In this sense, understanding how interfaces and their defects are formed, how we can avoid them, and how occurs Li-ion migration (through and within each material), is a fundamental point for the advancement in the development of commercial batteries. Therefore, supported by MODALIS^{2}, this work aims at exploring, from a theoretical point of view, the formation, stability, and properties of the interfaces formed between the stable surface (110) of β-Li_3PS_4 solid electrolyte[2] with the Li-anode and Li_2S, a passivating material that should stabilize the Li_3PS_4/Li-anode interface. Furthermore, possible pathways for the migration of Li ions across the interfaces, and in each material, were hypothesized based on the electron density critical points obtained through topological analysis and confirmed with the simulations and barrier energies calculation.

[1] Homma, K.; Yonemura, M.; et al., Solid State Ion., 53–58 (2011).
[2] Marana, N. L.; Sgroi, M. F.; et al., Nanomaterials, 2795 (2022).

Abstract ID. T4P08

Structural and Vibrational Description of Major Oxides Constituents of Portland Cement Clinker: A Density Functional Theory Study

Jefferson Maul[1,2], Davide Mitoli[2], Alessandro Erba[1], Ricardo P. S. Dutra[2]
[1]Dipartimento di Chimica, Università di Torino, via Giuria 5, 10125, Torino, Italy
[2]Materials Science and Engineering Graduate Program, UFPB, João Pessoa, 58051-900, Brazil
jeffdandrade@gmail.com

Computational modeling is increasingly gaining space in materials science, due to the large range of properties that can be simulated, some that experimentally would be not feasible either technically or financially, or even could contain immense health risks to the analyst [1]. This interest rapidly expands to study materials considered traditional as the ones employed in civil construction. The cement industry is undoubtedly one of the most relevant of this segment, due to the high mechanical properties and availability of raw materials for cement manufacturing. The clinker is the heart of Portland cement, probably the most common type of cement, it is produced by burning limestone (80%) with clay (20%), and it is composed by four main calcium based structures C_3S (Alite, $3CaO.SiO_2$) represents 42-60%, C_2S (Belite, $2CaO.SiO_2$) represents 14-35%, C_3A (Calcium Aluminate, $3CaO.AlO_3$) represents 6-13% and C_4AF (Calcium Aluminoferrite, 4CaO.Al2O3.Fe2O3) represents 5-10% [2]. Using Density Functional Theory (DFT) for solids (CRYSTAL program [3]) one is able to explore mechanical and spectroscopic features of these materials. However, the amount of polymorphs presented by some of these compositions can be very tricky. For example, using the most common polymorph structures for the C_3S composition studied in literature, with the current setup, we were unable to find the global minimum (crystal symmetry *C*m(M_3), *P*-1 (T_1), and *P*c(3<M>)). The structures and a good correlation with experimental Raman spectra of each DFT optimized structures are shown in Figure 1. Also, analyzing the elastic constants we observe that Born conditions are satisfied.

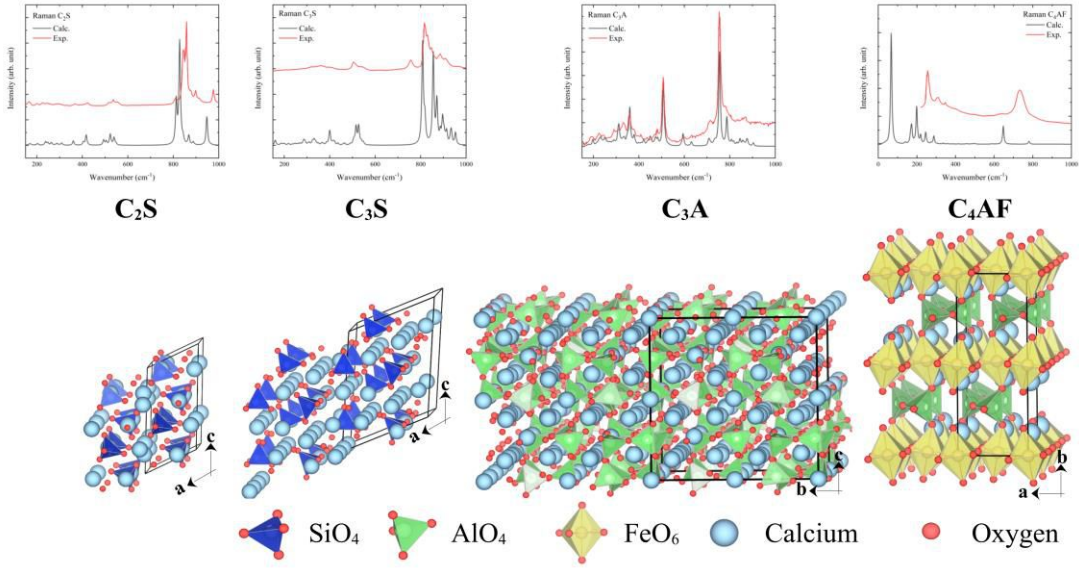


Figure 1: Structure and Raman spectra (experimental data taken from [4-6]) of four constituents of Clinker (C_2S (*P*2_1/m), C_3S (*P*c; <M>), C_3A (*P*a-3) and C_4AF (*I*ma2)).

[1] J. Neugebauer and T. Hickel Wiley Interdiscip. Rev. Comput. Mol. Sci. 3 (2013) 438-448.
[2] P.K. Mehta and P. J. M. Monteiro McGraw-Hill Education, (2014).
[3] A. Erba et al. J. Chem. Theory Comput., (2022) DOI: 10.1021/acs.jctc.2c00958
[4] J. Ibáñez et al. Raman Spectrosc. 38 (2007) 61-67.
[5] D. Torréns-Martín et al. J. Am. Ceram. Soc. 96 (2013) 3589-3595.
[6] L. Black et al. Adv. Appl. Ceram. 105 (2006) 209-216.

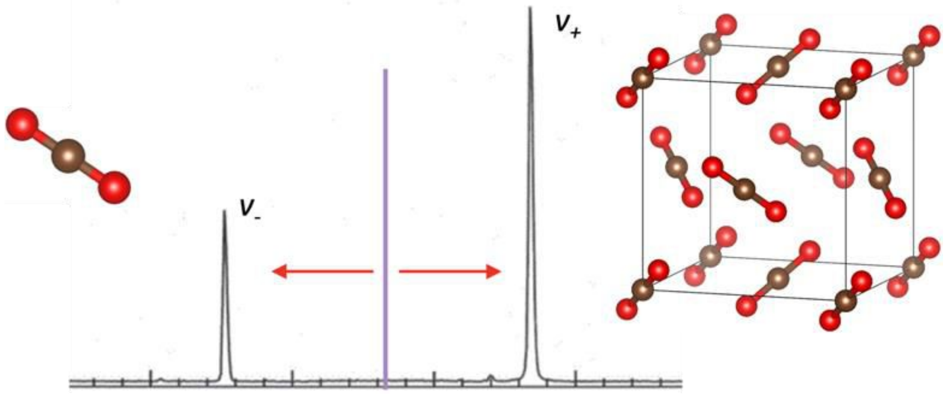
Fermi Resonance in Dry Ice Finally Explained: A Quantum-Mechanical Description

Davide Mitoli[1], Jefferson Maul[1] and Alessandro Erba[1]
[1]*Dipartimento di Chimica, Università di Torino, via Giuria 5, 10125 Torino, Italy*
davide.mitoli@unito.it

One of the most peculiar anharmonic features of infrared and Raman spectra is the so-called Fermi resonance (FR), according to which two (or more) vibrations in a molecule or a crystal couple in such a way to split the single harmonic peak into two distinguished ones. Such phenomenon was first interpreted by Fermi himself [1] and its occurrence in the CO_2 molecule represents the corresponding standard textbook example. As such, the physico-chemical interpretation of the FR in the CO_2 molecule is fully rationalized in quantum-mechanical (QM) terms.

A FR is also observed in dry ice, the molecular crystal of CO_2. Despite a number of works have been published so far on this topic, there is still no consensus on the subtle nature of this phenomenon in the solid, as a rigorous and complete QM characterization is still lacking. In order to provide an accurate description of FRs, methods which are capable of taking into account, among other anharmonic terms, nuclear quantum effects (NQEs) [2] must be employed. For such a reason, approaches like *ab initio* Born-Oppenheimer Molecular Dynamics (ai-BOMD) and Vibrational Self-Consistent Field (VSCF) fail.

On the other hand, Vibrational Configuration Interaction (VCI) allows for an explicit account of phonon-phonon coupling and represents the most appropriate theoretical framework to be employed in order to model such phenomena [3]. A developmental version of the CRYSTAL23 code [4], where the calculation of anharmonic vibrational states as well as their intensities [5] is available, has been used. In this study, we adopt a quartic-force field representation of the potential energy surface (PES) [6,7]. Results clearly show that 3-mode coupling (null in the CO_2 molecule) plays instead a fundamental role in the FR of dry ice.



[1] F. Enrico. Z. Phys. 71 (1931) 250-259
[2] T. E. Markland and M. Ceriotti. Nat. Rev. Chem. 2.3 (2018) 0109
[3] A. Erba et al. J. Chem. Theory Comput. 15.6 (2019) 3766-3777
[4] A. Erba et al. J. Chem. Theory Comput. (2022) DOI: 10.1021/acs.jctc.2c00958
[5] P. Carbonnière et al. J. Chem. Theory Comput. 16.5 (2020) 3343-3351
[6] A. Erba et al. J. Chem. Theory Comput. 15.6 (2019) 3755-3765
[7] D. Mitoli et al. Cryst. Growth Des. (2023) DOI: 10.1021/acs.cgd.3c00104

Argyrodite Li_6PS_5Cl solid electrolyte: A Raman theoretical study

Eduardo Oliveira[1], Fabrizio Silveri[2], Alessandro Damin,[1] Naiara Leticia Marana[1], Maddalena D'Amore[1], Mauro Sgroi[1], Lorenzo Maschio[1], Anna Maria Ferrari[1],
[1]*Dipartimento di Chimica, Università di Torino, via Giuria 5, 10125 Torino, Italy*
[2]*Gemmate Technologies s.rl. Buttigliera Alta, Italy*
eduardo.deoliveiragomes@unito.it

The rapid development of electrical vehicles and mobile electronic devices has motivated the enormous demand for batteries. For this reason, the urgent development of high-energy-density and low-cost batteries is nowadays a huge goal[1]. Conventional lithium batteries with oxide cathode materials have been widely used, but the low theoretical capacity of these oxide cathode materials and liquid composition problems limit their applications. One of the most promising strategies to solve these issues is to replace the liquid electrolytes with solid-state electrolytes (SSEs). The SSEs have shown good results, in addition to improved safety and lifetime, they promise a good energy density, packaging, and operating temperature range[2]. Among various kinds of inorganic SSEs, Argyrodites Li_6PS_5Cl has been reported as a promising electrolyte with a high ionic conductivity and easy synthesis methods[3]. Li_6PS_5Cl is reported to be cubic ($F\bar{4}3m$ structure), but our recent investigation[4] shows that the bulk structure, as reported in the literature, appears to be metastable, with spontaneous symmetry breaking yielding to pseudocubic structures of P1 symmetry. In this study, we calculated Raman spectra of all relevant structures, as Raman spectrum has been widely proved to be a valuable tool for the structural recognition of isocomposites. Computed results have been compared with available experimental data. All calculations have been performed at the DFT level combining hybrid functional with large basis set and by employing the CRYSTAL code[5]. This study is part of the MODALIS² (MODelling of Advanced LI Storage Systems) project and will allow us to contribute significantly to this project.

[1] S. Wang *et al.*, "High-Conductivity Argyrodite Li_6PS_5Cl Solid Electrolytes Prepared via Optimized Sintering Processes for All-Solid-State Lithium-Sulfur Batteries," *ACS Appl. Mater. Interfaces*, vol. 10, no. 49, pp. 42279–42285, 2018, doi: 10.1021/acsami.8b15121.
[2] and M. S. Hans-Jorg Deiseroth,* Shiao-Tong Kong, Hellmut Eckert, Julia Vannahme, Christof Reiner, Torsten Zaiß, "Angew Chem Int Ed - 2008 - Deiseroth - Li_6PS_5X A Class of Crystalline Li-Rich Solids With an Unusually High Li Mobility.pdf." .
[3] Z. Zhang *et al.*, "Design and synthesis of room temperature stable Li-argyrodite superionic conductors: Via cation doping," *J. Mater. Chem. A*, vol. 7, no. 6, pp. 2717–2722, 2019, doi: 10.1039/c8ta10790d.
[4] M. D'Amore *et al.*, "From symmetry breaking in the bulk to phase transitions at the surface: a quantum-mechanical exploration of Li_6PS_5Cl argyrodite superionic conductor," *Phys. Chem. Chem. Phys.*, vol. 24, no. 37, pp. 22978–22986, 2022, doi: 10.1039/d2cp03599e.
[5] R. Dovesi *et al.*, "Quantum-mechanical condensed matter simulations with CRYSTAL," *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, vol. 8, no. 4, pp. 1–36, 2018, doi: 10.1002/wcms.1360.

Development of a theoretical-computational approach for the study of chemical reactions at different temperatures

Alessio Olivieri[1], Alessandro Nicola Nardi[1], Andrea Amadei[2], Marco D'Abramo[1]
[1]Department of Chemistry, "Sapienza" University of Rome, Rome, Italy
[2]Department of Chemistry, "Tor Vergata" University of Rome, Rome, Italy
alessio.olivieri@uniroma1.it

The development of theoretical models and computational methods aimed at the study of chemical reactions is an appealing topic because they can provide new insights of reactions that are difficult to study experimentally. For example, the uncatalysed hydrolysis of the phosphodiester bond has a half-life of millions of years at room temperature allowing this reaction to be observed experimentally only at elevated temperatures [1,2]. Information about the rate of an uncatalyzed reaction can be used to estimate the enhancement of the reaction rate by the nucleases. Here, the phosphodiester bond (P-O) basic cleavage (Fig.1a) has been studied by means of MD-PMM [3] using dineopentyl phosphate (Np2P) as a model compound. The neopentil- substituents have been chosen due to their steric hindrance preventing the cleavage of the C-O bond, as observed in the dimethyl phosphate, and to carry out a comparison with the Eyring plot determined from the rate constants experimentally observed by K. G. Schroeder et al. for the same reaction [1,2]. As shown in Fig.1b, our theoretical model is rather in good agreement with the experimental data, in particular near ambient temperature where atomistic force fields are usually parametrized.

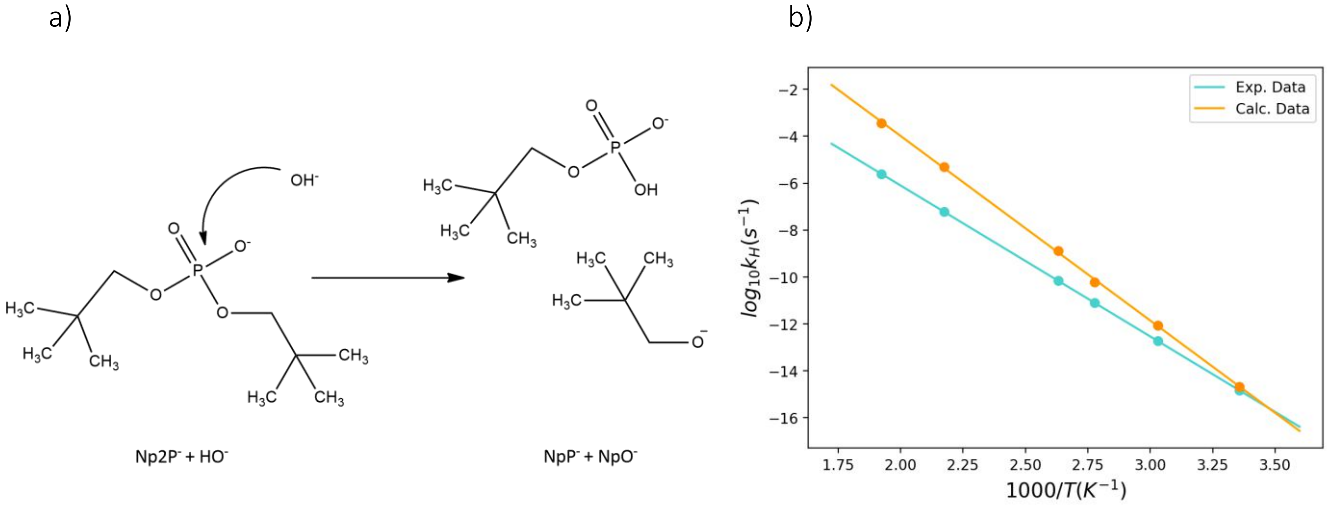


Figure 1. a) Basic Hydrolysis of the dineopentyl phosphate, b) Eyring plot of the experimentally observed rate constants (cyan) and calculated rate constants (orange).

[1] R. Wolfenden et al. J. Am. Chem. Soc. 120 (1998) 833
[2] K. G. Schroeder et al Proc. Natl. Acad. Sci. U.S.A. 103 (2006) 4052
[3] L. Zanetti-Polzi et al. Phys. Chem. Chem. Phys. 20 (2018) 24369

A machine learning approach for the prediction of atomic charges of metal- organic frameworks

Herald Paja[1], Lorenzo Donà[1], Jacopo Battaglia[2], Federico Schinco[3], Gianpaolo Perego[2], Luisa Spairani[3] and Bartolomeo Civalleri[1].
[1] Department of Chemistry, University of Turin, via Pietro Giuria 5, 10125, Torino TO, Italy
[2] Aethia s.r.l., Via Ribes, 5, 10010 Samone TO, Italy
[3] Netsurf s.r.l., Corso Vercelli, 444, 10015 Ivrea TO, Italy
herald.paja@unito.it

Metal-organic frameworks (MOFs) are very versatile materials because of their modular structure since the framework is composed by the combination of two secondary building units (SBU): an inorganic unit (metal ion or cluster) and an organic ligand. Therefore, a plethora of combinations are available, thus allowing MOFs to cover a huge chemical space. High-throughput computational screenings are then useful to explore all the chemical and physical properties of such materials but low-cost computational methods such as tailored force-fields are required to speed up the calculation [1]. To that purpose, accurate atomic charges are crucial to correctly predict long-range electrostatic interactions. They can be derived either from quantum-mechanical calculations or generated on the fly through simplified geometrical schemes or, more recently, through Machine Learning (ML) predictive models. The latter requires suitable databases of structure and properties to be used to train the ML model. Different databases of MOFs and their properties are now available such as CoReMOF [2], QMOF [3] and ARC-MOF [4].

In this work, we present the results of the prediction of atomic charges derived from (i) a new database and (ii) the QMOF database.

On the one hand, we built a dataset of 237 structures, with up to 3000 atoms in the unit cell, for which Hirshfeld-type charges (>80000) were computed with the low-cost hybrid HF/DFT composite method PBEsol-3c [5] on the fully relaxed structures. The CRYSTAL program [6] has been used to exploit the space group symmetry and use the efficient parallelization of the code. Then, we trained a ML model by using XGBoost with atomic and environmental descriptors. The work was carried out in collaboration with Aethia srl and NetSurf srl within the ATTRACTOR project. The so-built ML model has been made available through the ATTRACTOR web site [7] where it is possible to predict the Hirshfeld-type charges by processing the CIF file of a generic MOF.

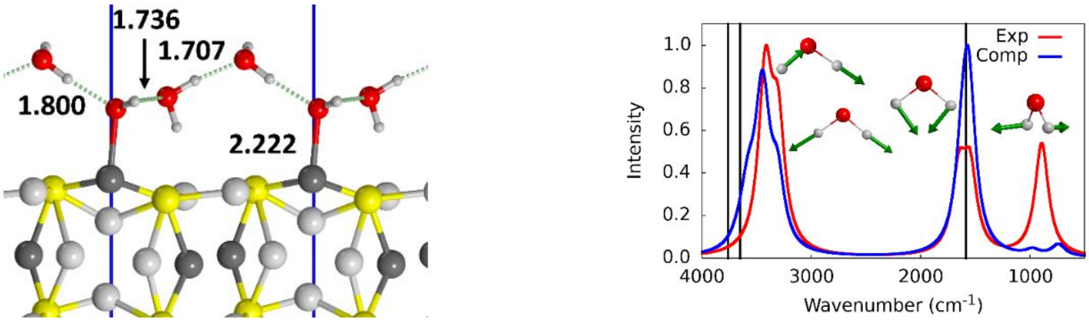
On the other hand, the QMOF database that contains more than 20000 cleaned up experimental structures (< 300 atoms in the unit cell) for which DDEC charges are available, was analysed to understand how the size and composition (i.e. metal ion types) of the training dataset affects the prediction of the atomic charges. Accurate predictions can be obtained by referring to a smaller dataset of 500 structures. Based on this result, the ATTRACTOR dataset has then been extended to have a more balanced composition in terms of different metal ions, by including some of the QMOF structures, for a better prediction of the Hirshfeld-type charges.

[1] P. Xu, X. Ji, M. Li, e W. Lu, npj Comput. Mater. 9 (2023) 42
[2] Y. G. Chung, E. Haldoupis, B. J. Bucior, M. Haranczyk, R. Snurr, et al. (2020). CoRE MOF 2019 Dataset (1.1.3). https://doi.org/10.5281/zenodo.3677685
[3] J. Burner et al., Chem. Mater., 35 (2023) 900.
[4] A. S. Rosen et al., Matter 4 (2021) 1578–1597.
[5] A. Erba, J.K. Desmarais, S. Casassa, B. Civalleri, L. Donà, I.J. Bush, B.G. Searle, et al. J. Chem. Theory Comput., https://doi.org/10.1021/acs.jctc.2c00958
[6] L. Donà, J. G. Brandenburg, B. Civalleri, J. Chem. Phys., 156 (2022) , doi: 10.1063/5.0080359.
[7] http://attractor.netsurf.it/

Water reactivity on Schreibersite: from phosphites to phosphates

S. Pantaleone[1], M. Corno[1], A. Rimola[2], N. Balucani[2], and P. Ugliengo[1]
[1]Dipartimento di Chimica and Nanostructured Interfaces and Surfaces (NIS) Centre, Università degli Studi di Torino, via P. Giuria 7, I-10125, Torino, Italy
[2]Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia, Spain
[3]Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto 8, I-06123 Perugia, Italy
Presenter's e-mail address: stefano.pantaleone@unito.it

Phosphorus is an element of primary importance for all living creatures, being present in many biological activities in the form of phosphate (PO_4^{3-}). However, there are still open questions about the origin of this specific element and on the transformation which allowed it to be incorporated in biological systems. The most probable source of prebiotic phosphorus is the intense meteoritic bombardment during the Archean era, few million years after the solar system formation, which brought tons of iron-phosphide materials (schreibersite) on the early Earth crust [1]. It was recently demonstrated that by simple wetting/corrosion processes from this material various oxygenated phosphorus compounds are produced [2]. In the present work, the wetting process of schreibersite (Fe_2NiP) was studied by computer simulations using density functional theory, with the PBE functional supplemented with dispersive interactions through a posteriori empirical correction (D*0) [3,4]. Therefore, the two stable (110) and (001) Fe_2NiP surfaces were used simulating different water coverages, from which structures, water binding energies and vibrational spectra have been predicted. The computed (an-)harmonic infrared spectra have been compared with the experimental ones, thus confirming the validity of the adopted methodology and models (see Figure 1) [5,6]. Moreover, water reactivity was inspected in several possible deprotonation reactions, also increasing the number of water molecules in order to lead to the formation of phosphonic and phosphoric acids and their corresponding deprotonated forms.



a) Structure

b) IR spectrum

Figure 1: PBE-D*0 optimized geometry of water monolayer on the (110) Fe_2NiP surface (left) and simulated vs experimental IR spectrum (at 125 K). Atom color legend: H in white, O in red, P in yellow, Fe in light grey, Ni in dark grey.

[1] Gulick A. (1955) *Am. Sci.*, *43*, 479-489
[2] Pasek M. A. and Lauretta D. S. (2005) *Astrobiology*, *5*, 515-535
[3] Pantaleone S., Corno M., Rimola A., et al. (2021) *ACS Earth Space Chem.*, *5*, 1741-1751
[4] Pantaleone S., Corno M., Rimola A., et al. (2022) *J. Phys. Chem. C*, *126*, 2243-2252
[5] La Cruz N. L., Qasim D., Abbott-Lyon H., et al. (2016) *Phys. Chem. Chem. Phys.*, *18*, 20160-20167
[6] Qasim D., Vlasak L., Pital A., et al. (2017) *J. Phys. Chem. C*, *121*, 13645-13654.

Computational understanding of disordered cubic Li_2TiS_3 as a novel material for Lithium-Ion batteries

Riccardo Rocca[1,2], Mauro Francesco Sgroi[1], Bruno Camino[3], Maddalena D'Amore[1] and Anna Maria Ferrari[1]
[1]Department of Chemistry and NIS, University of Turin, 10125 Torino, Italy
[2]Centro Ricerche FIAT S.C.p.A, 10043 Orbassano, Italy
[3]Chemistry Department, University College (UCL), London, United Kingdom
Presenter's e-mail address: riccardo.rocca@unito.it

Lithium-ion batteries are well-known power components of portable electronic devices, nevertheless these batteries can play a much bigger role in our modern society as energy storage device for powering electric vehicles. They are particularly interesting due to their attractive properties such as: high energy efficiency, lack of memory effect, high energy density, long cycle life and high-power density. In this perspective Sulfide-based cathodes has been studied in recent times. Different transition metals such as Ti, Sn, Nb has been considered to improve stability, performance and safety. In particular Li_2TiS_3 arouse a lot of interest for many reasons: the high stability, the high reported capacity (more than 400 mAh/g [1]), low cost and the absence of critical raw materials (such as Cobalt and Nickel). Cubic Li_2TiS_3 structure is not very well defined in literature, it is a system with structural disorder where Lithium and Titanium randomly occupies the same reticular position. For the generation of the system a solid solution approach was applied, considering 18 Lithium atoms 9 of them were substituted with Titanium. A total of 4023 structures were obtained and were classified based on the structural organization. A batch of 20 structures was selected and studied with CRYSTAL code [2]. Electronic properties and Raman spectra were simulated and a strong correlation between structure and electronic/spectroscopic properties was highlighted[3]. Since during the cell charge and discharge the cathode undergoes lithium extraction and insertion (respectively), the overall structure changes and different phenomena can occur. A deep investigation of the structure evolution during lithium extraction and insertion was carried out under different point of view: the structural evolution, changes in volume, distortion; the electronic properties; the energy required for lithium extraction; the OCV/SOC curve evaluation; the transport properties of lithium.

[1] A. Sakuda *et al.*, «A Reversible Rocksalt to Amorphous Phase Transition Involving Anion Redox», *Sci. Rep.*, vol. 8, fasc. 1, p. 15086, dic. 2018, doi: 10.1038/s41598-018-33518-4.
[2] R. Dovesi *et al.*, «Quantum-mechanical condensed matter simulations with CRYSTAL», *WIREs Comput. Mol. Sci.*, vol. 8, fasc. 4, lug. 2018, doi: 10.1002/wcms.1360.
[3] R. Rocca, M. F. Sgroi, B. Camino, M. D'Amore, e A. M. Ferrari, «Disordered Rock-Salt Type Li2TiS3 as Novel Cathode for LIBs: A Computational Point of View», *Nanomaterials*, vol. 12, fasc. 11, p. 1832, mag. 2022, doi: 10.3390/nano12111832.

Abstract ID. T4P15

Simulating electronic properties in aqueous environments with a hybrid multiconfigurational self-consistent field/fluctuating charge model

Chiara Sepali[1], Linda Goletto[1], Tommaso Giovannini[1], Chiara Cappelli[1]
[1]Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy
chiara.sepali@sns.it

Multi-reference self-consistent field methods (MCSCF) are currently widely used to overcome the limitations of single-determinant quantum mechanical approaches. [1,2,3] These methods incorporate many electronic configurations into what are known as multiconfigurational wave functions, allowing for a more accurate description of complex electronic structures. In fact, this is crucial in several cases, for example for carotenoids in photosensitive proteins and for transition-metal enzymes. [4,5] Since chemical and biological processes often occur within complex environments that can significantly influence molecular properties, a focused modeling strategy has emCDerged as an effective approach to studying such systems. [7,9] In this work, we present a novel approach, in which we couple an MCSCF theory (CASSCF) with the fluctuating charges model (FQ), [8] to investigate complex systems in an aqueous solution. This hybrid QM/FQ [9,10] model can accurately capture the complex multi-configuration nature of molecules and the effect of the external environment, making it a promising tool for future research in various biological and industrial applications.

[1] J. Hinze et al. J. Chem. Phys. 59 (1973) 6424
[2] E. Dalgaard, P. Jorgensen. J. Chem. Phys. 69 (1978) 3833
[3] B. Roos at al. Chem. Phys. 48 (1980) 157
[4] R. Spezia et al. J. Chem. Phys. 108 (2004) 6763
[5] F. Neese et al. Coord. Chem. Rev. 251 (2007) 288
[6] B. Mennucci et al. Nat. Rev. Chem. 3 (2019) 315
[7] H. Lin. Theor. Chem. Acc. 117 (2007) 185
[8] S. W. Rick et al. J. mol. Liq. 65 (1995) 31
[9] T. Giovannini et al. Chem. Soc. Rev. 49 (2020) 5664
[10] C. Cappelli. Int. J. Quantum Chem. 116 (2016) 1532

From Atom to Anode: the MODALIS^2 multiscale approach to modelling Si/C anodes for lithium-ion batteries

Fabrizio Silveri[1,2], Andrea Bertinetti[2], Matteo Alberghini[2], Alessio Tommasi[1], Martin Petit[3], Vivien Esnault[3], Jerome Bikard[4], Chen Zhao[4], Lorenzo Maschio[1], Mauro Sgroi[1], Gaetan Damblanc[5], Franck Sellier[5]
[1]Dipartimento di Chimica, Università di Torino, Via Pietro Giuria 7, 10125 Torino (TO), Italy
[2]Gemmate Technologies s.r.l., Via Reano 31, 10090 Buttigliera Alta (TO), Italy
[3]IFP Energies nouvelles, Rond-Point de l'échangeur de Solaize, Solaize, France
[5]Siemens Digital Industries Software, Lyon, France
f.sil@live.com

As new generations of batteries are being developed to ensure higher performing, safer and cheaper electric vehicles, new developments are needed at the material scale. In such scope, the MODALIS^2 project (funded by the European Union's Horizon 2020 research and innovation program under grant agreement No 875193) aims to contribute with an novel development process based on integrated multiscale numerical tools. In this work we present the application of the MODALIS^2 approach to the case-study of a Si/C composite anode material, whose properties have been studied at a variety of interlinked modelling scales. Building on experimental data, Density Functional Theory model systems were created within the Quantum Espresso code [1, 2] to study the electronic and mechanical properties of each phase as the state of charge (SoC) is increased; *ab-initio* Molecular Dynamics (AIMD) simulations granted valuable information on the morphology of the amorphous Li_xSi phases that make up the Si/C anode, and allowed for the computation of the dependency of elastic properties and volumetric parameters on the anodic SoC. Informed by DFT data, Finite-Element Method (FEM) models were employed to investigate the evolution of isolated Si/C particles during the lithiation and delithiation processes; the particle was modelled according to the core-shell structure identified by experimental characterization of the anode, but employed DFT-based elastic properties and volumetric expansion parameters as a function of Li concentration in order to evaluate the mechanical evolution of the particles during battery operation and homogenized data for the composite particle. In turn, FEM data could be used in the mechanical and electrochemical modelling of the entire anode. The MODALIS^2 project is addressing the material characterization of next-generation Li-ion cells in different physical domains and aims to demonstrate how an interlinked approach in material modelling can provide accurate parameters and faster time-to-market for next generation cells.

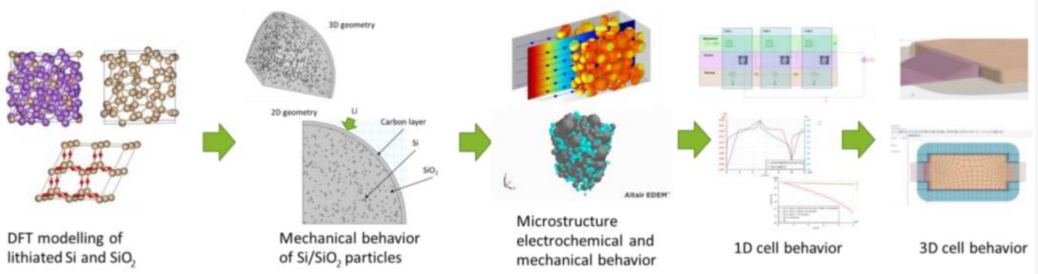


Figure 1. *An overview of the application of the MODALIS^2 toolchain to the modelling of Si/C-based batteries.*

References:

[1] P. Giannozzi et al., J.Phys.: Condens.Matter 21, 395502 (2009)
[2] P. Giannozzi et al., J.Phys.: Condens.Matter 29, 465901 (2017)

Bulk and surface properties of lithium-indium alloy anodes for Li-ion battery applications

Fabrizio Silveri[1,2], Eduardo de Oliveira Gomes[1], Anna Maria Ferrari[1]
[1]Dipartimento di Chimica, Università di Torino, Via Pietro Giuria 7, 10125 Torino (TO), Italy
[2]Gemmate Technologies s.r.l., Via Reano 31, 10090 Buttigliera Alta (TO), Italy
f.sil@live.com

As new generations of batteries are being developed to ensure higher performing, safer and cheaper electric vehicles, new developments are needed at the material scale. Lithium-alloy anodes have recently gained traction as materials for next-generation batteries due to their high theoretical capacity and the potential to limit the negative effects of pure-Li anodes such as dendrite formation and quick performance degradation. Here we present an *ab initio* computational investigation of the bulk and surface properties of lithium-indium alloys for all-solid-state battery applications.

Recent years have seen an increasing interest in lithium-indium anodes for solid-state batteries due to their proven constant voltage operations [1] and resistance to dendrite formation [2]. Computational literature in this field is however scarce, so we decided to investigate the electronic structure of the alloy in its bulk and at the interface, as well as its interaction with lithium ions during the charging process of the battery. Using the CRYSTAL [3, 4] and Quantum Espresso [5, 6] codes we investigated the nature of the lithium-indium interaction and its effect on the reactivity of the alloy. By extending the study to the low-index surfaces of the alloy, we were able to identify its most stable terminations and identify a correlation between the stability of the anode and its electronic properties. Furthermore, we analysed the mechanisms underlying the improved stability of LiIn alloy anodes over pure-Li anodes and the effect of lithium nucleation on the material, obtaining promising results.

The present study is part of the MODALIS^2 project (funded by the European Union's Horizon 2020 research and innovation program under grant agreement No 875193), which aims to provide faster implementation for novel materials in Li-ion batteries by joining the skills of material manufacturers, cell manufacturers and OEMs with model developers at a variety of modelling scales. In the work presented here we aimed to elucidate the electronic properties of the Gen4 LiIn-based anode and its improved dendrite prevention characteristics.

References:
[1] A. L. Santhosha et al. Batteries & Supercaps 2019, 2, 524–529
[2] S. Luo et al. Nat. Comm (2021) 12:6968
[3] R. Dovesi et al., WIREs Comput Mol Sci. 8, e1360 (2018)
[4] R. Dovesi et al., CRYSTAL17 User's Manual (University of Torino, Torino, 2017)
[5] P. Giannozzi et al., J.Phys.: Condens.Matter 21, 395502 (2009)
[6] P. Giannozzi et al., J.Phys.: Condens.Matter 29, 465901 (2017)

Quantum chemical investigation of multi-redox states in organic conjugated redox ladder type polymers for electrochemical energy storage systems

Shuailong Wang, Daniele Fazzi
Department of Chemistry "Giacomo Ciamician", University of Bologna, via F. Selmi 2, 40126 Bologna (Italy)
Presenter's e-mail address: shuailong.wang@studio.unibo.it

Electrochemical energy storage (EES) devices, such as batteries and supercapacitors, play a vital role in our modern society.[1] The request of materials able to storage and release the electrical energy at demand is continuously growing, challenging the actual state of the art of EES technologies. Lithium ion batteries (LIB), as composed by inorganic electrode materials (e.g., cobalt-based alloys), have been largely investigated and used, however they present limits related to their environmental sustainability and low charge capacity.

Organic conjugated redox polymers (**OCRP**) can be considered an effective alternative to inorganic based EES materials, being environmental friendly, easy to design and fabricate. However little is known about their fundamental *structure vs. redox-property* relationships.

In this contribution, we investigate via quantum-chemical calculations the structural and electronic properties of a special class of **OCRPs**, namely ladder polymers.[2] They are characterized by a rigid and highly conjugated backbone, leading to semi-crystalline solid state morphologies featuring high charge and ion mobilities. The ladder **OCRPs** we considered are polyquinoxalines (**PQL**) and **SBBL**, which is a simplified derivative of benzobisimidazobenzophenanthroline (**BBL**), a well known polymer with high charge, thermal and ion mobility.[3, 4]

By combining density functional theory (DFT), broken-symmetry DFT (BS-DFT) and fragment orbital density analysis (FOD) we revealed the poly-radicaloid character of the electronic structure of neutral and multi-redox states.[5] We found that negative (electron) and positive (hole) charges, here defined polarons, relax on localized states of the polymer chain, thus featuring different structural and electron-phonon coupling properties. Multi-charged species, revealed complex electronic structures, as characterized by quasi-degenerate multiplet states showing various spin multiplicities (e.g., doublet, triplet, quartet, quintet, etc.) and response properties.

Our computational study provides insights towards the understanding of multi-redox processes for the last generation of **OCRPs**, active materials for EES and biomimetic applications.

[1] Tarascon, J.M. and M. Armand etal. Nature, 2001. **414**(6861): p. 359-367.
[2] Lee, J., et al. etal. Chem Sci, 2017. **8**(4): p. 2503-2521.
[3] Wang, S., et al. etal. Adv Mater, 2016. **28**(48): p. 10764-10771.
[4] Fazzi, D. and F. Negri etal. Advanced Electronic Materials, 2020. **7**(1).
[5] Fazzi, D., et al. etal. Journal of Materials Chemistry C, 2019.

KEYNOTES

T5. Physical Chemistry approach to catalysis

Silver nanoflower as single platform for in situ photocatalytic reactions

Marcello Condorelli,[1],* Antonio Brancato[1], Cristiana Longo[1], Giuseppe Compagnini[1], and Luisa D'Urso[1]
[1] *Dipartimento di Scienze Chimiche, Università di Catania, Viale A.Doria 6, Catania 95125 Italy*
*(*marcello.condorelli@unict.it)*

In this work, we successfully synthesized silver nanoflower (AgNFs) via a facile wet chemical method and studied plasmon stimulated catalysis of a probe molecule attached to their surfaces[2]. We followed the reaction OF 4-Nitrothiobenzene to 4,4'dimetilmarcaptoazobenzene[1]. To obtain high catalytic properties, we deposed single AgNFs by drop-casting a diluted colloidal dispersion of each nanoparticle on a silicon wafer. The reaction processes were monitored and identified through in situ surface-enhanced Raman spectroscopy based on the confocal Raman microscope system. Moreover, to asset if the reaction is strictly related to the excitation wavelength and to the hot electrons production, tougher than thermal effects, we excited the system with three different wavelength , 532 nm, 633 nm , 785 nm. This study provides a simple and fast method to improve the catalytic property of the noble nanoparticles.

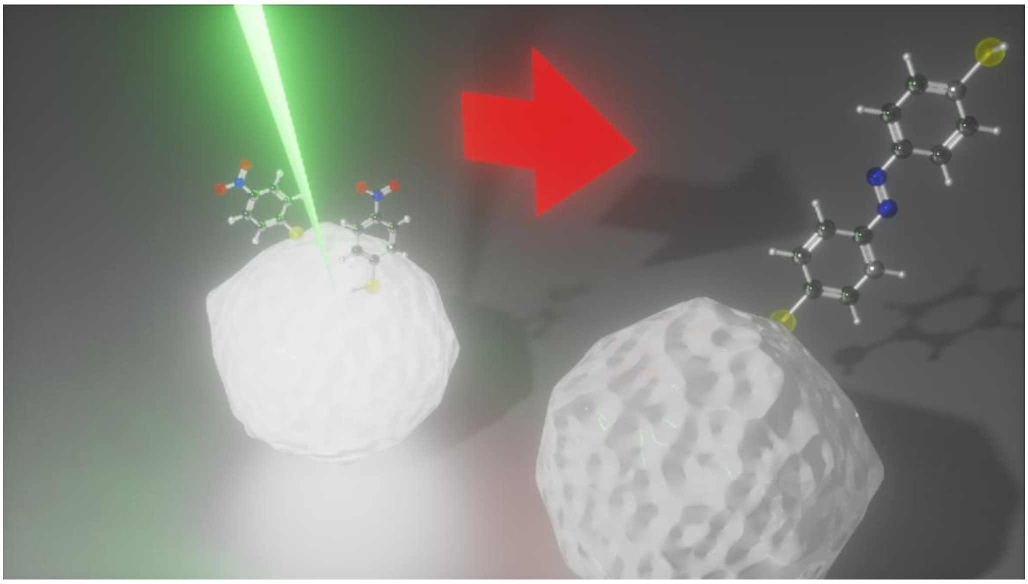


Figure 1: Graphical representation of the plasmon stimulated catalytic process.

[1] Fu, Xiaoli, et al. "AgAu Hollow Hexagonal Nanoplates for Ultrasensitive Tracking of Pesticides and Plasmonic Photocatalysis by Surface-Enhanced Raman Spectroscopy." *ACS Sustainable Chemistry & Engineering* (2022)
[2] Chang, Qing, et al. "Broadband plasmonic silver nanoflowers for high-performance random lasing covering visible region." *Nanophotonics* 6.5 (2017): 1151-1160.

Cu+ bipyridine based homoleptic complexes for hydrocarbons oxygenations reactions

Alessandro Damin,[1] Matteo Bonomo,[1] Barbara Centrella,[1] Gabriele Deplano,[1] Matteo Signorile,[1] Claudia Barolo,[1] Silvia Bordiga[1]
[1]*Dipartimento di Chimica, NIS and INSTM, Università di Torino, Via P. Giuria 7, 10143 Torino, Italia*
alessandro.damin@unito.it

The direct conversion of methane by oxygen into methanol and, more in general, selective oxidation of abundant C-H-containing molecules into valuable products, constitutes nowadays a highly desired goal. Taking inspiration by what is supposed to be the active site in p-MMO enzyme [1,2] and from previous literature [3], a possible direction of work is considering metallorganic complexes based on 2,2'-bipyridine ligands complexing Cu species. One of these (*i.e.* 6,6'-dimethyl-2,2'-bipyridine, dmbpy) has already demonstrated to be useful in preparing tetrahedral $[Cu(dmbpy)_2]^+(PF6)^-$ complex (see Figure 1, hereafter CuBP-M) as efficient redox mediator in dye sensitized solar cells [4].

Figure 1: CuBP-M ((PF6)- omitted for clarity) complex (on the left) and a tentative structure of the oxidized one (on the right) bearing a generic O species (purple sphere).

In this case, the steric hindrance induced by $-CH_3$ groups is supposed to destabilize the square planar coordination favoured for Cu^{2+} ions, so increasing the possibility to continuously cycle between Cu^+ and Cu^{2+} species: the observed extreme reversibility between the Cu oxidation states could be exploited in obtaining an active catalyst in partial oxidation reactions, after the transformation of Cu^+ to a $[CuO_{active}]^+$ species by a suitable O containing agent. CuBP-M was studied in CH_2Cl_2 solutions, following its modification upon the interaction with tert-butyl-hydroperoxide (tBu-OOH), the chosen oxidant agent. The simultaneous use of *in situ* UV-Vis and Resonance Raman Spectroscopy, supported by Cyclovoltammetry and DFT based calculations (B3LYP functional), allowed to identify a) the change in the oxidation state of Cu, b) modification of the local structure of Cu site, possibly transformed in $[Cu(O/OH)]^+$ species. In the case of CuBP-M complex, the relevance of the formed $[CuO_{active}]^+$ was confirmed by its reactivity with cyclo-hexene that showed the restoration of the original Cu^+ and the formation of oxygenated products (mainly cyclo-hexenol and cyclo-hexenone).

- Acknowledgements:

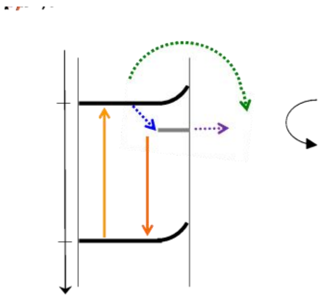
ERC-SyG project CUBE (project nr. 856446) is acknowledged for financial support.
Project CH4.0 under the MUR program "Dipartimenti di Eccellenza 2023–2027" (CUPD13C22003520001) is also acknowledged.

[1] B. Park B. *et al.* Frontiers in Chemistry 7 (2019) 1 and References therein
[2] P. Tomkins *et al.* Acc. of Chem. Res. 50 (2017) 418
[3] A. Sobkowiak *et al.* J. Am. Chem. Soc. 115 (1993) 609.
[4] Y.Saygil *et al.* J. Am. Chem. Soc. 138 (2016) 15087.

Photo(electro)catalytic and time-resolved spectroscopy characterization of metal oxide semiconductor materials for solar energy conversion

Elena Selli, Maria Vittoria Dozzi, Ivan Grigioni, Annalisa Polo
Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133 Milano, Italy
elena.selli@unimi.it

Solar energy conversion into hydrogen is a valuable approach to capture the energy that is freely available from sunlight and to turn it into a clean fuel. To this aim, photoelectrocatalytic (PEC) water splitting is an established powerful technology requiring the development and optimization of efficient oxide-based semiconductor materials to be employed to fabricate either photoanodes for water oxidation, the kinetic bottleneck of the overall PEC water splitting process, or metal – based photocathodes for proton reduction into hydrogen. Bismuth vanadate has emerged as a leading photocatalyst for the oxygen evolution reaction. Its PEC performance has been improved either i) by doping with hexavalent metal ions such as Mo^{6+}, leading to increased electron conductivity of $BiVO_4$, longer lifetimes of photoproduced holes, evidenced by transient absorption spectroscopy (TAS), and reduced interfacial charge transfer resistance [1,2]; or ii) by coupling it with WO_3 in a heterojunction, with an excitation wavelength-dependent efficiency in photoproduced charge separation, as revealed by TAS [3,4]. This technique in operando conditions, together with spectroelectrochemical measurements, also provided direct evidence of an electron spillover from $BiVO_4$ intraband gap states to WO_3 when the $WO_3/BiVO_4$ heterojunction is formed [5]. $CuWO_4$ can also be used as photoanode material, provided its internal charge recombination issues are overcome, as ascertained by a PEC investigation coupled with ultrafast TAS analysis [6]. A 50% Mo^{6+} for W^{6+} substitution results in $CuW_{0.5}Mo_{0,5}O_4$ electrodes with a greatly enhanced visible light-induced photoactivity compared to pure $CuWO_4$, with an optimal compromise between light absorption and photogenerated charge carriers separation [7]. On the other hand, efficient materials for hydrogen production are obtained by doping titanium dioxide with fluorine and nitrogen (N,F-doping), followed by noble metal (NM) nanoparticles (NPs) deposition. In this case, time-resolved photoluminescence (TR-PL) spectroscopy provided a clear correlation between the long – lasting PL decay component and the photocatalytic performance of the materials [8], demonstrating that long-living surface defect trap states improve the separation efficiency of photogenerated electron-hole couples. TR-PL spectroscopy also clarified that Au, rather than Pt NPs, strongly interact with the charge carriers trapped at surface defect sites and that the synergistic effects on photocatalytic hydrogen production attained with Au NPs – modified N,F-doped TiO_2 results from an efficient electron transfer path from luminescent defective trap states to Au NPs, where proton reduction occurs [9].



[1] A. Polo et al. Appl. Surf. Sci. 556 (2021) 149759
[2] A. Polo et al. Solar RRL (2022) 2200349
[3] I. Grigioni et al. ACS Energy Lett. 2 (2017) 1362
[4] I. Grigioni et al. J. Am. Chem. Soc. 140 (2018) 14042
[5] I. Grigioni et al. ACS Energy Lett. 4 (2019) 2213
[6] I. Grigioni et al. J. Phys. Chem. C 125 (2021) 5692
[7] A. Polo et al. ACS Appl. Energy Mater. 3 (2020) 6956
[8] M.V. Dozzi et al. J. Phys. Chem. C 117 (2013) 25586
[9] M.V. Dozzi et al. J. Phys. Chem. C 122 (2018) 14326

Abstract ID. T5K03

ORALS

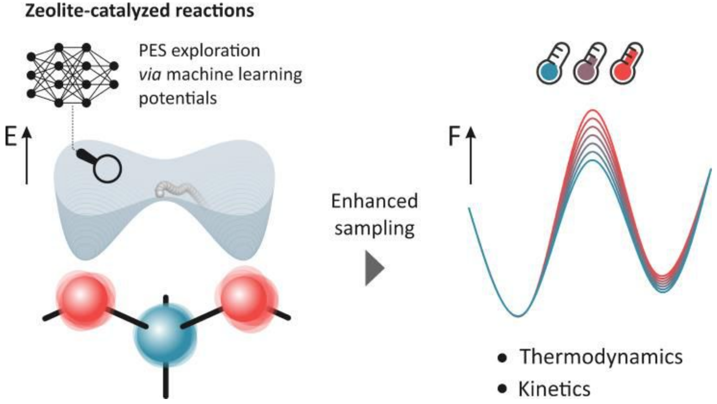
T5. Physical Chemistry approach to catalysis

Machine Learning Potentials for Accurate Simulations of Zeolite-Catalyzed Reactions

Massimo Bocus[1], Sander Vandenhaute[1], Veronique Van Speybroeck[1]
[1]*Center for Molecular Modeling, Ghent University, Technologiepark 46, 9052 Zwijnaarde (Belgium)*
massimo.bocus@ugent.be

Brønsted-acidic zeolites are microporous crystalline aluminosilicates widely used as catalysts in the chemical industry. Each aluminium substitution in the framework is charge-balanced by the addition of a proton, the Brønsted Acid Site (BAS). The BAS is the standard active site on which most zeolite-catalysed chemical conversions take place. An accurate theoretical investigation of reactive events in zeolites is far from trivial. Enhanced sampling techniques based on molecular dynamics are ideally suited to appropriately include temperature effects, the presence of co-adsorbed species and the confinement effect of the micropores.[1] Unfortunately, these techniques are also extremely expensive, requiring the system Potential Energy Surface (PES) to be evaluated hundreds of thousands of times at an *ab initio* level of theory. This means that – first – it is very challenging to obtain well-converged results and – second – it is fundamentally impossible to go beyond standard Density Functional Theory (DFT) methods, which are known to suffer accuracy issues for many relevant zeolite-catalysed reactions.[2]

Within this contribution, we showcase how Machine Learning Potentials (MLPs) can be used to remarkably speed up and extend dynamic simulations of zeolite-catalysed reactions. MLPs are numerical models based on deep neural network architectures. They take as input the atomic coordinates of the system and return the total energy and forces. The outstandingly large number of optimizable parameters in a typical MLP means that the system PES can be learned with high accuracy based on a limited set of training structures, evaluated at the desired level of theory. We show how MLPs can describe with excellent accuracy the DFT PES of the proton hopping reaction in zeolites and can be used to perform enhanced sampling simulations with full thermodynamic transferability.[3] The reaction consists in a simple hydrogen hop between two oxygens in the first coordination sphere of the aluminium defect. Additionally, we exploit an active learning procedure developed within our group[4] to massively reduce the required amount of training data, allowing to perform molecular dynamics beyond DFT accuracy. Alkene conversion is chosen as case study, given the known dependence of the reaction intermediates stability on the chosen level of theory.[2]



[1] L. Grajciar et al. Chem. Soc. Rev. 47 (2018) 8307-8348.
[2] T. J. Goncalves et al. ChemCatChem 11 (2019) 4368-4376.
[3] M. Bocus et al. Nat. Comm. 14 (2023) 1008.
[4] S. Vandenhaute et al. Npj Comput. Mater. 9 (2023) 19.

ATOMICALLY PRECISE METAL NANOCLUSTERS: INSIGHTS INTO THEIR PHOTOLUMINESCENCE PROPERTIES AND CATALYTIC ACTIVITIES

Sara BONACCHI[1], Sabrina ANTONELLO[1], Tiziano DAINESE[1], Christine M. AIKENS,[2] Flavio MARAN[1,3]

[1]Department of Chemical Sciences, University of Padova, 35131 Padova, Italy; [2]Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, United States. [3]Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269, United States.

sara.bonacchi@unipd.it

Monolayer-protected metal nanoclusters (NCs), with defined mass, size, and shape are emerging as ideal candidates for various applications in bioimaging and catalysis.[1] The molecule-like behavior of these NCs can now be controlled with atomic precision by exploiting synthetic strategies such as, metal doping and ligand exchange reactions, thus paving the way for the design of novel nanoclusters with tunable properties and functionalities (Fig. 1).[2] Despite the electronic and structural properties of most of the NCs are well understood, the origin of their peculiar near-infrared photoluminescence (NIR) remains an open question.[3]

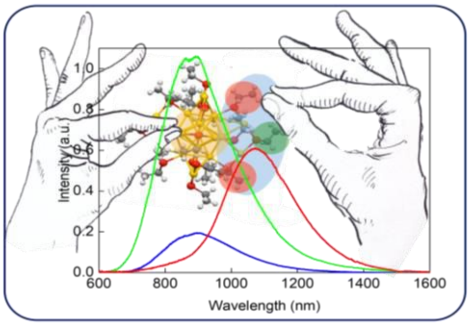


Figure SEQ Figure * ARABIC 1 Single-crystal XRD of $Au_{25}(SR)_{18}$ nanocluster.$Au_{25}(SR)_{18}$ NCs photoluminescence spectra as function of its

Here we describe *in situ* photoluminescence spectroelectrochemical analysis and electron and nuclear dynamic studies of a series of gold and metal-doped NCs [$Au_{24}M(SPh)_{18}$] (M: Cd, Pt, Hg) to gain insight into the origin of their optical properties[4] as well as, into their sophisticated reactivity as singlet-oxygen photosensitizer.[5]

[1] Y. Li, M. Zhou, R. Jin, Adv. Materials, 2022, 33, 2006591
[2] S. Bonacchi, S. Antonello, T. Dainese, F. Maran. Chemistry – Eur. J. 2021, 27, 30-38.
[3] K. L. Dimuthu M. Weerawardene, C. M. Aikens, J. Am. Chem. Soc., 2016, 138, 11202 -11210
[4] S. Bonacchi, S. Antonello, T. Dainese, C.M. Aikens, F. Maran. Manuscprit in preparation.
[5] Agrachev, M.; Fei, W.; Antonello, S.; Bonacchi, S.; Dainese, T.; Zoleo, A.; Ruzzi, M.; Maran, F. Chem. Sci. 2020, 11, 3427–3440.

A multi-technique study of acido-basicity of apatitic surfaces and their evolution with temperature

Sebastiano Campisi[1], Simone Sprio[2], Aline Auroux[3], Antonella Gervasini[1]
[1] Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133 Milano, Italy
[2] Institute of Science and Technology for Ceramics (ISTEC), CNR, via Granarolo 64, 48018 Faenza, Italy
[3] Université Claude Bernard Lyon1, CNRS, IRCELYON, 2 avenue Albert Einstein, F- 69626, Villeurbanne Cedex, France
sebastiano.campisi@unimi.it

The surface properties of hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) mediate the interactions with the surrounding and determine its functionality in several applications, from biomedicine to wastewater-treatment, from drug-delivery to catalysis [1]. Among the various strategies used to control the surface features of HAP, ion incorporation is the most appropriate. Indeed, HAP can undergo partial or total substitution of one of its three constitutive ions (Ca^{2+}, PO_4^{3-}, and OH^-) by several foreign ions (monoatomic or polyatomic groups) [2]. Herein, HAP and carbonate HAP (CHAP) with calcium ions partially substituted by Mg^{2+} and Sr^{2+} ions (MgSrHAP and MgSrCHAP) were prepared by wet precipitation and then calcined at different temperatures (300, 400, 500, 600°C). The influence of carbonation and type of ionic substitution on the surface properties was investigated as a function of thermal treatment. Emphasis was put on acidity/basicity of samples using a multi-technical approach that combines X-ray photoelectron spectroscopy, calorimetric-volumetric measurements of NH_3 and SO_2 adsorption, titrations with phenylethylamine and benzoic acid in cyclohexane, infrared spectroscopy, thermogravimetric analysis and N_2 adsorption-desorption isotherms. Both MgSrHAP and MgSrCHAP presented the typical amphoteric character of apatitic materials (typical acid/basic site ratio, A/B, ~1.2), with a slight predominance of basic sites (A/B ~0.77). Microcalorimetric measurements confirmed this amphoteric nature imparted by acidic and basic sites of intermediate strength with a plateau of nearly constant differential heat of adsorption at 50 - 65 kJ mol^{-1}. In the MgSrHAP sample, a remarkable dependence of the strength and heterogeneity of both acidic and basic sites on the temperature of thermal treatment was observed. In contrast, MgSrCHAP possessed highly heat-stable basic sites and suffered just from a slight decrease in the amount of weak acidic sites, probably due to the occurrence of decarbonation above 300°C (Fig. 1).

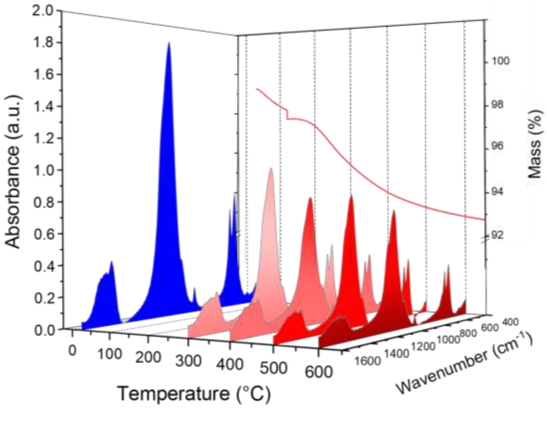


Figure 1. FT-IR spectra of MgSrCHAP and TGA profile as a function of temperature.

[1] H. Yook et al. Adv. Mater. (2023) 2204938
[2] M. Ibrahim, et al. Journal of Hazardous Materials 383 (2020) 121139

Sampling the real-time atomic dynamics of metal nanoparticles via combination of experiments, simulations and machine learning

Matteo Cioni[1], Massimo Delle Piane[1], Giovanni M. Pavan[1,2]
[1]*Department of Applied Science and Technology, Politecnico di Torino,*
Corso Duca degli Abruzzi 24, I-10129 Torino, Italy
[2]*Department of Innovative Technologies, University of Applied*
Sciences and Arts of Southern Switzerland, Polo Universitario Lugano,
Campus Est, Via la Santa 1, CH-6962 Lugano-Viganello,
Switzerland
matteo.cioni@polito.it

Recent advancements in the characterization of metallic nanoparticles (NPs) have opened new possibilities for understanding their physical and chemical properties. A new technique based on local minima search algorithms has been developed to reconstruct the 3D structure of metallic NPs, using atomic resolution annular dark-field scanning transmission electron microscopy (ADF STEM) images[1]. However, the identity of the atoms is unknown, making it difficult to reconstruct their dynamics.

To address this limitation, atomistic simulations have been employed to capture and track individual atomic movements over time, which makes them particularly useful for understanding the internal dynamics of complex molecular systems [2]. Recent advancements in machine learning techniques, such as unsupervised clustering and statistical analysis of smooth overlap of atomic positions (SOAP) data[3], have also been applied to analyze molecular dynamics trajectories of complex systems, including Au NPs[4]. By integrating both methods, it is possible to obtain a complete characterization of these systems in terms of actual equilibrium structures and reconstruction of internal dynamics.

Starting from the experimental samples, physically relevant 3D configurations can be used as initial points from which molecular dynamics simulations can be run to obtain a sampling of the atomic dynamics within the NPs. In particular, we propose to apply our approach to gain insights into the structural and dynamic complexity of the NPs obtained through ADF STEM, each one separated by 0.6 s, as reported in ref 1. Each of these structures is characterized by a low temporal resolution, making it inaccessible to understand the internal dynamics between them. However, our approach is specifically designed to bridge this gap and enable the reconstruction of the system's internal dynamics between each experimental structure.

Then SOAP vectors have been used to categorize and distinguish atomic environments that appear during the molecular dynamics simulations of these nanoparticles, enabling the identification of key structural and dynamic features that govern their behaviour. Overall, this integrated approach combining experimental techniques and computational simulations provides a powerful tool for understanding the complex dynamic behaviour of metallic NPs and for designing new catalytic materials, with potential applications in various fields.

[1] Arslan Irmak, Ece, et al. Small Methods 5.12 (2021): 2101150.
[2] Cioni, Matteo, et al. The Journal of Chemical Physics 158.12 (2023): 124701.
[3] Bartók, Albert P. Physical Review B 87.18 (2013): 184115.
[4] Rapetti, Daniele, et al. chemrxiv.org (2022).

Capturing probabilities and complexity in reactive systems: from host-guest systems to heterogenous catalysis on metals

Massimo Delle Piane[1], Luca Pesce[2], Matteo Cioni[1], Giovanni M. Pavan[1,2]
[1] Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
[2]Department of Innovative Technologies, University of Applied Sciences and Arts of Southern Switzerland, Polo Universitario Lugano, Campus Est, Via la Santa 1, 6962 Lugano-Viganello, Switzerland
massimo.dellepiane@polito.it

Nature masterfully leverages spatial confinement to achieve unprecedented efficiency in controlling chemical reactions, such as in the case of enzymes. Inspired by this principle, supramolecular metal-organic cages, which encapsulate guest molecules and govern their reactions under confinement, are gaining traction. However, the dynamic complexity of these host-guest systems, wherein reactants and products continuously shuttle in and out, often obscures the key factors driving reactivity.

We have developed a comprehensive computational framework to decipher structure-dynamics-property relationships in various reactive host-guest systems. Two applications are highlighted. Firstly, we probed the isomerization of azobenzene guests within a Pd(II)-based coordination cage host in water through molecular models.[1] Secondly, we investigated a coordination cage capable of encapsulating amide guests and boosting their hydrolysis by favouring their mechanical twisting towards reactive molecular configurations under confinement. Employing an innovative multiscale simulation approach, we characterized the dynamic equilibrium of the amide guests within the cage and their hydrolysis reaction constants. The collected kinetic and thermodynamic data were integrated, offering a statistical estimation of reaction acceleration in the host-guest system, aligning well with experimental trends.[2]

Intriguingly, the probability-based principles used for these host-guest systems can be seamlessly translated to heterogeneous catalysis on metal surfaces. Here, the likelihood of a reaction occurring can be correlated with the lifespan of reactive atomic environments on metal surfaces, as determined using sophisticated machine learning data analysis methods.[3-4] Thus, this research bridges the gap between supramolecular host-guest systems and heterogeneous catalysis, enhancing our understanding of reactivity in complex, dynamic systems.

[1] L. Pesce, C. Perego, A. Grommet, R. Klajn, G. M. Pavan J. Am. Chem. Soc. 142 (2020) 9792–9802
[2] M. Delle Piane, L. Pesce, M. Cioni, G. M. Pavan Chem. Sci. 13 (2022) 11232-11245
[3] M. Cioni, D. Polino, D. Rapetti, L. Pesce, M. Delle Piane and G. M. Pavan J. Chem Phys. 158 (2023) 124701
[4] D. Rapetti, M. Delle Piane, M. Cioni, D. Polino, R. Ferrando and G. M. Pavan ChemRxiv (2022), DOI:10.26434/chemrxiv-2022-7wfm9

In-situ IR spectroscopy studies on Layered Double Hydroxides as possible electrocatalysts for CO_2 reduction reaction to CO

Melodj Dosa[1], Margherita Cavallo[1], Ryosuke Nakazato[2], Natale Gabriele Porcaro[1], Matteo Signorile[1], Silvia Bordiga[1], Nataly Carolina Rosero-Navaro[2], Kiyoharu Tadanaga[2], Valentina Crocellà[1], Francesca Bonino[1]
[1]Department of Chemistry, NIS and INSTM Reference Centers, Università di Torino, Via Quarello 15/A, 10135 Torino, Italy
[2]Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Hokkaido, Japan
Presenter's e-mail address: melodj.dosa@unito.it

Among the CO_2 electrochemical reduction products, CO is particularly of interest since it is used as a base chemical for methanol and liquid hydrocarbon production. For electrocatalytic application, the Layered Double Hydroxides (LDHs) can be considered a valid alternative to precious metal electrode catalysts thanks to their properties [1,2]. A previous work [3] investigated different LDHs composition, namely Zn-Al, Ni-Fe, and Ni-Al. The Zn-Al LDH exhibited a different carbonates profile evolution compared to Ni-Fe and Ni-Al ones [3]. In this work, the Zn-Al LDH was studied at different chemical compositions, namely 1:2, 1:1, and 2:1. The in-situ ATR-IR spectroscopical characterization was performed in order to mime the electrocatalytic conditions without electric potential. A deposition of a thin layer of LDH was done on the ATR crystal and then it was flowed with H_2O in which dry N_2 gas was bubbled (30 min). After that, the inlet gas was switched to CO_2 (further 30 min). Figure 1 reports the results of the in-situ ATR-IR spectroscopic study. It was evidenced a different profile for each sample, which can be ascribed, thanks to a careful deconvolution work, to different amounts and species of carbonates. Moreover, in order to better discriminate monodentate, bridged or chelated carbonates, the in-situ ATR-IR analyses were performed in presence of cyclohexane instead of water, whose large and intense band at about 1640 cm^{-1} covers the carbonates formed in this region.

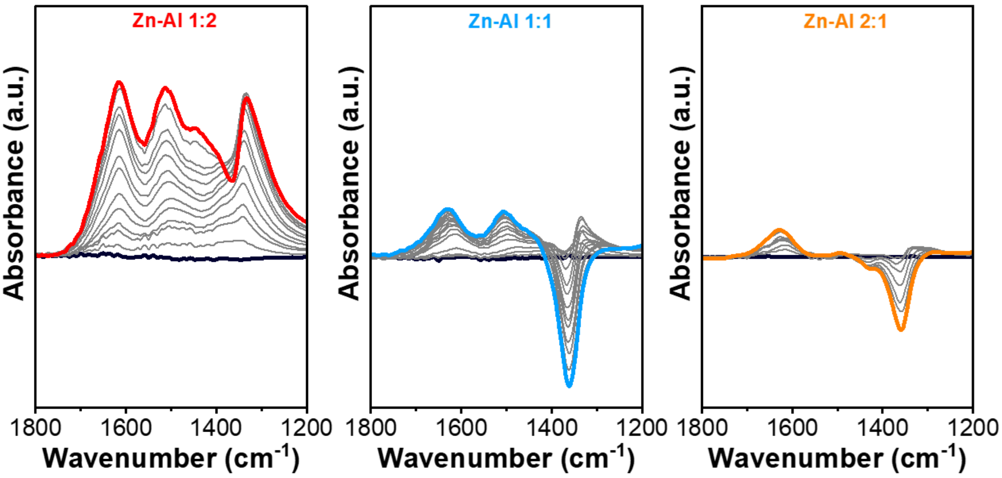


Fig. 1 ATR-IR spectra of Zn-Al LDHs, in water. The initial state (black line), intermediate (gray lines) and maximum carbonate evolution (coloured curves) are reported. The spectra are normalized to the structural carbonates.

This work is part of the Horizon2020 European Founding project "4AirCRAFT" Air Carbon Recycling for Aviation Fuel Technology (No. 101022633).

[1] Y. Furukawa et al. Solid State Ion. 192 (2011) 185
[2] X. Duan et al. Adv. Mater. 29 (2017) 1701784
[3] R. Nakazato et al. RSC Sustain. (2023), submitted

Influence of the architecture of the gas diffusion layer on the performances of Cu-based electrodes for the CO_2 electroreduction in flow cells

Marco Etzi[1], Julien Dangbegnon[1], Angelica Chiodoni[1], Fabrizio Pirri[1,2]

[1] *Center for Sustainable Future Technologies, Istituto Italiano di Tecnologia, Torino, Italy*
[2] *Department of Applied Science and Technology, Politecnico di Torino, Torino, Italy*

marco.etzi@iit.it

The electrocatalytic CO_2 reduction reaction is a promising technology to convert CO_2 into fuels and building blocks for chemicals using renewable energy. Cu is the only known metal catalyst converting CO_2 into a wide range of hydrocarbons and alcohols (mainly methane, ethylene, and ethanol). Flow cells employing gas diffusion electrodes (GDEs) instead of simple H-cells are used to increase current densities and thus the production rates. In a GDE, CO_2 diffuses from the back of the electrode through a porous gas diffusion layer and reaches the active sites located in the catalyst layer. The gas diffusion layer is thus an important element that only recently has attracted attention for the CO_2RR [1,2], while the role of its structure has been deeply studied for fuel cells.

With this regard, our work aims to establish how the architecture and structure of the gas diffusion electrodes affect the Faradaic Efficiencies (FEs) in a flow-cell CO_2 electrolyzer. Commercial Cu nanoparticles were used as electrocatalyst and a wide range of market-available carbon fiber papers were screened to understand which factors influence the selectivity. We show that the structure, composition, and type of cracks of GDE greatly influence the FE of CO, H_2, and ethylene. For instance, larger and more abundant cracks are detrimental to ethylene production. Filling the cracks with higher carbon black to PTFE ratio changes the selectivity by increasing the CO to ethylene ratio. Using a crack-free GDE is advantageous for getting high ethylene FEs. This work highlights the importance of choosing the proper substrate depending on the target product.

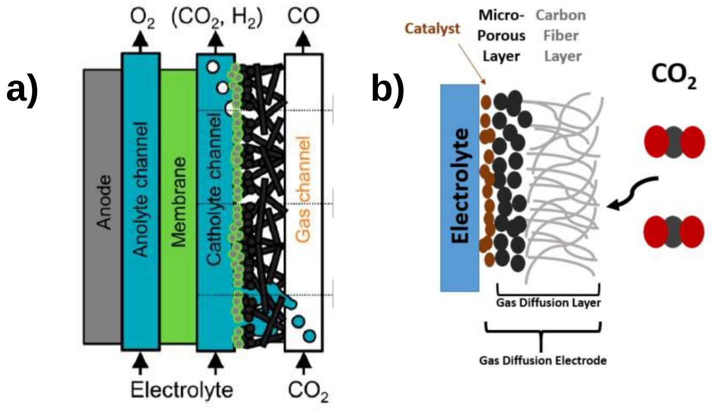


Figure 1. a) Flow cell CO_2 electrolyzer (ref. 3); b) scheme of gas-diffusion electrode.

[1] Y. Kong et al. Small methods 6 (2022) 2200369.
[2] A.A. Samu et al. Communications Chemistry (2023), 6:41.
[3] L. Baumgarten et al. ACS Appl. Energy Mater. 5 (2022), 15125−15135.

Piezo-photocatalytic application of $BiFeO_3$-based systems for pollutants degradation in water

Nicolò Ghibaudo[1], Pierfrancesco Maltoni[2], Tapati Sarkar[2], Maurizio Ferretti[1], Stefano Alberti[1] and Davide Peddis[1]
[1]*Chemistry and Industrial Chemistry Department, Via Dodecaneso 31, 16146, Genova (Ge), Italy*
[2]*Department of Engineering Sciences, Uppsala University, Box 534, SE-75121 Uppsala, Sweden*
nicolo.ghibaudo@edu.unige.it

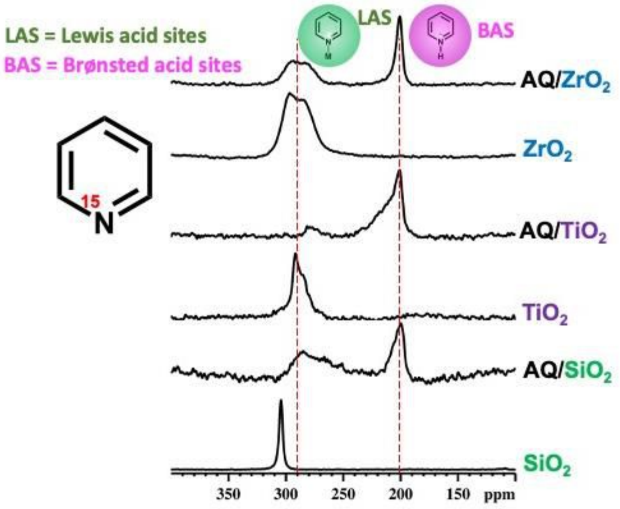
BFO represents a multiferroic system, owing to the complex perovskite structure made of specific metal oxides: the ferro-electric behavior is due to the location of Bi in the A-sublattice, while the magnetic order is induced by the 3d cation in the B-sublattice. $BiFeO_3$ is ferroelectric with a large spontaneous polarization along the [111] direction. These features make $BiFeO_3$ a potential piezo-photocatalytic material [1]. The pure $BiFeO_3$ system was prepared by a simple one-pot sol-gel synthesis method with glycine as chelating agent, followed by an annealing step (first, at 300 °C for 30 min, then at 500 °C for 1h) [2]. The particles are agglomerated, with an average crystallite size of 30 nm, as obtained by the analysis of XRPD pattern. In order to test the potential piezo-photocatalytic activity of this material, photocatalytic experiments were performed for the degradation of methylene blue, used as a model pollutant, in different conditions. A Xenon solar lamp (300 W) was used as the irradiation source while the mechanical vibration to highlight the piezoelectric features of the material was provided by an ultrasonic bath (35 kHz, 120 W); degradation tests were performed against 10 ppm dye solutions, with a concentration of $BiFeO_3$ equal to 0.5 g/L. The experiments were performed for 2 hours while the temperature was kept around 25 °C. Both photocatalytic and piezo-photocatalytic experiments have been carried out to show the effect of ultrasonic vibration and to specifically address the experimental outcomes of the materials' features.

[1] S. Lan et al. Nano Energy 93 (2022) 106792
[2] T. Sarkar et al. Nanoscale 10 (2018) 22990

Multi-site organic-inorganic porous hybrid catalysts

Enrica Gianotti[1], Ivana Miletto[2], Julio C. Fernandes P. Brito[1], Geo Paul[3], Leonardo Marchese[3]
[1]Department for Sustainable Development and Ecological Transition, Università del Piemonte Orientale, P.zza Sant'Eusebio 5, 13100, Vercelli, Italy.
[2]Department of Pharmaceutical Sciences, Università del Piemonte Orientale, Largo Donegani 2, I-28100 Novara, Italy.
[3]Department of Science and Technological Innovation, Università del Piemonte Orientale, V. T. Michel 11, 15100 Alessandria, Italy.
enrica.gianotti@uniupo.it

Organic-inorganic porous hybrid materials, formed by the combination of inorganic materials and organic compounds, are attractive for the purpose of creating high-performance or highly functionalized heterogeneous catalysts. Since they combine the advantages of inorganic solids (high mechanical, thermal, and structural stability) and organic molecules (flexibility and functionality), they are suitable for a wide range of applications, including catalysis, adsorption, separations, non-linear optics, microelectronics or sensing. Hybrid porous catalysts in which active sites with different nature coexist within the same architectures allow to perform multi-step reactions, optimizing the overall catalytic process [1]. The attractiveness of hybrid catalytic materials comes from the observation of the success of nature, which has developed catalysts, enzymes, to achieve more selective and specific chemical reactions in living organisms, where selectivity is a key factor for the survival of the species. Hybrid materials can be classified according to the interactions between organic and inorganic building blocks. In Class I hybrids, weak interactions between two phases, such as van der Waals, hydrogen bonding or weak electrostatic interactions are present. Nevertheless, the need of more robust and stable functional solids through the covalent interaction among organic and inorganic units allowed the development of novel synthesis approaches to obtain Class II hybrid materials, that are suitable in the field of heterogeneous catalysis [2,3]. In this contribution, several examples of multi-site porous hybrid catalysts will be presented, highlighting the role of the inorganic supports and the use of multi-technique approaches for their physico-chemical characterization together with their application in tandem reaction processes. In particular, spectroscopic techniques (FTIR and ssNMR) augmented by the use of molecular probes allowed assessing the strength, location and accessibility of catalytic sites, thus highlighting correlations between the hybrid catalysts architecture and the catalytic properties.



^{15}N MAS NMR of ^{15}N pyridine adsorbed on different hybrids based on Aquivion polymer (AQ) supported onto different oxides, and on the pure supports.

[1] S. Chongdar, S. Bhattacharjee, P. Bhanja, A. Bhaumik, Chem. Commun. 58 (2022) 3429.
[2] I. Miletto, C. Ivaldi , E. Gianotti, G. Paul, F. Travagin, G.B. Giovenzana, A. Fraccarollo, D. Marchi, L. Marchese, M. Cossi, J Phys. Chem. C 125 (2021) 21199.
[3] M.C. Hernández-Soto, A. Erigoni, C. Segarra, F.Rey, U. Díaz, E. Gianotti, I. Miletto, M. Pera-Titus, Appl. Catal. B 643 (2022) 118710.

Monitoring CO-induced surface phenomena in supported metal catalysts by IR spectroscopy

Paolo Lazzarini [1], A. Ricchebuono[1], E. Vottero[1], A. Piovano[2], R. Pellegrini[3] and E. Groppo[1]

[1]*Department of Chemistry, INSTM & NIS Centre, University of Torino, via Quarello 15, Torino, I-10135, Italy*
[2]*Institut Laue-Langevin (ILL), 71 avenue des Martyrs, Grenoble, 38042, France*
[3]*Chimet SpA-Catalyst Division, Via di Pescaiola 74, Viciomaggio Arezzo, I-52041, Italy*
Presenter's e-mail address: *paolo.lazzarini@unito.it*

Modifications in either surface structure or oxidation state of metal nanoparticles (NPs) induced by (reactive) adsorbates are often-recurring phenomena in catalysis with an influence over catalytic performances [1]. Among the adsorbates, CO is one of the most used probe molecules for characterizing metal NPs, and it is also a reactant in many reactions of industrial and/or environmental interest. Here we focus on three highly dispersed 5 wt.% Pt/Al_2O_3, Pd/Al_2O_3 and Ru/Al_2O_3 industrial catalysts and their interaction with CO. We pointed out coverage-dependent CO-induced modifications by means of *in-situ* IR spectroscopy of adsorbed CO on M/Al_2O_3.,This allowed rationalizing the differences in reactivity of the three metals. IR spectra collected dosing small incremental CO pulses allow to differentiate NPs adsorption sites and to trace restructuring phenomena. For Pt/Al_2O_3 (Fig. 1A) a standard coverage-dependent behavior is observed, with no spectroscopic evidence of CO-induced restructuring. However, above a certain coverage, disproportionation of CO is observed. Conversely, for Pd/Al_2O_3 (Fig. 1B) at high CO coverage the band ascribed to bridged carbonyls on the Pd(100) facets decreases in favor of that due to linear carbonyls, suggesting a CO-induced shrinking of the Pd(100) facet in favour of more corrugated ones. Finally, for Ru/Al_2O_3 CO adsorption leads to the appearance of novel Ru^{x+} adsorption sites above a coverage threshold, due to the CO-induced oxidative disruption of Ru NPs [2]. The observed reactivity of the three metals towards CO (Pt<Pd<Ru) can be rationalized based on their "nobility" degree. IR spectroscopy, coupled with other characterization techniques, allows us to evaluate quantitatively the impact of CO-induced modifications.

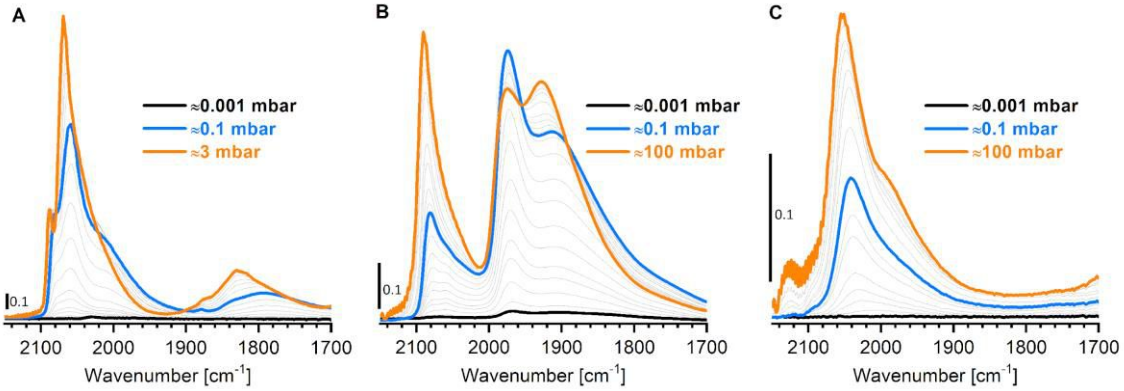


Figure 1 *In-situ FT-IR spectra collected dosing incremental CO pulses on A) 5 wt.% Pt/Al_2O_3, B) 5 wt.% Pd/Al_2O_3 and C) 5 wt.% Ru/Al_2O_3.*

[1] Sápi et al., *Catalysis Letters* **151** (2021): 2153-2175.
[2] Chen et al., *Journal of Catalysis* **373** (2019) 103–115.

Immobilization of enzymes on magnetic nanoparticles for polymer synthesis

Francesco Papatola[1]*, Sawssen Slimani[1,2], Davide Peddis[1,2], Alessandro Pellis[1]
[1]*Università di Genova, Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31, 16146, Genova, Italy.*
[2]*CNR, Istituto di Struttrua della Materia, nM2-Lab, Monterotondo Scalo (Roma), 00015, Italy.*
*francesco.papatola@edu.unige.it

To satisfy the increasing request for environmentally friendly polymers, in line with the "European green deal"[1], the ability of enzymes to transform natural and non-natural compounds into polymers is considered as an environmentally friendly alternative to the traditional chemical synthetic pathways[2]. Improving enzyme's activity and stability as well as preserving selectivity is a must and can be achieved by immobilizing the biocatalyst on the surface of metal oxide nanoparticles[3]. Recently the possibility to assemble nanoparticles in ordered magnetic porous nanostructures open interesting new perspectives in several field (e.g., to deliver and to harvest specific biomolecules; bio-sensing, magnetic hyperthermia)[4], and they could result particularly important also for synthetic applications. The aim of this work is to design a smart platform consisting of spinel iron oxides ($MeFe_2O_4$; Me: Fe^{2+} and Co^{2+}) nanoparticles arranged in spherical structurally iso-oriented nanostructures (SSN) with optimized morpho structural (i.e., particles size, shape and crystallinity), textural (i.e., high surface area) and magnetic properties. Transmission electron microscopy (TEM) shows that the primary nanocrystalline particles (~7 nm) assemble into SSN with an average size of about 50-60 nm. Magnetization measurements, investigated by Vibrating Sample Magnetometer (VSM), show superparamagnetic behavior at 300 K. *Candida antarctica* lipase B (CaLB) was immobilized on nanoparticles' surface investigating the optimal bioconjugation conditions. At this point, CaLB immobilized on magnetic nanoparticles surface was tested for enzymatic polymerization reaction to synthetize polyesters starting from renewable monomers such as adipic acid and 1,8-octanediol. The percentage of conversion of substrate monomers was studied by Nuclear Magnetic Resonance analysis (NMR), and the specific molecular weight was analysed by gel permeation chromatography (GPC).

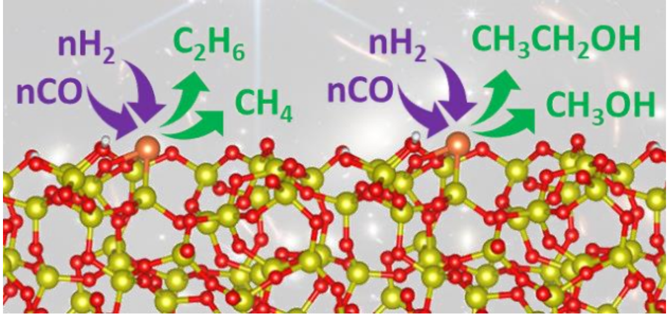
1. Tao, J. & Kazlauskas, R. *Biocatalysis for Green Chemistry and Chemical Process Development*. *Biocatalysis for Green Chemistry and Chemical Process Development* (2011). doi:10.1002/9781118028308.
2. Pellis, A., Cantone, S., Ebert, C. & Gardossi, L. Evolving biocatalysis to meet bioeconomy challenges and opportunities. *New Biotechnology* (2018) doi:10.1016/j.nbt.2017.07.005.
3. Vaghari, H. *et al.* Application of magnetic nanoparticles in smart enzyme immobilization. *Biotechnology Letters* (2016) doi:10.1007/s10529-015-1977-z.
4. Cannas, C. *et al.* Surfactant-assisted route to fabricate CoFe2O4 individual nanoparticles and spherical assemblies. *J. Colloid Interface Sci.* (2010) doi:10.1016/j.jcis.2009.12.007.

True astrocatalysis, iron catalysed formation of interstellar complex organic molecules.

Gerard Pareras[1] & Albert Rimola[1]
[1]*Departament de Química, Universitat Autònoma de Barcelona, Barcelona, Catalunya, Spain.*
Gerard.pareras@uab.cat

Life on earth, and concretely, how the simplest organic matter not only appeared but also evolved to more complex systems is still one of the unsolved enigmas of the origin of life. The most scientifically accepted scenario assumes that the simplest organic molecules were formed over the interstellar dust during the star formation process to be later incorporated to bigger bodies. During this same process such molecules evolved to more complex ones with prebiotic relevance.[1] Nevertheless, the mechanisms from which this complexation happened are yet under debate. Recent studies shed some light to this matter as they demonstrated the presence of transition metals (TMs) incorporated within the structure of the dust.[2] Matter of fact, the observation of this later-incorporated-to-the-dust TMs opens a new perspective in the branch of the Astrochemistry, the Astrocatalysis. Due to the relatively large abundancies of diatomic molecules such as H_2, CO and N_2, catalytical processes such as Fischer-Tropsch (FT) and Haber-Bosch (HB) are perfect candidates to convert those simple molecules to more complex ones with probiotic potential as acetaldehyde (CH_3CHO) and formamide (NH_2CHO). Moreover, the omnipresence of the dust grains during the different stages of the planetary formation, makes these synthetic routes triggers for the chemical evolution not only in the outer space but also in the first periods of the Earth formation.[3]

Despite the inherent relevance of the catalytical processes, studies trying to rationalize such processes as well as their reaction mechanisms in the context of the astrochemistry are still missing. In this work we report for first time computational studies to unveil the reaction mechanisms for the catalytic formation of methanol, ethanol, and by-products such as methane and formaldehyde from the direct coupling of CO and H_2. Considering also that TMs can be allocated on dust grains as either single atoms (SA) or in low number of atomic aggregations as metal-nanoclusters (NC).



[1] E. Herbst et al. Int. Rev. Phys. Chem. 36 (2017) 287–331.
[2] J. A. Nuth III et al. Meteorites Early Sol. Syst. II. 147 (2006) 147–167.
[3] W. F.Bottke et al. Nature. 485 (2006) 78–81.

The influence of the surface area and the thiophenic groups concentration on the Pt NPs, a synergic effect for the increment of the Catalytic activity vs. the Oxygen Reduction

Mattia Parnigotto[a], *Riccardo Brandiele*[a], *Maria Chiara Dalconi*[b], *Gregorio Dal Sasso*[b], *Gian Andrea Rizzi*[b], *Christian Durante*[a,*]
[a] *Department of Chemical Sciences University of Padova via Marzolo 1, 35131 Padova (Italy)*
[b] *Department of Geoscience University of Padova via Gradenigo 6, 35131 Padova (Italy) via Marzolo 8, 35131 Padova (Italy)*
Mattia.parnigotto@phd.unipd.it

Several strategies are oriented to improve the Pt catalyst performance for Oxygen Reduction Reaction (ORR), to reduce its loading. One way is to trigger an interaction between the Pt metal NPs and the support, which can generally affect the catalytic activity by influencing the NP morphology and dimension, inducing strain on the NP because of lattice mismatch, and changing the electronic structure via charge transfer processes. Sulphur-doped mesoporous carbons (SMCs) have been shown to exert a great metal-support interaction on Pt NPs (*1*). In this contribution, SMCs with different amounts of S (1 $\%_w$ to 14 $\%_w$) were synthesized by pyrolysis (fig 1), following a hard template method that employed mesoporous silica as the template. The degree of graphitization and the surface area were tuned by a successful steam treatment at high temperature for different exposure times. During steam treatment, the sulfur content gradually decreases, while the surface area increases to 1750 $m^2\ g^{-1}$. The Pt NPs were allowed to grow on the carbon supports by thermal treatment of $Pt(acac)_2$ under H_2 flow. Small and wide-angle synchrotron XRD characterization, together with TEM characterization, allowed us to explore the correlation between the steam treatment time and the content of S with the Pt nanoparticle growth and kinetic (fig.2). The catalysts were characterized in 0.1 M $HClO_4$ towards ORR. Mass activity and specific activity showed a correlation with both the sulphur content, the specific surface area and with the Pt specific surface area, thus the best performance was observed at intermediate values of the two parameters (Fig. 1). The results were rationalized based on a metal-support interaction and the mass transport and conduction properties of the synthetized materials.

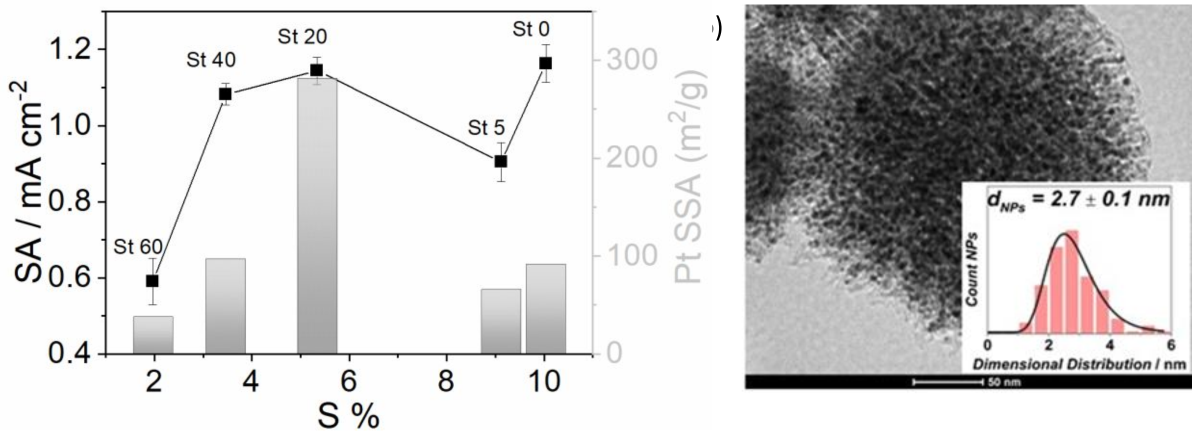


*Figure SEQ Figure * ARABIC 1 Figure SEQ Figure * ARABIC 1: a) Sulphur content, specific activity and total specific surface area of Pt as function of the steam treatment, TEM image and distribution of Pt-SMC steam treated catalyst.*

[1] V. Perazzolo et al. *ACS Publ.* 8, (2017), 1122–1137.

Combination of MnO_2 and persulfate as oxidants for degradation of water pollutants at low temperatures

Stefano Salvestrini[1], Angelo Fenti[2], Lin Qian[3] and Frank-Dieter Kopinke[3]
[1]Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, University of Campania "Luigi Vanvitelli", via Vivaldi 43, 81100, Caserta, Italy.
[2]Department of Engineering, University of Campania "Luigi Vanvitelli", Via Roma 29, 81031 Aversa (CE), Italy.
[3]Department of Environmental Engineering, Helmholtz Centre for Environmental Research – UFZ, Permoserstr. 15, D-04318 Leipzig, Germany.

stefano.salvestrini@unicampania.it

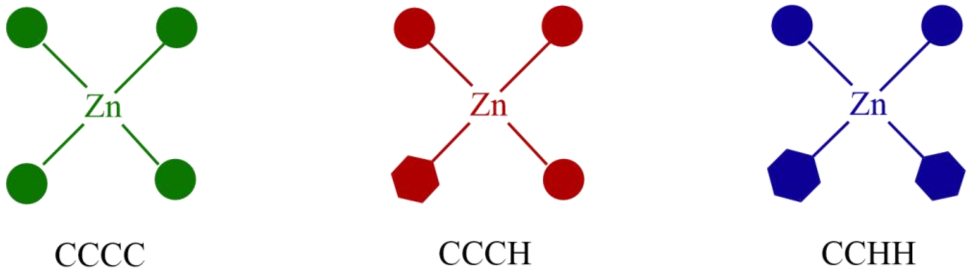
MnO_2 can be used in persulfate-based advanced oxidation processes to activate persulfate and generate reactive sulfate ($SO_4^{-\bullet}$) for the abatement of water organic contaminants. Alternatively, one can focus on MnO_2 as particulate oxidant which, contrary to PS, is active already at low temperatures. This low-temperature activity is particularly attractive for *in situ* groundwater treatment. The roles of PS and MnO_2 as oxidant and catalyst, respectively, may invert: MnO_2 functions as primary oxidant and PS works as re-oxidant of reduced Mn-oxides. This way, the limited oxidation capacity of particulate MnO_2 can be overcome. So far, such reaction systems have not been extensively explored. In the present study, the degradation of 4-hydroxybenzoic acid (HBA) by PS+MnO_2 was studied under various experimental conditions, by varying reaction temperature, reagent concentrations, and water matrix. Both PS and MnO_2 alone have the ability to effect the oxidation of HBA. In the co-presence of PS and MnO_2, a fast removal of HBA from water was achieved even at low temperatures (15 °C), owing to a synergic effect between the two components.

Quenching experiments indicate a heterogeneous step for oxidation of HBA, beyond radical attack in aqueous solution. This was also confirmed by applying the PS+MnO_2 oxidation system onto the highly recalcitrant target compound perfluorooctanoic acid.

Reactivity of zinc fingers in oxidizing environments: insight from molecular models through activation strain analysis

Davide Zeppilli[1], Andrea Madabeni[1], Laura Orian[1]
[1]Dipartimento di Scienze Chimiche, Università degli Studi di Padova, Via Marzolo 1, 35131 Padova, Italia.
davide.zeppilli@phd.unipd.it

Zinc fingers (ZFs) are small, independent and structurally diverse protein domains, characterized by the presence of a Zn^{2+} ion coordinated to four amino acids, mostly cysteine (Cys) and histidine (His) [1]. They are also formed by a hydrophobic core and other residues, *e.g.*, α-helix, responsible of intra- and intermolecular interactions, fundamental for their stability and functionality [2]. In particular, these domains can recognize DNA and RNA by interacting selectively with them, thus possessing an apparently crucial role in the nucleic acid duplication processes [3]. In this work, fundamental aspects of ZFs chemistry are investigated *in silico* to understand their behavior in oxidizing conditions. All the analyses are conducted in the framework of Kohn-Sham Density Functional Theory (DFT) [4], combined with the activation-strain model [5] and molecular orbital (MO) theory.



Three zinc complexes are considered, differing for the Cys/His ratio: CCCC has four Cys coordinated to the central Zn^{2+} ion, CCCH has three Cys and one His, and CCHH has two Cys and two His, respectively. Firstly, the structure and conformation of the most common ZF models were systematically explored. Then, their reactivity with H_2O_2 was investigated, using a benchmarked level of theory. Lastly, based on the very recent hypotheses that selenolates can act as pro-oxidant agents targeting ZFs [7], the reactivity of ZF models with selenolates and thiolates was investigated, identifying a possible mechanism of ZF disruption with potential antiviral and antitumoral applications.

[1] J. Miller et al. EMBO J. 4 (1985) 1609-1614
[2] J.M. Berg Proc. Nat. Acad. Sci. 85 (1988) 99-102
[3] K. Kluska et al. Coord. Chem. Rev. 367 (2018) 18-64
[4] F.M. Bickelhaupt et al. Rev. Comput. Chem. 15 (2000) 1-86
[5] F.M. Bickelhaupt et al. Angew. Chem. Inter. Ed. 56 (2017) 10070-10086
[6] C. Tidei et al. Tetraedron Lett. 53 (2012) 232-234
[7] P.A. Nogara et al. Redox chemistry and biology of thiols, Elsevier (2022) 643-665

POSTERS

T5. Physical Chemistry approach to catalysis

TOF-SIMS investigation of pollutants photodegradation mechanism directly at the surface of photocatalytic materials

Alessandro Auditore, Enrica Maria Malannata, Antonino Licciardello
Dipartimento di Scienze Chimiche, Università degli Studi di Catania, v. A. Doria 6, 95125 Catania (Italy)
alessandro.auditore@unict.it

Nowadays, the presence of contaminants in water is an increasingly large and difficult problem to solve. The efficient removal of these contaminants from aqueous solutions requires advanced oxidation processes (AOP). This can be accomplished by several methods, such as electrocatalysis, photocatalysis, and photo-electrocatalysis, which involve the use of materials that allow rapid removal of pollutants with high degradation rates [1].

The most widely used material in this regard in the photocatalysis approach is TiO_2 [2], in the form of powder or thin films deposited on inert substrates such as silicon wafers or glass.

Complete mineralization of the pollutant is desirable for an efficient process. Monitoring the intermediate products of degradation is crucial to be sure that chemical species more toxic than the initial substance are not formed. This type of investigation involves several techniques such as HPLC analysis and mass spectrometry by taking aliquots of the aqueous matrix under investigation [3].

In this study, we performed the study of photodegradation products directly on the surface of TiO_2-based photocatalytic material and on substrates that did not present photocatalytic properties (silicon wafer or glass). This was made possible by using secondary ion mass spectrometry (TOF-SIMS).

TOF-SIMS allows monitoring of photocatalytic reactions on the photoactive material surface by mass spectrometry of desorbed surface species [4] providing information on the degradation pathway that occurs on the surface of photoactive materials under simulated solar irradiation. This study involved a target molecule that is a common dye, Rhodamine B, and other emerging persistent pollutants. Understanding the degradation pathways that occur at the surface is a promising way to obtain information about the rate determining step of pollutants' abatement and to improve the specific functionalization of the materials under investigation and experimental conditions.

This peculiar application of TOF-SIMS technique makes it possible to evaluate the effect of interaction between the target pollutant system and the photocatalytic material and to verify in situ the formation of environmentally harmless/harmful by-products.

[1] Dengsheng Ma et al. Chemosphere 275 (2021) 130104
[2] A. Ajmal et al. RSC Adv. 4, 37003 (2014).
[3] S. Rasalingam et al. ACS Appl. Mater. Interfaces 7, 4368 (2015).
[4] A. Orendorz et al. Appl. Surf. Sci. 255 (2008) 1011–1014

This work has been partially funded by European Union (NextGeneration EU), through the MUR-PNRR project SAMOTHRACE (ECS00000022)

Application of chemometric approaches to a photocatalytic pilot plant for environmental issues and study of the material recovery

Nicolò Ghibaudo[1], Maurizio Ferretti[1], Mohamed O. Amin[2], Entesar Al-Hetlani[2], Metwally Madkour[3] and Stefano Alberti[1]
[1]*Chemistry and Industrial Chemistry Department, Via Dodecaneso 31, 16146, Genova (Ge), Italy*
[2]*Chemistry Department, Faculty of Science, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait*
[3]*Chemistry Department, Faculty of Science, Arish University, Al-Arish 45511, Egypt*
nicolo.ghibaudo@edu.unige.it

Environmental problems related to the presence of emerging pollutants within the environment are finally receiving the proper attention, due to the dangerous side-effects that arise due to the presence of these biologically active compounds (pharmaceuticals and personal care products, PPCPs) in water bodies. Therefore, it's mandatory to find proper water treatment technologies able to efficiently counteract the spread of these new contaminants, as actual wastewater treatments are not able to deal with these kinds of micro-contaminants [1]. In this context, heterogeneous photocatalysis as an Advanced Oxidation Process represent a promising approach for the abatement of PPCPs in water. In this work, the performance of powdered TiO_2-based materials for the photocatalytic degradation of different dyes has been evaluated in a photocatalytic pilot plant (Figure 1) under solar simulated light, with a treatment volume of 10L. Different materials were tested in the pilot plant, and a chemometric approach (Full Factorial model) was applied to compare the photocatalytic performances of each tested material on a different scale. Finally, the recovery of the photocatalyst was studied following a new recuperation method, by reaching the isoelectric point (pH_{IEP}) of each sample, by means of pH modifications of the solution, for the precipitation of TiO_2 nanoparticles, annulling their surface charge [2].

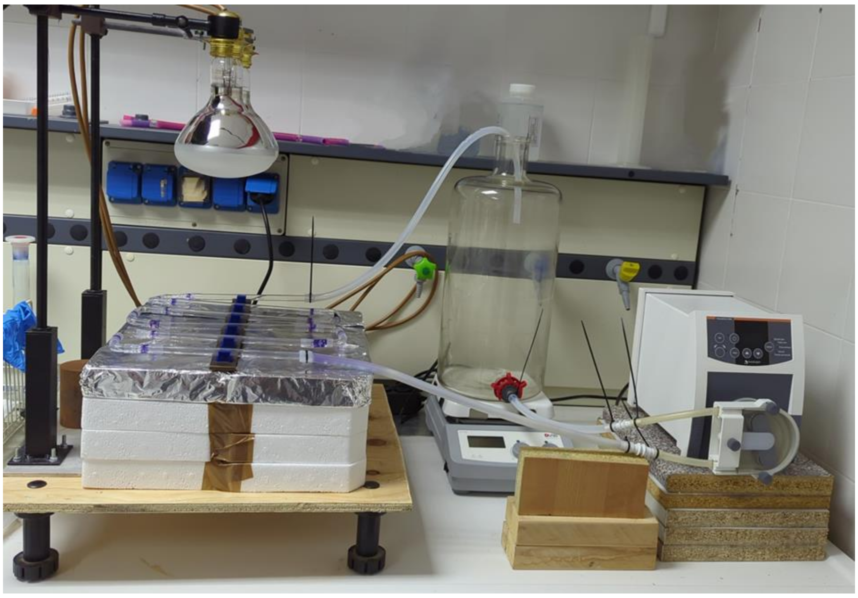


Figure 1. The tested photocatalytic pilot plant with a treatment volume of 10L for abatement of micro-contaminants.

[1] J.J. Rueda-Marquez et al. J. Clean. Prod. 258 (2020) 120694
[2] F. Azeez et al. Sci. Rep. 8 (2018) 7104

Insights on the vital role of stabilized Copper single-atom on a Ce-MOF for the CO oxidation reaction

Andrea Jouve[1], Sergio Rojas-Buzo[1], Edoardo Bracciotti[1], Francesca Bonino[1], Unni Olsbye[2] and Silvia Bordiga[1]

[1]Department of Chemistry and NIS Centre, University of Turin, Via Giuria 7, 10125 Turin, Italy
[2]Department of Chemistry, Centre for Materials and Nanoscience, SMN, University of Oslo, Blindern, 0315 Oslo, Norway
e-mail address: a.jouve@unito.it

The CO oxidation, one of the most extensively reaction studied, is nowadays increasing its importance due to the urgency of pure hydrogen production, cleaning air, or lowering automotive emissions.[1–3] Single-atom catalysts (SACs) have exhibited outstanding performance for plenty different heterogeneous reactions including carbon monoxide oxidation.[4] Metal–organic frameworks (MOFs), can offer an excellent supports to stabilize single atoms due to their unique metal-support interactions, beside to offer an elevated specific surface area (SSA).[5] In addition, MOFs features can be also tailored by controlling the nature of the organic functional ligands and/or metal oxoclusters included in their structure. Among the different SACs explored for CO oxidation, CeO_2-based ones have shown some of the most promising results.[6] For these reasons we have synthesized, by means of a so-called metal node stabilization approach, a copper single-atom catalyst supported in a Ce-MOF (Cu/UiO-67(Ce), Cu loading: 2.27 wt.%).

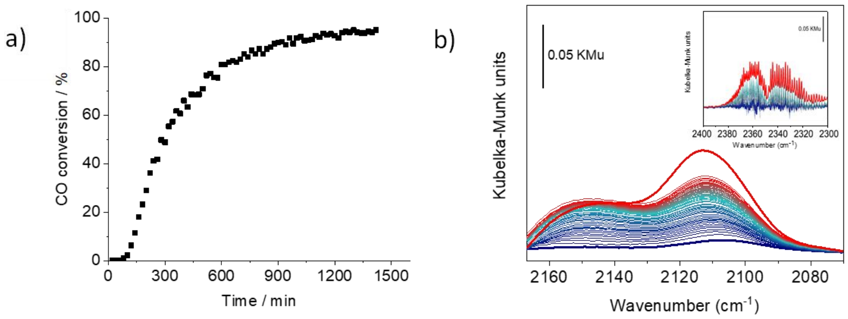


Figure 1a. CO conversion to CO_2 during time on stream; cat.: 80 mg, Cu/UiO-67(Ce); flux: 15 mL/min, 6,7%$_{mol}$ CO e 3,3%$_{mol}$ O_2 (in He); T=200°C. Figure 1b. In-situ DRIFTS spectra collected during CO oxidation and focused on the CO adsorption and CO_2 formation (inset); from blue to red spectra: 0 - 1000 minutes.

The catalyst, after passing an initial activation phase, reaches a remarkable activity (> 90% conv.) on stream at 200 °C (Fig. 1a); this experiment, which lasted about 24h, gives insights on the stability of the system and proofs the reversibility of Cu^{1+}/Cu^{2+} species. On the other hand, time-resolved *in-situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurements provided long term information; the sequence of DRIFTS spectra shows a clear formation and evolution of the band at ≈2115 cm^{-1} assigned to related CO-Cu^{1+} adduct (Fig. 1b). At the same time, the roto-vibrational feature of gaseous CO_2, evident in the range 2250–2000 cm^{-1} (Fig.1b inset), demonstrates the increase on the catalytic activity during Cu^{2+} reduction. In conclusion, we were able to observe a remarkable catalytic activity and follow the intermediates and reaction products formation and evolution, proving the reduction of the Cu species, monitored by means of *in situ* DRIFT spectroscopy.

[1] M. Shelef et al. Catal. Today 62 (2000) 35–50
[2] A. Manasilp et al. 37 (2002) 17–25
[3] S. Dey et al. Appl. Surf. Sci. 441 (2018) 303–316
[4] H. Zhang et al. Catal. Rev. Sci. Eng. 64 (2022) 491–532
[5] A. M. Abdel-Mageed et al. J. Am.Chem. Soc. 141 (2019) 5201–5210
[6] L. Nie et al. Science 358 (2017) 1419–1423

Abstract ID. T5P03

Operando X-ray absorption spectroscopy for tracking catalytic active sites in Pd nanoparticles supported on TiO_2

Elizaveta Kozyr,[1] Francesco Pellegrino,[1] Silvia Bordiga,[1] Elena Groppo,[1] Riccardo Pellegrini,[2] Alina Skorynina,[3] Aram Bugaev,[4] and Lorenzo Mino[1]

[1]Department of Chemistry and NIS Centre, University of Torino, Torino, Italy
[2]Chimet SpA - Catalyst Division, Via di Pescaiola 74, Viciomaggio Arezzo, Italy
[3]CELLS-ALBA Synchrotron Light Source, Cerdanyola del Valles, Barcelona, Spain
[4]SuperXAS beamline, SLS, Paul Scherrer Institute, Villigen, Switzerland
elizaveta.kozyr@unito.it

An attractive green way to generate hydrogen is the photocatalytic water splitting over nanomaterials [1, 2]. In this field, TiO_2 is a well-studied material and researchers tried to engineer the TiO_2 structure, particle size and morphology to improve overall efficiency [3, 4]. Pd is often employed as co-catalyst for its stability and high activity in the catalytic reaction [5]. Despite numerous studies, an open issue in this area is the mechanism of deposition of the metal cocatalyst and changes in its local structure during H_2 evolution. In this contribution we address this problem investigating the photodeposition mechanism of Pd on TiO_2 and the subsequent hydrogen photoproduction in comparison with Pd/TiO_2 samples of industrial interest produced by Chimet S.p.A., following the deposition precipitation method.

The samples were characterized by Transmission Electron Microscopy (TEM) and FT-IR spectroscopy of adsorbed CO to study the structure, morphology, particle size and distribution of the supported palladium nanoparticles (NPs). Then, the metal behavior under reaction conditions was studied by *operando* time-resolved XAS spectroscopy and correlated with online mass spectrometry data. XANES and EXAFS data were acquired at ALBA synchrotron (Barcelona, Spain). The measurements were carried out in a self-made photocatalytic cell in liquid phase, in fluorescence and transmission modes. We monitored the evolution of Pd species from precursor to NPs during photodeposition by XAS, where the components for the synthesis procedure were systematically varied (such as concentration of metals, UV light power and time of irradiation, the concentration of the sacrificial agent). The growth of Pd^0 contribution by XAS was correlated with the growth of the signal of the produced H_2. According to the XAS data, the Pd NPs obtained by photodeposition showed a stronger interaction with the TiO_2 substrate with respect to the Pd NPs obtained by deposition-precipitation. Combining XAS and TEM results, we rationalized the dependence of the nanoparticle size on UV light power and irradiation time and methods of deposition NPs.

The results of this study help in disclosing the synthesis-properties-activity relationships for Pd/TiO_2 systems to obtain design rules to produce more efficient photocatalysts.

[1] J. Hyun Kim et al. Chem. Soc. Rev. 48 (2019), 1908
[2] H. Nishiyama et al., Nature (2021) 598, 304
[3] F. Pellegrino et al., ACS Catal. 9 (2019) 6692
[4] Y. Wang et al., Appl. Catal. B: Environ. 318 (2022) 121783
[5] B. Rusinque et al. Catalysts 11 (2021), 405.

Cu shielding effect on Al against dealumination of CHA during hydrothermal aging

V. Saltão[1,2 *], V. Crocellà[2], S. Bordiga[2], G. Berlier[2]
[1]Umicore AG & Co KG, Automot Catalysis Div, Res & Dev, Hanau, Germany
[2] Department of Chemistry, and NIS Centre, Università di Torino, Via P. Giuria 7 – 10125 Italy
[*]Presenter's e-mail address: vascoantnio.correiasalto@unito.it

Keywords: NH3-SCR, chabazite, Cu, hydrothermal aging, dealumination, IR spectroscopy

The emission of polluting NOx from combustion engines is usually reduced via NO_X selective catalytic reduction by NH_3 (NH_3-SCR). Of all known catalysts for NH_3-SCR, Cu-zeolites, and specifically Cu-CHA, present the best hydrothermal stability and performance in the 180-300 °C range, maintaining it for higher temperatures [1,2]. As increasing fuel efficiency drives down combustion temperatures [2], Cu-CHA relevance as a NH_3-SCR catalyst increases. However, repeated exposure to the high temperatures and water present in engine exhaust systems may dealuminate the catalyst [3], thus deactivating it, since the Cu active sites are stabilized by the negative charge induced on the framework by Al atoms. Therefore, this project aims to study the structure of Al and Cu after dealumination, and how differently dealumination affects zeolites with different Cu and Al contents. Fresh and hydrothermally treated (650 °C for 100 hours) Cu-CHA catalysts with different Si/Al ratio (6.7 and 15) and Cu content (0, 0.8 and 3.2 wt%) were characterized using XRD, in situ IR spectroscopy under N_2 flow at 350 °C and volumetric measurements using Ar at 87 K.

XRD measurements indicate that after aging the crystallinity of the samples is maintained. However, Ar-volumetric measurements show an increase in the surface area (Figure 1) and micropore volume of the samples after aging, resulting from the removal of Al from the framework. This change is more pronounced on the samples without Cu, suggesting that Cu atoms shield Al atoms from dealumination. The collected IR spectra support this claim, showing the Brønsted sites signals decreasing after aging and the intensity of the partial extraframework AlOH slightly increasing, with this effect being more pronounced in the samples without Cu. Further studies are ongoing to investigate the nature of the defective sites and the effect of dealumination on the Cu sites active in NH_3-SCR reaction.

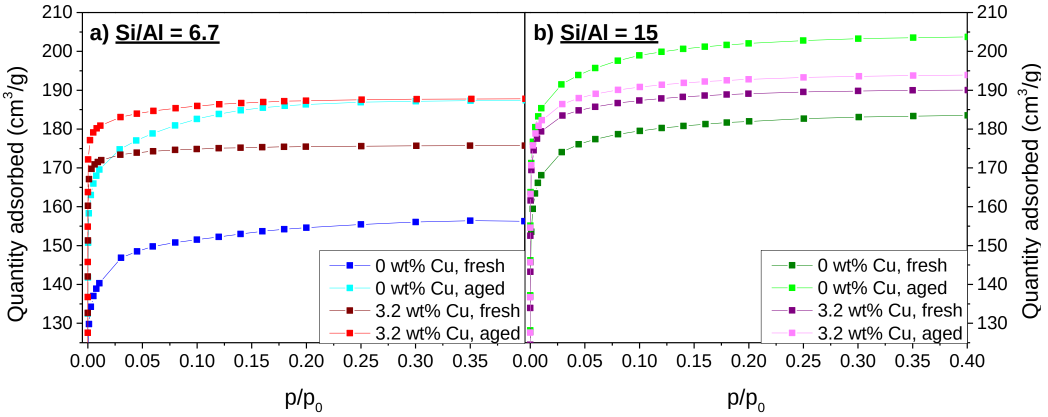


Figure 1 - Isotherms of Ar adsorption on Cu-CHA and protonic CHA. a) Si/Al = 6.7; b) Si/Al = 15

[1] I. Nova and E. Tronconi, Eds., Urea-SCR Technology for deNOx After Treatment of Diesel Exhausts. New York, NY: Springer New York, 2014. doi: 10.1007/978-1-4899-8071-7.

[2] A. M. Beale, F. Gao, I. Lezcano-Gonzalez, C. H. F. Peden, and J. Szanyi, "Recent advances in automotive catalysis for NO x emission control by small-pore microporous materials," Chem Soc Rev, vol. 44, no. 20, pp. 7371–7405, 2015, doi: 10.1039/C5CS00108K.

[3] Y. J. Kim, J. K. Lee, K. M. Min, S. B. Hong, I.-S. Nam, and B. K. Cho, "Hydrothermal stability of CuSSZ13 for reducing NOx by NH3," J Catal, vol. 311, pp. 447–457, 2014, doi: 10.1016/j.jcat.2013.12.012.

KEYNOTES

T6. Reactive processes in gas, liquid and solid phases

Circuit Theory for Chemical Reaction Networks

Francesco Avanzini[1], Nahuel Freitas[2], Massimiliano Esposito[3]
[1] *Department of Chemical Sciences, University of Padova, via Marzolo 1, I-35131 Padova, Italy*
[2] *Departamento de Física, FCEyN, UBA, Pabellón 1, Ciudad Universitaria, 1428 Buenos Aires, Argentina*
[3] *Complex Systems and Statistical Mechanics, Department of Physics and Materials Science, University of Luxembourg, L-1511 Luxembourg City, Luxembourg*
francescoavanzinih@gmail.com

We lay the foundation of a circuit theory for chemical reaction networks [1]. Chemical reactions are grouped into chemical modules solely characterized by their current-concentration characteristic, as electrical devices by their current-voltage (I-V) curve in electronic circuit theory. This, combined with the chemical analog of Kirchhoff's current and voltage laws, provides a powerful tool to predict reaction currents and dissipation across complex chemical networks. The theory can serve to build accurate reduced models of complex networks as well as to design networks performing desired tasks.

[1] F. Avanzini et al. arxiv:2210.08035 accepted in Phys. Rev. X

Hydrophobic hydration and pairwise hydrophobic interaction of Lennard-Jones and Mie particles in different water models

Giuseppe Graziano[1], Karolina Zieba,[2] Cezary Czaplewski,[2] Adam Liwo[2]
[1]Department of Science and Technology, University of Sannio, 82100 Benevento, Italy
[2]Faculty of Chemistry, University of Gdańsk, Wita Stwosza 63, 80-308 Gdańsk, Poland
graziano@unisannio.it

The study provides a deep computational analysis of the thermodynamic and structural features associated with the hydration of xenon, Xe, and its pairwise hydrophobic interaction (i.e., the potential of mean force, PMF), over a large temperature range [1]. Xe is described both as a Lennard-Jones particle, LJ-Xe, and as a Mie particle [2], Mie-Xe (pseudo hard sphere). Three different water models are used: TIP3P-Ew, SPCE and TIP4P-2005. Mie-Xe is more hydrophobic than LJ-Xe due to the lack of the attractive energetic interactions with water molecules; its hydration, around room temperature, is opposed by a large and negative entropy change and a positive enthalpy change. The PMF of Mie-Xe is characterized by a deep minimum at contact distance whose depth increases with temperature, and whose magnitude is significantly larger than that obtained for LJ-Xe. The contact minimum configuration of Mie-Xe is favoured by a large positive entropy change and contrasted by a positive enthalpy change. These results are qualitatively the same regardless of the water model used. There is no clear connection between the values determined for the thermodynamic functions and the structural features of the hydration shells surrounding the single Mie-Xe and the couple of Mie-Xe particles in the contact minimum configuration. This confirms that the structural reorganization of water associated with such processes is characterized by an almost complete enthalpy-entropy compensation [3,4].

[1] K.Zieba, C.Czaplewski, A.Liwo, G.Graziano, Phys.Chem.Chem.Phys. 22 (2020) 4758
[2] J. Jover, A.J. Haslam, A. Galindo, G. Jackson, E.A. Müller, J.Chem.Phys. 137 (2012) 144505
[3] B. Lee, Biophys.Chem. 51 (1994) 271
[4] J.D. Dunitz, Curr.Biol. 2 (1995) 709

ORALS

T6. REACTIVE PROCESSES IN GAS, LIQUID AND SOLID PHASES

The double activation energy to ionic conduction in doped ceria: a journey through impedance and Raman spectroscopy

Cristina Artini[1,2], Sara Massardo[1], Sabrina Presto[3], Massimo Viviani[3], Marcella Pani[1,4]
[1] *DCCI, University of Genova, Via Dodecaneso 31, 16146 Genova Italy*
[2] *CNR-ICMATE, Via De Marini 6, 16149 Genova, Italy*
[3] *CNR-ICMATE, c/o DICCA-UNIGE, Via all'Opera Pia 15, 16145 Genova , Italy*
[4] *SPIN-CNR, Corso Perrone 24, 16152 Genova, Italy*
artini@chimica.unige.it

Ceria doped by trivalent rare earths (RE) ions is widely studied for its high ionic conductivity in the intermediate temperature range, namely between 773 and 973 K, which makes it a promising electrolyte for solid oxides cells (SOCs). In addition to the well known Gd- and Sm-doped systems, especially interesting are co-doped systems, since co-doping by two or more ions is considered as one of the most effective methods to improve ionic transport thanks to the expected lowering of activation energy to ionic conduction and, in the end, the enhancement of ionic conductivity.

In many systems two different values of activation energy to ionic conduction occur within different temperature ranges, with the low/high temperature crossover being located at ∼750 K. This evidence has been observed both in singly [1,2] and in co-doped systems [3,4], and it seems to be an intrinsic property of the material. Roughly in correspondence of the threshold temperature, even the Raman shift and the linewidth of the ceria most intense Raman signal present a slope change which can be hardly explained by applying the most common models. On the contrary, all these features find a comprehensive interpretation in the light of the defect chemistry of these oxides, which points at the presence of different defect aggregates having a well-known crystal structure and hindering ionic conductivity. The evaluation of their stability with increasing temperature based on their configurational entropy, suggests a key for the understanding of the observed transport and spectroscopic features.

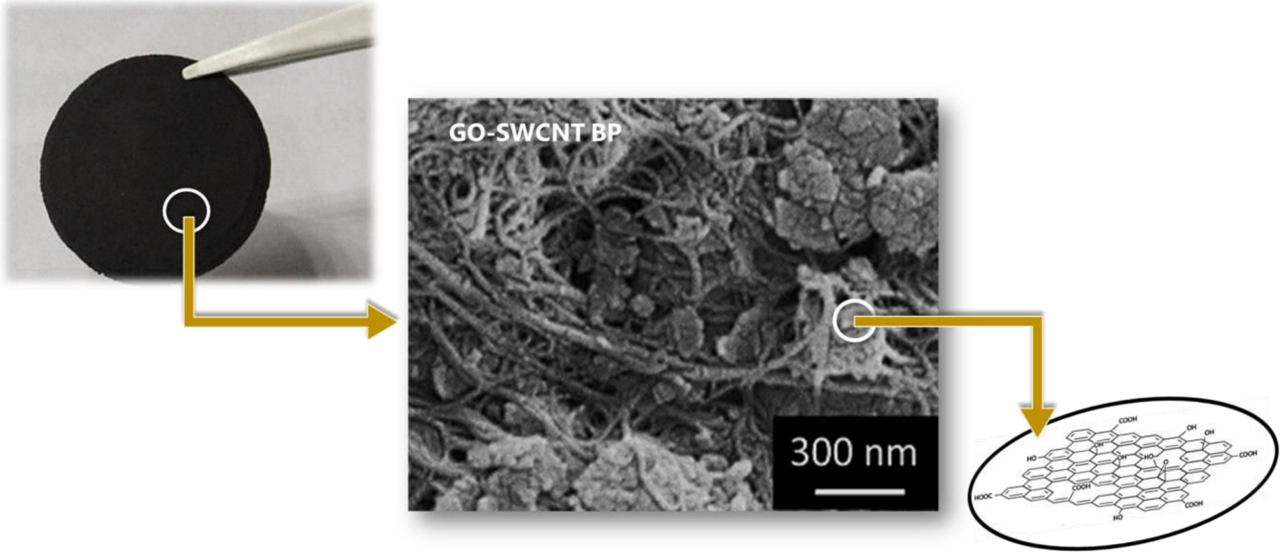
Results obtained on several singly (Gd, Sm-) and doubly (GdSm-, NdTm-, NdDy-) doped systems will be discussed, also in comparison with literature data.

[1] S. Omar, E.D. Wachsman, J.L. Jones, J.C. Nino, J. Am. Ceram. Soc. 92 (2009) 2674-2681.
[2] C. Artini, S. Presto, S. Massardo, M. Pani, M.M. Carnasciali, M. Viviani, Energies 12 (2019) 4148.
[3] C. Artini, S. Presto, M. Viviani, S. Massardo, M.M. Carnasciali, L. Gigli, M. Pani, J. Energy Chem. 60 (2021) 494-502.
[4] C. Artini, M. Viviani, S. Presto, S. Massardo, M.M. Carnasciali, L. Gigli, M. Pani, Phys. Chem. Chem. Phys. 24 (2022) 23622-23633.

Removal of Non-Steroidal Anti-Inflammatory Drugs from Drinking Water Sources by GO-SWCNT Buckypapers

Mariafrancesca Baratta[1], Antonio Tursi[1], Manuela Curcio[2], Giuseppe Cirillo[2], Aleksey Vladimirovich Nezhdanov[3], Alexandr Ivanovic Mashin[3], Fiore Pasquale Nicoletta[2], Giovanni De Filpo[1]
[1]*Dipartimento di Chimica e Tecnologie Chimiche (CTC), Università della Calabria, Rende 87036 Cosenza, Italy;*
[2]*Dipartimento di Farmacia e Scienze della Salute e della Nutrizione, Università della Calabria, 87036 Rende, Italy;*
[3]*Applied Physics & Microelectronics, Lobachevsky State University of Nizhni Novgorod, 603022 Nizhni Novgorod, Russian Federation;*
mariafrancesca.baratta@unical.it

Pharmaceutical products such as antibiotics, analgesics, steroids, and non-steroidal anti-inflammatory drugs (NSAIDs) are new emerging pollutants, often present in wastewater, potentially able to contaminate drinking water resources. Adsorption is considered the cheapest and most effective technique for the removal of pollutants from water, and, recently, membranes obtained by wet filtration method of SWCNT aqueous solutions (SWCNT buckypapers, SWCNT BPs) have been proposed as self-standing porous adsorbents [1]. In this work, the ability of graphene oxide/single-walled carbon nanotube composite membranes (GO-SWCNT BPs) to remove some important NSAIDs, namely Diclofenac, Ketoprofen, and Naproxen, was investigated at different pH conditions (pH 4, 6, and 8), graphene oxide amount (0, 20, 40, 60, and 75 wt.%), and initial NSAIDs concentration (1, 10, and 50 ppm). For the same experimental conditions, the adsorption capacities were found to strongly depend on the graphene oxide content. The best results were obtained for 75 wt.% graphene oxide with an adsorption capacity of 118 ± 2 mg g^{-1} for Diclofenac, 116 ± 2 mg g^{-1} for Ketoprofen, and 126 ± 3 mg g^{-1} for Naproxen at pH 4. Overall, the reported data suggest that GO-SWCNT BPs can represent a promising tool for a cheap and fast removal of NSAIDs from drinking water resources, with easy recovery and reusability features.



[1] Baratta, M., Mastropietro, T. F., Bruno, R., Tursi, A., Negro, C., Ferrando-Soria, J., Mashin, A. I., Nezhdanov, A., Nicoletta, F. P., De Filpo, G., Pardo, E., Donatella Armentano, D., ACS Appl. Nano Mater., 2022, 5, 4, 5223.

The nitroxide/oxammonium cation redox couple as mediator for water oxidation

Antonio Barbon[1], Abdirisak Ahmed Isse[1], Itzhak Bilkis[2], Lev Weiner[3]
1. Dept. of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova, Italy
2. Dept. of Organic Chemistry, Weizmann Institute of Science, Rehovot 76100, Israel
3. Fac. of Agric., Food and Environ. Sciences, Hebrew Un., Rehovot 76100, Israel

Oxammonium cation, having a reduction potential of 0.8-1.0 V vs NHE in water, are known reagents that are used to selectively oxidize organic groups like primary alcohols to aldehydes or carboxylic acids or N-alkyl anilines to quinolones [1].

We produced an oxammonium cation starting from the 3-carboxy proxyl radical by electrolysis at a rather low potential (0.8 V). We observed that the produced cations are able to oxidize water in slightly basic solutions (pH=8-10), obtaining oxygen as a product. This electric potential is much lower than that required for the direct outer-sphere electron transfer (redox potential of the couple $OH^\bullet/OH^-$ is 2-2.6 V *vs* NHE). The reaction kinetic of the oxammonium cation back to its corresponding radical form was followed be electron paramagnetic resonance (EPR) methods and by cyclic voltammetry (CV).

The kinetic was better observed producing the oxammonium cation by photostimulated chemical oxidation of the corresponding nitroxide in the presence of Ru(II) and ammonium persulfate as formation of oxammonium cations occur in the time scale of microseconds, a timescale much shorter than the recovery rection.

We also have studied the reaction rate as a function of the redox potential for a series of nitroxides and found a linear relation between the redox potential and the rate for the recovery reaction.

Finally, water oxidation in $H_2{}^{17}O$ leads to a partial isotopic substitution for the nitroxide group.

A hypothesis of the reaction mechanism, also supported by DFT calculations [2], will be presented.

[1] W. F. Bailey, J. M. Bobbitt, K. B. Wiberg J. Org. Chem. 72 (2007) 4504
[2] A. Barbon, A. A. Isse, A. Gennaro, R. Carmieli, I. Bilkis, L. Weiner Mater. Adv. 3 (2022) 8149

Investigating the Eutectic Mixtures formed by Choline Chloride and Hydroxyphenol Isomers

Paolo Casu[1], Matteo Palluzzi[1], Matteo Busato[1], Paola D'angelo[1]
[1]*Department of Chemistry, Sapienza University, Piazzale Aldo Moro 5, Rome, Italy*
paolo.casu@uniroma1.it

Deep Eutectic Solvents (DESs) are mixtures formed by a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), having a melting point significantly lower than the ideally predicted one for the eutectic composition. DESs exhibit negligible vapor pressure, non-flammability, high conductivity, high solvation capabilities, and low toxicity, making them safer and more sustainable solvents compared to the most common organic ones [1]. Besides these advantages, DESs are also "designing" solvents: this means that it is possible to produce *ad hoc* media for a specific purpose by changing one of the components or introducing new substituents into an existing one. Several DESs found in the literature contain choline chloride as HBA and an enormous variety of chemical species acting as HBDs, thus leading to diverse characteristics and physical properties.

In this work, we aim to demonstrate how structural modifications in the HBD component can induce serious changes in the thermal properties of these systems, which are ultimately correlated to the interactions occurring in solution at atomistic level. To this purpose, we decided to study three archetypical systems formed by choline chloride with isomers of the hydroxyphenol component, where the two hydroxyl groups are respectively in *ortho*- (catechol), *meta*- (resorcinol), and *para*-positions (hydroquinone) (Figure 1a). To do so, we performed differential scanning calorimetry (DSC) measurements (Figure 1b) on mixtures formed between these components at various molar ratios to unveil the thermal behaviour of these systems through all the explored composition range. Infrared spectra have been recorded and the inspection of the O-H stretching region allowed to retrieve information about the extent of hydrogen-bonding formation. Molecular dynamics simulations have been carried out as this method is the ideal candidate to provide a detailed picture about the nature of the interactions among the components. This multidisciplinary approach allowed us to unveil the structure-property relationship in these systems, and the obtained results will be fruitful as a starting point for the synthesis and the development of novel DESs for different purposes.

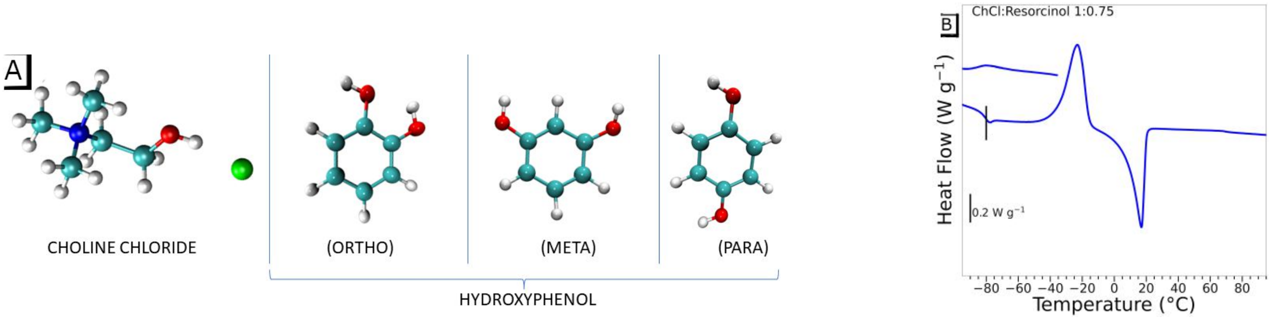


Figure 1: A) Molecular structure of the mixtures components and B) DSC thermogram of the mixture formed by choline chloride and resorcinol in 1:0.75 molar ratio.

[1] E. L. Smith, A. P. Abbott and K. S. Ryder, Chem. Rev. 2014, 114, 11060.

A QM/MM strategy for the study of interstellar surface diffusion

Stefano Ferrero[1], Albert Rimola[1] and Piero Ugliengo[2]
[1]Departament de Quimica, Universitat Autonoma de Barcelona, Bellaterra, 08193, Catalonia, Spain
[2]Dipartimento di Chimica and Nanostructured Interfaces and Surfaces (NIS) Centre, Università degli Studi di Torino, via P. Giuria 7, 10125, Torino, Italy
Presenter's e-mail address: Stefano.ferrero@uab.cat

Surface diffusion of astrochemical species plays a vital role in the Langmuir-Hinshelwood reaction processes that occur on interstellar grains.[1] It is therefore crucial to provide accurate diffusion parameters that can be used in astrochemical models to predict correct chemical abundances in the interstellar medium.[1]

In this study, we present a quantum mechanics/molecular mechanics (QM/MM)[2] strategy to investigate the diffusion of astrochemical species on interstellar ice surfaces.

Our approach allows for the calculation of both binding energies and diffusion barriers of the species under study, providing both valuable information for understanding the behavior of astrochemical species on interstellar ices and also accurate parameters for astrochemical models.

The obtained results were used to perform kinetic Monte Carlo (KMC)[3] simulations to model the long timescale dynamics of the species under study and calculate their diffusion coefficients on interstellar ice surfaces.

The obtained computational results are discussed, and their potential implications for astrochemistry are explored. The study provides insights into the mechanisms that govern the surface diffusion of astrochemical species and their impact on interstellar chemistry. The discussion also addresses the assumptions and approximations inherent in astrochemical modeling and how these can affect the accuracy and relevance of the obtained results.

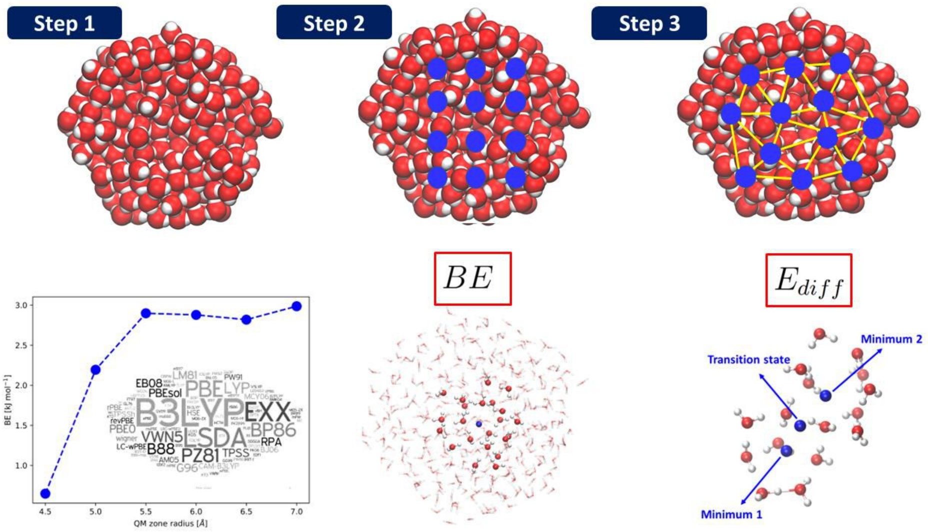


Figure 1 Steps involved in the QM/MM strategy aiming to calculate binding energies and diffusion barriers

[1] Cuppen, H. M., et al. "Grain surface models and data for astrochemistry." Space Science Reviews 212 (2017): 1-58.
[2] Warshel, A., & Levitt, M. (1976). Journal of molecular biology, *103*(2), 227-249
[3] Andersen, Mie, Chiara Panosetti, and Karsten Reuter, Frontiers in chemistry 7 (2019): 202.

Computational Insights into CO_2 Formation on Interstellar Water

Harjasnoor Kakkar[1], Albert Rimola[1]
[1]*Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia, Spain*
Harjasnoor.kakkar@uab.cat

Solid CO_2 has been detected in various physical environments in the interstellar medium (ISM) since its first observation in 1989.[1] Despite being one of the most abundant species in the ISM and a significant component of ice mantles on dust grains, the formation route of CO_2 remains uncertain.[2] The low abundance of CO_2 in the gas phase suggests that it is exclusively formed on the solid ice surface. Moreover, there is no clear, efficient process that can account for the majority of CO_2 formation.[3] In this study, we investigate three well-known radical-neutral reaction pathways (CO with O, CO with OH, and HCHO with O) on pure water ice clusters using quantum chemical calculations. Multiple density functional theory (DFT) functionals are employed to carry out the preliminary benchmarking study on the model gas-phase reactions and determine an accurate method for describing the reaction properties. With the selected functional, potential energy surfaces of the reactions are obtained on ice models i.e., two water clusters consisting of 18 and 33 molecules. First insights will be presented based on the computational investigation that aims to determine the energetically feasible reaction mechanisms. The astrophysical implications of the results will be discussed in combination with observations from experiments and astrochemical models of these widely studied reactions.

[1] J. E. Roser, G. Vidali, et al. *Astrophys. J*. **2001**, 555, L61-L64.

[2] M. Minissale, E. Congiu, et al. *Astron. Astrophys*. **2013**, 559, A49.

[3] R. T. Garrod, T. Pauly. *Astrophys. J*. **2011**, 735, 15.

Organo-modified silicas for the removal of dye molecules from water media

Lorenzo Maccarino[1], Vanessa Miglio[1], Leonardo Marchese[1], Chiara Bisio[1,2]
[1] *Dept of Sciences and Technological Innovation, University of Eastern Piedmont, viale T. Michel 11, 15121 Alessandria*
[2] *CNR-SCITEC Institute of Chemical Science and Technology "Giulio Natta", Via G. Venezian 21, 20133 Milano*
lorenzo.maccarino@uniupo.it

Many anthropogenic activities unfortunately introduce pollutant species that deteriorate the quality of water, one of the essential life components. Various methods can be used to remove pollutants from water (*e.g.*, filtration, precipitation, electrochemical methods, bioremediation, catalysis, etc.), but adsorption onto solids (such as clays, zeolites, porous silicas) is considered an advantageous, cost-effective, and high-performance method [1]. For this purpose, interest was directed towards the study of an organic-inorganic hybrid silica material named Swellable Organically Modified Silica (Silica-SOM), which possesses the unique property of swelling, *i.e.*, expanding porous volume under appropriate conditions, being potentially capable of storing significant amounts of pollutants [2]. Silica-SOM is synthesized by sol-gel method involving the polycondensation of bis(trimethoxysilylethyl)benzene using tetrabutylammonium fluoride as a catalyst. As the gel ages, a three-dimensional network of Si-O-Si bonds with aryl and aromatic groups forms, producing a porous and flexible material [3]. The physico-chemical properties of the Silica-SOM were determined by means of a multi-technique approach: the morphology was found to be composed of aggregates of particles of submicron size and irregular shapes; as Silica-SOM are hydrophobic, the particle size in aqueous suspension is higher (700 nm) than in organic solvents (< 250 nm), as they tend to aggregate in water; the material is mesoporous with a surface area of 414 m^2/g and possesses a negative surface charge at pH values above 3.7.

The adsorption performance of Silica-SOM against two soluble organic dye pollutants in the aqueous phase (Rhodamine B and Methyl orange) was studied. Silica-SOM was placed in contact with an aqueous dye solution and the solutions were analyzed for successive times up to a maximum of 24 hours. Silica-SOM showed very promising removal capacities: after 1 hour of contact 99.5% of Rhodamine B (Fig. 1) and more than 98% of Methyl Orange (Fig. 2) was removed. Adsorption cycles of Rhodamine B were carried out, after desorption of the pollutant in alcohol solution by sonication. These tests showed that Silica-SOM is fully regenerable and reusable under the studied conditions.

Finally, the synthesis procedure of Silica-SOM was optimized using an experimental factorial design approach to decrease the synthesis time.

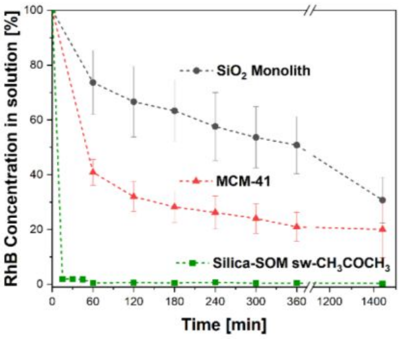


***Figure SEQ Figure * ARABIC 1**: Rhodamine B residual percentual concentration in solution over time. A comparison of different materials studied at same conditions: Silica monoliths (●), MCM-41 (▲) and Silica-SOM pre-swollen with acetone (■).*

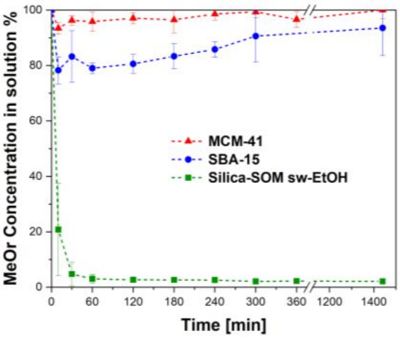


Figure 2: *Methylorange residual percentual concentration in solution over time. A comparison of different materials studied at same conditions: SBA-15 (●), MCM-41 (▲) and Silica-SOM pre-swollen with ethanol (■).*

[1] Karthigadevi, G. et al. Bioresource Technology vol. 324, 124678, 2021
[2] C. M. Burkett e P. L. Edmiston, Journal of Non-Crystalline Solids, vol. 351, n. 40–42, pagg. 3174–3178, 2005
[3] P. L. Edmiston e L. A. Underwood, Separation and Purification Technology, vol. 66, n. 3, pagg. 532–540, 2009

A theoretical characterization of bimolecular reactions leading to the formation of interstellar phosphorus- and silicon-bearing molecules

Luca Mancini[1], Marzio Rosi[2], Dimitrios Skouteris[3], Fernando Pirani[1], Nadia Balucani[1]
[1]*Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, 06123 ,Perugia, Italy*
[2]*Dipartimento di Ingegneria Civile e Ambientale, Università degli Studi di Perugia, 06125, Perugia, Italy*
[2] *Master-Tec, Via Sicilia 41, 06128 Perugia, Italy*
luca.mancini2@studenti.unipg.it

Silicon and phosphorus, together with carbon, oxygen, hydrogen and nitrogen, are among the most important elements in the interstellar medium (ISM). Silicon in the form of silicates is one of the main constituents of the core of dust grains, while the chemistry of phosphorus has strong implications for prebiotic chemistry. In recent years, phosphorus has been clearly identified in the coma of comet 67P/Churyumov-Gerasimenko[1] and in different regions of the interstellar medium, including the shocked region L1157-B1, where PO and PN are the main P-bearing compounds[2,3]. The presence of silicon in the gas phase is mainly related to violent events, such as shocks. As soon as silicon is released in the gas phase, it can immediately react and it is mostly converted into SiO, which is considered a useful target to probe shock regions[4]. Interestingly, in the same L1157-B1 shock region, another fascinating Si-bearing molecule (silicon sulfide, SiS) has been detected with a surprisingly high abundance in a well-localized region around the protostar, suggesting a different chemical origin for SiO and SiS[4]. Thus, understanding the chemistry of these species is pivotal to explain the formation mechanism of interstellar silicates starting from silicon and its gaseous compounds, as well as the formation of phosphorus bearing molecules with a strong prebiotic potential. Given the difficulties associated with the experimental investigation of most of the postulated interstellar reactions, theoretical quantum chemistry calculation appears to be essential to elucidate the chemistry of silicon-bearing and phosphorus-bearing species. In the present contribution, we present new possible formation mechanisms for interstellar PO, PN, and SiS, focusing on ion-neutral reactions. Additionally, the proton transfer to ammonia [5] has been studied for protonated precursors of neutral PO and SiS.

In our approach, we make use of DFT calculations for geometry optimization and frequency analysis coupled to a CCSD(T) reevaluation of the energy for each identified stationary point of the reaction potential energy surface. The data coming from electronic structure calculations are then used to perform a kinetic analysis using a Rice-Ramsperger-Kassel-Marcus (RRKM) code implemented by us to derive the rate coefficients and branching ratios of the different product channels. The use of a semi-empirical (Improved Lennard-Jones)[6] formulation for the initial long-range interactions allows us to obtain more reliable values of the rate constant to include in current astrochemical models.

[1] K. Altwegg et al. Sci Adv 2(5) (2016)
[2] B. Lefloch et al. MNRAS 462 (2016) 3937-3944
[3] V. M. Rivilla et al. ApJ 826(2) (2016) 161
[4] L. Podio et al. MNRAS Lett. 470 (2017) L16-L20
[5] V. Taquet et al. ApJ 46 (2016) 821
[6] F. Pirani et al. PCCP 10 (2008) 5489

Abstract ID. T6O08

Understanding Deep Eutectic Solvents Formation through L-Menthol Mixtures with Butylated Hydroxytoluene Derivatives

Giorgia Mannucci,[1] Matteo Busato,[1] Lorenzo Augusto Rocchi,[1] Maria Enrica Di Pietro,[2] Angela Capocefalo,[3] Elisa Zorzi,[1] Paolo Casu,[1] Daniele Veclani,[4] Franca Castiglione,[2] Andrea Mele,[2] Andrea Martinelli,[1] Paolo Postorino,[5] and Paola D'Angelo[1]
[1]Department of Chemistry, University of Rome "La Sapienza", P.le A. Moro 5, 00185 Rome, Italy
[2]Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milan, Italy
[3] Institute for Complex Systems, National Research Council, P.le A. Moro 5, 00185 Rome, Italy
[4]Molecular Photoscience Group, Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale Delle Ricerche, via P. Gobetti 101, 40129 Bologna, Italy
[5]Department of Physics, University of Rome "La Sapienza", P.le A. Moro 5, 00185 Rome, Italy
giorgia.mannucci@uniroma1.it

Deep eutectic solvents (DESs) are formed by two of more compounds that melt upon contact at a precise molar ratio and produce a mixture with a melting point (MP) lower than those the pure constituents [1]. DESs are generally defined as a mixture of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), although it is not a strict definition for these systems. Indeed, recently a new eutectic solvent formed by L-Menthol (MEN) and butylated hydroxytoluene (BHT) in a 1:3 molar ratio where no hydrogen bonds (H-Bonds) are played by the BHT molecules was presented [2]. Here, we present a study of MEN mixtures with BHT derivates, with the aim of studying in detail what are the different contributions to the eutectic formation. MEN with the BHT, 2-tert-butyl-p-cresol (TBC) and p-cresol (PC) compounds has been carried out, where TBC and PC are analogous to the BHT species but respectively with one and no tert-butyl groups in ortho position to the hydroxyl group. The structures of the studied systems and the used nomenclature are represented in Figure 1.

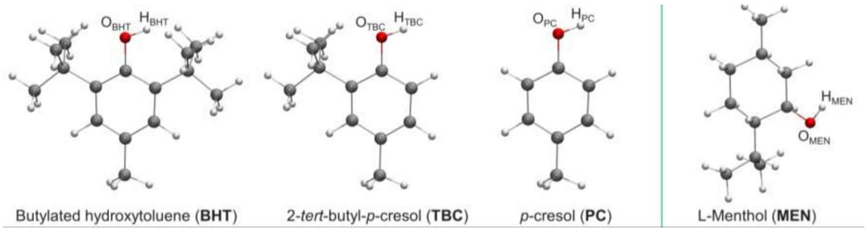


Figure 1. Molecular structures of the butylated hydroxytoluene (BHT), 2-tert-butyl-p-cresol (TBC), p-cresol (PC), and L-menthol (MEN) components within the employed atom nomenclature.

First, a thermal characterization of the systems was carried out by differential scanning calorimetry and polarized optical microscopy. The obtained results made us understand that the BHT:MEN mixture can be classified as a eutectic solvent (ES), while the TBC:MEN and PC:MEN ones as DESs. To investigate the nature of this different thermal behavior proton (^{1}H) nuclear magnetic resonance, Raman spectroscopy and ab-initio molecular dynamics simulations were performed. This combined approach confirmed that in the BHT:MEN mixtures almost no hydrogen-bond (H-bond) interactions are established between the components. Instead, in the TBC:MEN and PC:MEN DESs the driving force for the eutectic formation was found to be respectively the TBC-MEN donor-receptor H-bond and the intercalation of the PC molecules into the MEN H-bonded network. This combined approach was able to shed light into the various contributions ruling the structure-properties relationship in DESs.

[1] M. Francisco et al., Angew. Chem., 52 (2013) 3074–3085
[2] M. Busato et al., ACS Sustain. Chem. Eng., 10 (2022) 6337–6345

Insights on the NO bond

Assimo Maris, Sonia Melandri, Luca Evangelisti
Department of Chemistry G. Ciamician University of Bologna, via Selmi 2, 40126 Bologna, Italy
assimo.maris@unibo.it

It is well known that nitrogen monoxide (NO) is a stable radical. Its stability can be attributed to the delocalization of the unpaired electron to form a two-center three-electron π-type N-O bond, and characterizes a series of compounds that, broadly speaking, can be considered as nitrogen monoxide derivatives. Among them, we cite the heterocyclic aminoxyl radical and the di-tert-butyl nitroxide, whose stability is enhanced by both the steric shielding of the methyl groups surrounding the radical site and the absence of hydrogen atoms in the α-position to the nitrogen atom, that prevents hydrogen abstraction. Their stability is very important because it means that they are not reactive towards closed shell systems, while they are reactive towards free-radicals. These kinds of compounds are used to generate complex macromolecular architectures with well controlled stereochemistry, high chain end homogeneity and a very low polymer dispersity (nitroxide-mediated radical polymerization, NMRP). In particular, NMRP is a reversible-deactivation radical polymerization (RDRP), but, unlike other RDRP techniques, NMRP does not require the presence of transition metal complexes, which is favorable for some sensitive biological and electronic applications.

Hydroxylamines and alkoxyamines also contain the NO group, but they are not radical species.

However, when the homolysis of the OH/OR bond takes place, the produced NO radical is quite stable, opening up the possibility for their use in several fields, including NMRP. Large size alkoxyamines are also used as intermediates in the Denisov cycle, a catalytic process occurring in plastic materials added with hindered amine light stabilizers (HALS) in order to prevent their photo-degradation. Moreover, several studies explore alkoxyamines as precursors of radicals that can be used as therapeutic and theranostic agents.

The interest in hydroxylamines and alkoxyamines revolves essentially around the peculiar properties of the N-O bond that are affected by the intra- and inter-molecular interactions, which also determine the molecular geometry. With the purpose of modelling the physico-chemical properties of this class of compounds and to understand the factors controlling the homolytic cleavage, we characterized a series of model molecules by combining quantum mechanical calculations and a range of spectroscopic techniques (MW, NIR, XPS, NEXAFS). The molecular structure and dynamics will be discussed.

Insights on the Dissipation Process of the Nascent Reaction Energy in the Formation of Formamide on Interstellar Water Ice Surfaces

Berta Martínez-Bachs[1], Gerard Pareras[1], Joan Enrique-Romero[2], Albert Rimola[1]
[1]Universitat Autònoma de Barcelona, Departament de Química, 08193 Bellaterra, Spain
[2]Leiden Institute of Chemistry, Leiden, University, Leiden 2300 RA, The Netherlands
berta.martinez@uab.cat

Ice mantles covering dust particles provide a solid-state support for chemical reactions in the Interstellar Medium. Such water ice surfaces can act as third bodies by absorbing the energy released by surface reactions[1]. Indeed, the absorbing capacity of ice mantles is a crucial factor that will determine if newly formed species on their surfaces will remain adsorbed on the ices or will be desorbed and ejected into the gas-phase as it is commonly assumed by astrochemical models[2-4]. In this contribution, we analyze the third-body role of water ice mantles for the radical-radical coupling between NH_2 and HCO to form formamide, a reaction that presents a low energy barrier and is largely exothermic[5]. Its potential energy surface has been characterized on an amorphous water ice model using static quantum chemical methods. Ab initio molecular dynamics simulations have been performed to elucidate how the nascent reaction energy is dissipated through the amorphous water ice model. Results indicate that water ices present a high absorbing capacity and, therefore, the energy that remains on the newly formed formamide is not large enough to cause its ejection into the gas-phase.

[1] A. Potapov and M. McCoustra, Int. Rev. Phys. Chem. 40 (2021) 299
[2] S. Pantaleone et al. Astrophys. J. 897 (2020) 56
[3] S. Pantaleone et al. Astrophys. J. 917 (2021) 49
[4] S. Ferrero et al. Astrophys. J. 944.2 (2023) 142
[5] J. Enrique-Romero et al. ACS Earth Space Chem. 3 (2019) 2158

σ- and π-hole activation of aryl halides upon perfluorination: direct evidence from gas phase rotational spectroscopy

Sonia Melandri, Assimo Maris, Luca Evangelisti,
[1]Department of Chemistry, University of Bologna, via Selmi, 2 40126 Bologna, Italy
sonia.melandri@unibo.it

Non-covalent interactions (NCIs) play a very important role in many physical, chemical and biochemical processes and the interest in their experimental and theoretical characterization is testified by the large amount of literature on this theme.

In recent years, many kinds of NCIs involving different atoms or fragments that can replace the bridging proton of the hydrogen bond and attract an electron donor via a region of depleted electron density, have been a subject of great interest. This region is called a ‘‘hole’’ and, depending on whether it is in the direction of or perpendicular to the molecular σ-framework, it is called a ‘‘σ’’– or a ‘‘π–hole’’, respectively.

The presence of σ– or π– holes is evidenced by the accurate data on the structures and electronic properties of molecules and molecular complexes obtained by rotational spectroscopy performed in the cold isolated conditions of a free jet expansions.

Enhancement of the σ- and π- hole in aryl halides due to perfluorination of the ring is demonstrated and the results can be directly compared to the outcome of high-level quantum mechanical calculations obtained in the same isolated conditions.

Swellable Organically Modified Silicas for the removal of PFAS from aqueous solutions

Vanessa Miglio[1], Federico Begni[1], Andrea Bortoli[1], Claudio Cassino[1], Geo Paul[1], Leonardo Marchese[1], Chiara Bisio[1,2]
[1] *Dept of Sciences and Technological Innovation, University of Eastern Piedmont, viale T. Michel 11, 15121 Alessandria*
[2] *CNR-SCITEC Institute of Chemical Science and Technology "Giulio Natta", Via G. Venezian 21, 20133 Milano*
vanessa.miglio@uniupo.it

Although water is one of the essential components for life, there is a continuous deterioration of water quality due to numerous anthropogenic activities that result in the introduction of organic, inorganic, and biological pollutants into the various water sources. Of particular concern is fluorinated alkyl substances (PFAs), a class of amphiphilic organic molecules that differ in alkyl carbon chain length and polar functional group at the head of the chain[1]. Since their carbon chain is fully fluorinated, they are very stable and persistent, and they also exhibit hydrophobic and lipophobic properties. The presence of some PFAs in aquatic environment is of greater concern as toxicological data suggests an association to adverse human health effects[2]. For this reason, remediation of PFAs from the environment has rapidly increased; as a matter-of-fact PFAs are recalcitrant to conventional water treatment, adsorption is considered as a better technique due to its cost efficiency, eco-friendliness, and high efficiency[3]. For this purpose, different porous materials, such as silicas, zeolites, clays, resins and active carbon are used. A promising novel material for adsorption of these pollutants is Swellable Organically Modified Silica (SOMS), an organic-inorganic hybrid material[4]. The unique feature of this material is that its structure allows for an expansion of three to five times its volume in the presence of organic compounds, thus enabling their efficient adsorption[5]. During the synthesis, it is possible to functionalize these materials with quaternary amine groups, in order to obtain a positively charged material called QASOMS[6]. In this work, QASOMS was synthesized and used as adsorbent for the removal of three PFAs molecules from water within a concentration range between 50 and 800 ppm. The adsorption property of the hybrid QASOMS material is compared with the performances of commercially available ultra-stable high-silica Y zeolite and granular activated carbon. Perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS) and perfluorobutanesulfonic acid (PFBS) were used as model PFAs molecules.

^{19}F-NMR analysis was used for the identification and quantification of PFAs. The area of the CF_3 signal of PFOA was used to prepare a calibration curve that was then used for evaluating the PFAS concentration after 24h contact with the sorbent materials. QASOMS showed high affinity for all the three perfluoroalkyl compounds throughout the whole concentration range tested. (**Figure 1**).

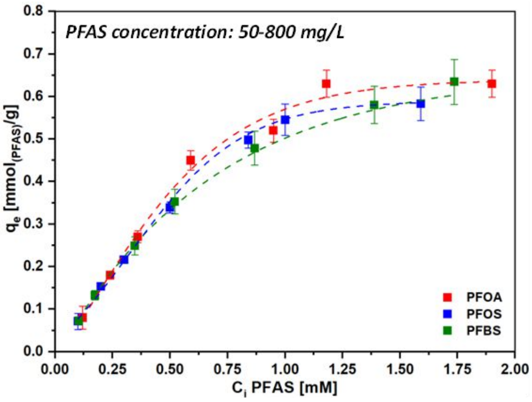


Figure 1 – Adsorption isotherms of PFOA; PFOS and PFBS on QASOMS.

[1] E. Panieri et al., Toxics, vol. 10, n. 2, pag. 44, gen. 2022
[2] I. Ross et al., Remediation, vol. 28, n. 2, pagg. 101–126, mar. 2018
[3] D. M. Wanninayake, Journal of Environmental Management, vol. 283, pag. 111977, apr. 2021
[4] C. M. Burkett e P. L. Edmiston, Journal of Non-Crystalline Solids, vol. 351, n. 40–42, pagg. 3174–3178, ott. 2005
[5] C. M. Burkett, et al., Chem. Mater., vol. 20, n. 4, pagg. 1312–1321, feb. 2008
[6] P. L. Edmiston et al., Adsorption, vol. 24, n. 1, pagg. 53–63, gen. 2018

The Interaction of Sulphur-Bearing Species With Olivine Clusters: A New Perspective on Sulphur Depletion In The Interstellar Medium

Jessica Perrero[1,2], Albert Rimola[1], and Piero Ugliengo[2]
[1] *Universitat Autònoma de Barcelona, Departament de Química, E-08193, Bellaterra, Spain*
[2] *Università degli Studi di Torino, Dipartimento di Chimica, I-10125, Torino, Italy*
jessica.perrero@uab.cat

Interstellar dust grains are irregular, micron-sized, solid aggregates of graphite and/or silicates found in the interstellar medium (ISM). Grains provide a surface where species can meet, accrete, and react. Indeed, they are thought to be responsible for most of the formation of H_2 and H_2O [1]. In diffuse molecular clouds, the mineral core of the grains can be exposed to the atoms and small molecules present in the gas phase. Sulphur depletion in the ISM is a long-standing issue, as its expected elemental abundance in dense molecular clouds cannot be achieved when considering only the species detected in the gas phase [2]. Therefore, it is our aim to understand how gas phase sulphur-bearing species interact with the grains on which OCS and, tentatively, SO_2 were observed [3]. Hence, a better understanding of sulphur chemistry is needed, starting from its behavior in diffuse clouds where only the core of the grains is present.

To simulate the olivine grain core, a family of silicates containing Mg and Fe and one of the most abundant minerals in the ISM, we performed a series of quantum mechanical benchmark calculations to find a suitable methodology for the characterization of their structures, represented by nanoclusters of $Mg_4Si_2O_8$ and $Mg_3FeSi_2O_8$ [4].

We used H_2S to fine tune the computational methodology, extending the study to other S-bearing species. Our calculations reveal that sulphur prefers to interact with Fe rather than with Mg, and that the strength of the interaction is such that the species are likely to stick onto the mineral surfaces, becoming part of the grain core. This may, in part, account for the S-depletion in the gas-phase.

[1] E.F. van Dishoeck et al. Chem. Rev. 113 (2013) 9043
[2] J.C. Laas and P. Caselli Astron. Astrophys. 624 (2019) A108
[3] A.A. Boogert et al. Annu. Rev. Astron. Astr. 53 (2015) 541
[4] M. Serra-Peralta et al. Phys. Chem. Chem. Phys. 24 (2022) 28381

X-ray absorption spectroscopy allows the detection of general Bromine oscillatory behaviour in the Belousov-Zhabotinskii reaction

Francesco Tavani[1], Federico Frateloreto[1], Daniele Del Giudice[1], Marika Di Berto Mancini[1], Giorgio Capocasa[1], Matteo Busato[1], Osvaldo Lanzalunga[1], Stefano Di Stefano[1] and Paola D'Angelo[1]
[1]Dipartimento di Chimica, Sapienza Università di Roma, Piazzale A. Moro 5, 00185 Rome, Italy
francesco.tavani@uniroma1.it

The Belousov-Zhabotinskii (BZ) reaction [1,2] involving the cerium ion catalyzed oxidation and bromination of malonic acid (MA) by bromate is the most extensively studied oscillating chemical reaction and continues to fascinate chemists to this day. A wide variety of chemical processes proceed in fact in a cyclic fashion exhibiting concentration periodic changes. Since the elucidation of the main mechanistic features of the BZ reaction by Field, Körös and Noyes (FKN) in 1972 [3] whose work laid the foundation to understand the temporal and spatial phenomena present in numerous BZ reagents, experimental and theoretical efforts have been devoted to investigate the BZ reaction mechanistic details, e.g. those regarding the reaction destabilizing, negative feedback processes. A revised semiquantitative model of the BZ reaction based on 80 elementary reactions and 20 concentration variables was proposed by György, Turányi and Field [4], and reaction pathways are still being added upon collection of additional experimental evidence.

Nonetheless, it appears clear that when tackling a chemical mechanism of this size with many unknown parameters the availability of experimental techniques that may accurately track the oscillating concentration time evolution of the key reaction intermediate species is of paramount importance. Herein, we tackle the previously unaddressed issue of gaining comprehensive real time spectroscopic insights into the speciation of the Br reactants during the BZ oscillatory reaction by resorting to X-ray absorption spectroscopy (XAS). XAS is advanced spectroscopic tool that stands out among the laboratory-based techniques routinely used to investigate reaction mechanisms. XAS may be in fact employed to investigate all periodic table elements, it is an element-specific probe due to core electron excitation and is frequently used to determine oxidation states since the energy shifts of the K (1s) edge often correlate well with the ionization energy of the core orbital. Notably, a multivariate statistical analysis of the XAS data may further complement the information acquired on the chemistry of the given reactive system.

In this presentation, we will provide new insights into the behaviour of the Br–related species of the cerium ion catalyzed BZ reaction and show that periodic oscillations not only occur in the concentrations of Br^-, $HBrO_2$, HOBr and Br_2, but also in those of the main reactants BrO_3^- and bromomalonate. Specifically, we measure detectable oscillations in the concentrations of BrO_3^- and bromomalonate by monitoring the BZ reaction through Br K-edge XAS. Further, by coupling XAS with UV-Vis spectroscopy, we simultaneously track the oscillatory time evolution of the Ce and main Br reactants. Multivariate Curve Resolution (MCR) and kinetic analyses are used to interpret the observed oscillatory patterns. Our work evidences collective oscillations in the BZ system and extends the use of X-ray spectroscopy to investigate the mechanisms of oscillatory chemical systems whose key species are often silent to conventional methods of detection.

[1] B. P. Belousov, Sbornik ReJeratov po Radiaisionnoi Meditsine (1958) 145 (in Russian)
[2] A. M. Zhabotinskii, Biofizika 9 (1964) 306 (in Russian)
[3] R. J. Field et al. J. Am. Chem. Soc. 94 (1972) 8649
[4] L. György et al. J. Phys. Chem. 94 (1990) 7162

Crossed **Molecular beam studies of elementary reactions relevant in combustion and astrochemistry:** O(^{3}P) + small aromatics

Gianmarco Vanuzzo[1], Giacomo Pannacci[1], Pedro Recio[1], Adriana Caracciolo[1], Marzio Rosi[2], Piergiorgio Casavecchia[1], Nadia Balucani[1]
[1]Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, 06123 Perugia, Italy
[2]Dipartimento di Ingegneria Civile Ambientale, Università di Perugia, 06125 Perugia, Italy
gianmarco.vanuzzo@unipg.it

Given the importance of aromatic compounds in numerous contexts ranging from atmospheric pollution to combustion chemistry and astrochemistry, we have started a systematic laboratory investigation of the reactions of atomic oxygen in its fundamental electronic state of ^{3}P with small aromatic compounds, namely benzene, pyridine, toluene, and thiophene. These compounds are quite common in the above-mentioned environments and can also be considered simple prototypes for polycyclic aromatic hydrocarbons (PAHs), nitrogen-containing polycyclic aromatic hydrocarbons (PANHs), and polycyclic aromatic sulfur heterocycles (PASHs). We have employed the crossed-molecular-beam (CMB) technique with universal, soft ionization, mass-spectrometric detection, and time-of-flight analysis to identify the reaction mechanism and the branching fractions (BFs) of the possible reaction products [1]. The interpretation of our experimental results has been supported by high-level ab initio electronic structure calculations of potential energy surfaces (PESs) and RRKM/Master Equation computations of product BFs (see, for instance, [2-6]). In particular, for the reactions occurring between O(^{3}P) with benzene and pyridine, two main groups of mechanisms were observed: 1) the H-displacement mechanisms, in which an oxygen atom replaces an H atom and 2) the ring contraction mechanisms, most likely leading to CO ([2-4]). The presence of the N atom in the aromatic ring of pyridine increases the yield of the ring-contraction mechanism. We will explore whether this is the case also for other heterocyclic compounds like thiophene. Conversely, the introduction of a methyl group linked to the aromatic ring allows the preservation of the six-member aromatic ring in the products formed from the reaction of oxygen atoms with toluene, as opposed to the case of benzene and pyridine [2-4 and *in preparation*].

The authors wish to thank the Italian MUR (PRIN 2020, "Astrochemistry beyond the second period elements", Prot. 2020AFB3FX)

[1] P. Casavecchia et al. Int. Rev. Phys. Chem. 34 (2015) 161
[2] C. Cavallotti et al., J. Phys. Chem. Letters 11 (2020) 9621
[3] G. Vanuzzo et al., J. Phys. Chem. A. 125 (2021) 8434
[4] P. Recio et al. Nature Chem. 14 (2022) 1405

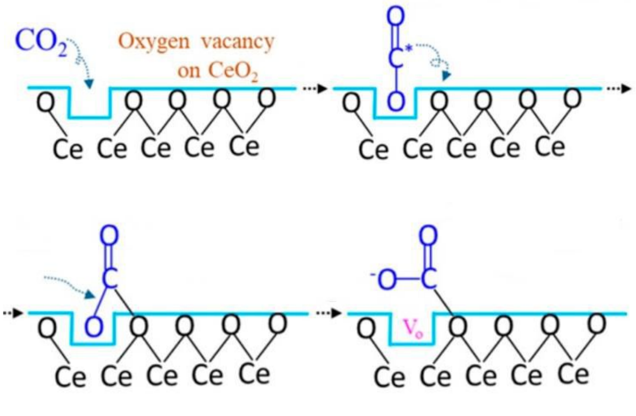
POSTERS

T6. REACTIVE PROCESSES IN GAS, LIQUID AND SOLID PHASES

Sustainable CO_2 conversion to DMC catalysed by MOF-derived Ce and Ce/Zr oxides

Edoardo Bracciotti[1], Sergio Rojas Buzo[1], Davide Salusso[1], Andrea Jouve[2], Matteo Signorile[1] and Silvia Bordiga[1]
[1] *Department of Chemistry and NIS Centre, University of Turin, Via Quarello 15, 10125 Turin, Italy*
[2]*Department of Drug Science and Technology, University of Turin, Via Giuria 9, Turin 10125, Italy*
edoardo.bracciotti@unito.it

Dimethyl carbonate (DMC), widely used for several applications that range from fuel additives to Li-ion batteries, is nowadays a valuable product of industrial synthesis. Its production from the direct reaction between CO_2 and methanol (CH_3OH) is a relevant process for short-term conversion of the huge amounts of CO_2 produced every year. Among a survey of studied catalysts, CeO_2, ZrO_2 and their solid solutions were found to show the highest activities and stability. Since it has recently been reported that the presence of Ce^{3+} in $CeZrO_x$ solid solutions favors CO_2 activation through bidentate carbonates formation, we have synthesized and fully characterized defective Ce and Ce/Zr MOFs and oxides derived by non-conventional calcination of MOFs Ce-UiO-66 and Ce/Zr-UiO-66[1]. The reaction has been carried and studied by *in situ* IR spectroscopy in both gas and liquid phases and the obtained data have been compared with pure CeO_2 and ZrO_2[2, 3]. It has been possible to deduce the spectral components of the reacting mixture by using the MCR-ALS protocol, which permitted to identify formates (HCOO), methoxides (OCH_3), and carbonates (CO_3) and to follow their complex evolution. By these methods it was also possible to observe that formate production inhibits the rapid monomethyl carbonate (MMC) and DMC production. To understand the role played by different oxidation states of the metals, the activity of Ce^{3+} was monitored through NAP-NEXAFS: the Ce oxidation state in the pure CeO_2 did not change after reaction. Moreover, the FT-IR and NAP-NEXAFS results confirmed that CO_2 is reduced to CO oxidizing Ce^{3+} whilst CH_3OH/CH_3O^- are oxidized to $HCOO^-$ hence reducing Ce^{4+} (which reduction increases at higher ZrO_2 content).



[1] Davide Salusso, Silvia Mauri, Gabriele Deplano, Piero Torelli, Silvia Bordiga, Sergio Rojas-Buzo; ***Nanomaterials***, (2023) 13, 272.

[2] Matteo Signorile, Davide Salusso, Valentina Crocellà, Maria Cristina Paganini, Silvia Bordiga, Francesca Bonino and Davide Ferri; ***Phys. Chem. Chem. Phys.***, (2023) 25, 8392-8402.

[3] Davide Salusso, Giorgio Grillo, Maela Manzoli, Matteo Signorile, Spyridon Zafeiratos, Mathias Barreau, Alessandro Damin, Valentina Crocellà, Giancarlo Cravotto, and Silvia Bordiga; *ACS Appl. Mater. Interfaces*, (2023) 15, 15396–15408.

Acknowledgements: Project funded by Centro Nazionale Mobilità Sostenibile MOST. Spoke 14, task 1.2.

CO_2 to e-fuels conversion using heterogenized metal complexes in MOFs

Edoardo Bracciotti[1], Sergio Rojas Buzo[1] and , Silvia Bordiga[1]
[1] *Department of Chemistry and NIS Centre, University of Turin, Via Quarello 15, 10125 Turin, Italy*
edoardo.bracciotti@unito.it

The environmental global problem of CO_2 dispersion in the atmosphere is largely due to transportations, which account almost for a quarter of total global production. When it comes to consider new types of fuels, the resources necessary to develop and to produce new engines are to be taken in account. Because of the great advance that there would be in producing fuels that are compatible with the existing technologies, the production of CO_2-neutral fuels (e-fuels) with properties similar to most conventional ones is considered an interesting and fertile field of research. Metal-Organic Frameworks (MOFs), despite combining the high surface areas needed for heterogeneous catalysts with well-defined structures that permit to accurately design catalytic centers within the framework, haven't been extensively studied as supports for metal complexes to be used in the direct thermal reduction of carbon dioxide[1]. The research will initially focus on the MOF Zr-UiO-67 as a promising starting material to be modified to host single-atom catalytic centers, for it conjugates good mechanical and chemical stability with large sized pores[2]. A survey of complexes that proved to be active catalysts in the homogeneous CO_2 reduction and some similar species adapted to fit into the MOF's structure will be synthesized and grafted inside the framework. The grafting will be exploited by post-synthetic modification of the MOF by the insertion of a preformed metal complex bearing a ligand able to exchange with the organic linkers of the structure. Other attempts will be carried out by trapping active catalysts into the cavities of the porous structure without been coordinatively bonded to the scaffolding. Ru and Ir organometallic complexes, which show among the highest conversion rates in CO_2 hydrogen reduction under mild conditions, will be the starting choice among active metal centers to be studied[3,4]. The catalytic activities of the obtained material will be tested in both batch and flow reactors and monitored via GC-MS analysis. The reactivity of those species that will prove to be more effective in gas phase CO_2 reduction will be further investigated and the intermediate species characterized by *in situ* FT-IR methods to understand reaction mechanisms and kinetics.

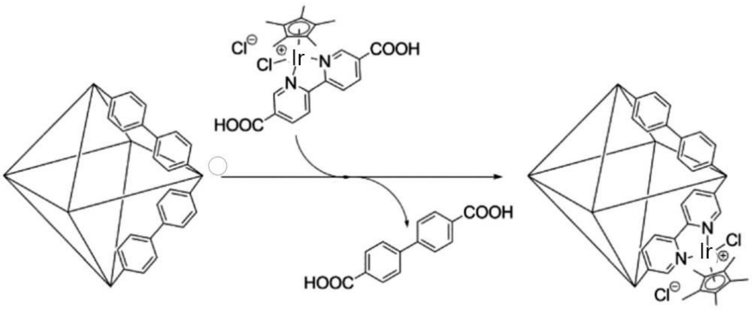


Fig: Schematic representation of an example of an iridium complex heterogenization in MOF UiO-67.

[1] S. De, A. Dokania, A. Ramirez, J.Gascon; *ACS Catalysis* (2020), 10, 14147-14185.
[2] A. H. Vahabi, F. Narouzi, E. Sheibani, M. Mahimi-Nasrabadi; *Coord. Chem. Rev.* (2021), 445, 214050.
[3] N. Onishi, Y. Himeda; *Coord. Chem. Rev.* (2022), 472, 214767.
[4] W. Chu, Z. Culakova, B. T. Wang, K. I. Goldberg; *ACS Catalysis* (2019), 9, 9317-9326.

Acknowledgements: Project funded by Centro Nazionale Mobilità Sostenibile MOST. Spoke 14, task 1.2. We also thank Chimet Spa for providing us with precious metal precursors.