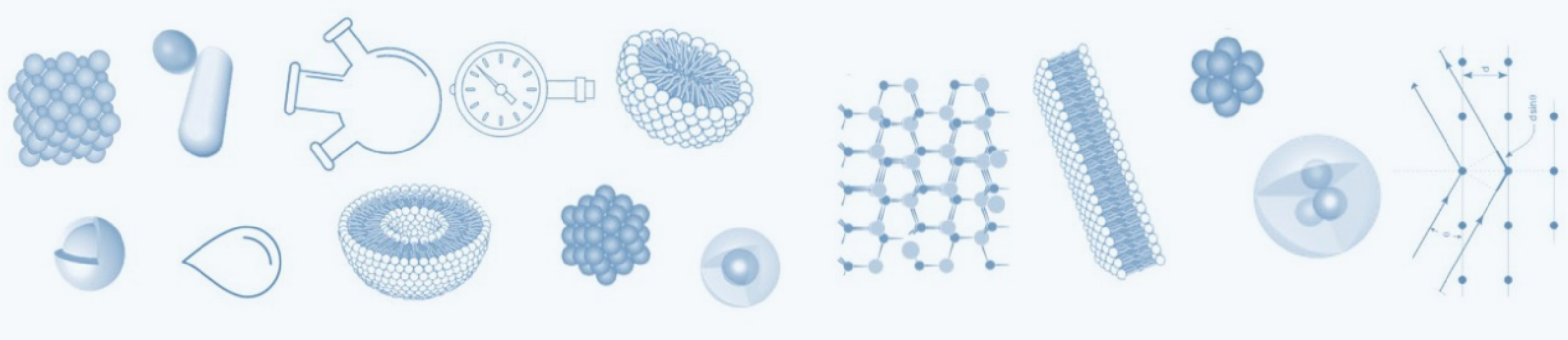

# $3^{rd}$ Edition International Workshop

# AIM 2022
# Advanced Inorganic Materials
## Green and Unconventional Synthesis: Approaches and Functional Assessment

Department of Physics
**University of Bari**
*June 23 – 24, 2022 Bari - Italy*

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Unconventional and Green Approaches for The Synthesis of Crystalline Inorganic Materials

**Guest Editors**
Dr. Marta M. Natile, Prof. Dr. Silvia Gross, Prof. Dr. M. Lucia Curri

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## Plenary Speakers

**Prof. Liberato Manna**, Italian Institute of Technology (IIT), Italy
*Halide Perovskite Nanocrystals: Their Synthesis, Chemical, Structural, and Surface Transformations*

**Prof. Sanjay Mathur**, University of Cologne, Germany
*Efficient Photon-harvesting Technologies for Water Splitting Reactions*

## Invited Speakers

**Dr. Íñigo Bretos**, Materials Science Institute of Madrid (ICMM-CSIC), Spain
*Low-temperature strategies to induce the crystallization of metal oxide thin films by wet chemical methods*

**Prof. Jawwad A. Darr**, University College London, United Kingdom
*Green unconventional supercritical water flow routes to energy materials discovery and Kg/h scale-up*

**Dr. Cinzia Giannini**, Institute of Crystallography (IC-CNR), Italy
*Structural and morphological X-ray studies of Inorganic nanomaterials*

**Prof. Simone Mascotto**, University of Hamburg (Germany)
*Self-regenerating supported metal nanoparticles for $CO_2$ conversion applications*

**Prof. Liberato Manna** Italian Institute of Technology (IIT), Italy

Liberato Manna received his Ph.D. in Chemistry in 2001 from the University of Bari (Italy) and worked at UC Berkeley (USA) as a visiting Student and subsequently at the Lawrence Berkeley Lab (USA) as a postdoctoral fellow until 2003. He was then scientist at the National Nanotechnology Lab in Lecce (Italy) and he moved to the Istituto Italiano di Tecnologia (IIT), Genova (Italy) in 2009 as head of the Nanochemistry Group. From 2010 to 2021 he has also been part-time professor at TU Delft (The Netherlands). Currently, he is also associate director of IIT for the Materials and Nanotechnology programs at IIT. His research interests include the synthesis and assembly of colloidal nanocrystals, the study of structural, chemical and surface transformations in nanoscale materials, and their applications in energy, photonics, and electronics.

**Prof. Sanjay Mathur** University of Cologne, Germany

Sanjay Mathur is the director of the Institute of Inorganic Chemistry at the University of Cologne in Germany. He is the Co-Director of the Institute of Renewable Energy Sources at the Xian Jiao Tong University, Xian, China and a World Class University Professor at the Chonbuk University in Korea. He also holds Visiting Professorships at the Central South University, China, Tokyo University of Agriculture and Technology, Japan and National Institute of Science Education and Research (NISER), India. He has been awarded the Honorary Doctorate of the Vilnius University in 2016.

**Dr. Íñigo Bretos** Materials Science Institute of Madrid (ICMM-CSIC), Spain

Íñigo Bretos received his PhD degree in Chemistry from the Universidad Autónoma de Madrid (Spain) in 2006. After a postdoctoral position in the RWTH Aachen University (Germany), in 2009 he joined the Materials Science Institute of Madrid (CSIC) where he recently (and finally) became CSIC Researcher (2022). His research interest is focused on the synthesis, processing and characterization of multifunctional materials (ferroelectrics, piezoelectrics, dielectrics, multiferroics or superconductors) for intelligent and sustainable electronic devices with application in the fields of digital information (memories, sensors and actuators), energy (photovoltaic and piezoelectric harvesters) and environment (photocatalysts for environmental remediation). Over the years, his research career has evolved from the area of microelectronics to the emerging technology of flexible electronics putting special emphasis on the development of synthetic approaches with low-energy consumption (low-temperature processing) and environmentally friendly (aqueous synthetic routes, lead-free materials). This fact motivated the development of his main research line: the low-temperature processing of metal oxide thin films by wet chemical methods.

**Prof. Jawwad Darr** University College London, United Kingdom

Professor Jawwad Darr is now one of the UK's leading industrially facing academics in advanced functional materials/nanomaterials process engineering, Professor of Materials Chemistry at University College London, UCL. He has published over 200 academic publications and 3 patents and has been awarded funding valued at over 20 million pounds and has graduated over 45 PhD students (as of 2021). From 2016 to 2021, he was vice dean of enterprise in the Maths and Physical Sciences faculty at UCL in, which he was supporting UCL's faculty engagement with industry.

He is visiting professor at Comsats University Islamabad (Lahore Campus) since 2008. In 2017, he co-founded the UPSIGN charity (UK-Pakistan Science and Innovation

Global Network; www.upsign.org.uk) that works to support, educate and connect British Pakistani and Pakistani academics. In his UPSIGN work, he is involved in public outreach workshops and lectures, training Pakistani academics and students, and developing training and workshops to support underprivileged undergraduate black and minority Asian students in research. He is a regular speaker at industrial forums and academic events in a wide range of topics. As well as his own latest research, he teaches on topics related to green chemistry, applications of advanced functional materials (including batteries) and at outreach lectures for (virtual/real) schools/universities in the UK globally.

**Dr. Cinzia Giannini** Institute of Crystallography (IC-CNR), Italy

Cinzia Giannini is the Director of the Institute of Crystallography, National Research Council (CNR), since July 1, 2021, and President of the CNR Research Area in Bari since May 1, 2022. She is President of the Italian Synchrotron Radiation Society (SILS) since 2021 and member of the board of Directors of the Italian Institute for Environmental Protection and Research (ISPRA) for the period 2022-2025.

She got her Ph.D. in Physics from University of Bari in 1996; worked as researcher at the CNRSM in Brindisi; and joined as researcher the CNR in 2001.

The aim of her research is to study the properties of materials, surfaces, nano systems, biomaterials, and tissues by means of X-ray scattering also with a focus on understanding structure and properties. This includes participating in the development of new X-ray imaging modalities with applications towards energy materials, environment and health and new X-ray methods for achieving high spatial/temporal resolution. Since 2021, she is also active in the time resolved x-ray scattering experiments, being part of the Review Panel for the Single Particle and Biomolecules/Serial Femtosecond Crystallography (SPB/SFX) Instrument of the European X-ray Free Electron Laser (XFEL).

**Prof. Simone Mascotto** University of Hamburg, Germany

Simone Mascotto (1981, Trento, Italy) is Assistant Professor of Inorganic Chemistry at the University of Hamburg, Germany. He received a MSc degree in Industrial Chemistry from the University of Padua (2006) and a PhD in Physical Chemistry from the Justus-Liebig-University of Giessen (2009). In 2010–2013 he was a Marie Curie postdoctoral fellow at the University of Trento, Italy and research associate at the Helmholtz-Zentrum Berlin, Germany. His research group focuses on the design ofmetal oxides with tailored surface properties and on the investigation of surface-related phenomena in nano- materials by scattering methods at large scale facilities

# AIM 2022 Workshop program

## Bari, 23-24 June, 2022

## Aula A Department of Physics – University of Bari Campus, via Orabona 4, 70126 Bari

**Abbreviations**

**PI** – Plenary lecture (35 minutes + 5 minutes discussion)
**KN** – Keynote lecture (30 minutes + 5 minutes discussion)
**OP** – Oral presentation (15 minutes + 5 minutes discussion)
**FP** – Flash presentation (7 minutes + 3 minutes discussion)

# 23th June 2022

| | | |
|---|---|---|
| **Opening Session** | | |
| **Chairperson**: Prof. M. Lucia Curri, University of Bari | | |
| 9:00 - 9:30 | **Opening welcome** | |
| 9:30 - 10:10 | **PI1** | **Prof. Liberato Manna** Italian Institute of Technology, IIT (Italy) *Halide Perovskite Nanocrystals: Their Synthesis, Chemical, Structural, and Surface Transformations* |
| 10:10 - 10:30 | **OP1** | **Dr. Alice Debot** University of Luxembourg (Luxembourg) *Inkjet printing of thin chalcogenide semiconductor layers for solar cell applications* |
| 10:30 - 10:50 | **OP2** | **Dr. Rosanna Mastria** Institute of Nanotechnology, NANOTEC-CNR (Italy) *Photoluminescence emission induced by localized states in halide-passivated colloidal two-dimensional* $WS_2$ *nanoflakes* |
| 10:50 - 11:30 | **Coffee break** | |
| 11:30 - 12:00 | **KN1** | **Prof. Jawwad A. Darr** University College London (United Kingdom) *Green unconventional supercritical water flow routes to energy materials discovery and Kg/h scale-up* |
| 12:00 - 12:20 | **OP3** | **Mrs. Franca Marina** University of Padua (Italy) *Unveiling the impact of doping ions on aluminum oxide as automotive catalyst support* |
| 12:20 - 12:40 | **OP4** | **Dr. Francesco Miccio** Institute of science and technology for ceramics, ISTEC-CNR (Italy) Geopolymer based catalysts and oxygen carriers for application in thermochemical processes |
| 12:40 - 13:00 | **OP5** | **Prof. Alessandro De Giacomo** University of Bari (Italy) *Nanostructures produced via Laser Ablation in Liquids* |
| 13:00 - 14:30 | **Lunch break & Poster session** | |
| **Afternoon Session** | | |
| **Chairperson:** Prof. Silvia Gross, University of Padua | | |
| 14:30 - 15:00 | **KN2** | **Dr. Cinzia Giannini** Institute of Crystallography, IC-CNR (Italy) *Structural and morphological X-ray studies of Inorganic nanomaterials* |
| 15:00 - 15:20 | **OP6** | **Mr. Filippo Colombo** University of Hamburg (Germany) *Bimetallic exsolution of Ni-Fe nanoparticles from perovskite oxides: an insight on mechanistic aspects through in-situ synchrotron measurements* |
| 15:20 - 15:40 | **OP7** | **Dr. Aurora Rizzo** Institute of Nanotechnology, NANOTEC-CNR (Italy) *Polymer-Assisted Perovskite Assembly* |
| 15:40 - 16:20 | **Coffee break** | |
| 16:20 - 16:30 | **FP1** | **Dr. Kioseoglou Effrosyni** Aristotle University of Thessaloniki (Greece) *Advanced Vanadium-Peroxido Materials in Sustainable Catalytic Systems* |
| 16:30 - 16:40 | **FP2** | **Dr. Leonarda Francesca Liotta** Institute of nanostructured materials, ISMN-CNR (Italy) *Ag/Cu supported on* $SiO_2$-$TiO_2$ *oxides as potential antifouling systems: Characterization of chemical physical and rheological properties* |
| 16:40 - 16:50 | **FP3** | **Mrs. Giada Mannias** University of Sassari (Italy) *Innovative and green perspectives of Iron (III) Trimesate Metal Organic Frameworks via Mechanochemical and Sonochemical approaches* |
| 16:50 - 17:00 | **FP4** | **Mrs. Zuharia Arshad** University College London (United Kingdom) Continuous Hydrothermal Flow Synthesis of Therapeutic Magnetic Nanoparticles |
| | | |
| 20:30 | **Social Dinner** | |

## 24th June 2022

| | | |
|---|---|---|
| **Morning Session** | | |
| **Chairperson**: Prof. Jawwad A. Darr, University College London (United Kingdom) | | |
| 9:00 - 9:40 | **PI2** | **Prof. Sanjay Mathur** University of Cologne (Germany) *Efficient Photon-harvesting Technologies for Water Splitting Reactions* |
| 9:40 - 10:00 | **OP8** | **Dr. Massimo Dell'Edera** Institute for chemical and physical processes, IPCF-CNR (Italy) *$CuO-CeO_2-TiO_2$ photocatalysts prepared in situ by Solution Combustion Synthesis for the efficient degradation of Methyl Blue and Nalidixic Acid under UV and Visible light* |
| 10:00 - 10:20 | **OP9** | **Mrs. Regina Del Sole** University of Bari (Italy) *Aerosol-Assisted Atmospheric Pressure Plasma Deposition of $TiO_2$/rGO nanocomposite coatings* |
| 10:20 - 11:00 | **Coffee break** | |
| 11:00 - 11:30 | **KN3** | **Prof. Simone Mascotto** University of Hamburg (Germany) *Self-regenerating supported metal nanoparticles for $CO_2$ conversion applications* |
| 11:30 - 11:50 | **OP10** | **Dr. Silvia Mostoni** University of Milano-Bicocca (Italy) *Porphyrin functionalized $ZnO/SiO_2$ hybrid nanoparticles as scintillator agents* |
| 11:50 - 12:10 | **OP11** | **Mr. Benjamin Rudolph** University of Hamburg (Germany) *Exsolution of Ni nanoparticles from nanostructured perovskite oxides for biogas reforming* |
| 12:10 - 12:30 | **OP12** | **Dr. Raffaella Soave** Institute of Chemical Science and Technology, SCITEC-CNR (Italy) *Ferrate salts as stand-alone catalysts for chemical fixation of $CO_2$ into epoxides and aziridines: a theoretical perspective* |
| 12:30 - 12:40 | **FP5** | **Mrs. Susanna Tinello** University of Padua (Italy) *Optimisation of a green synthesis of zinc oxide nanoparticles exploiting an algae-mediated biogenic approach* |
| 12:40 - 12:50 | **FP6** | **Dr. Giuseppe Dilauro** University of Bari (Italy) *Synthesis of Functionalized Oxygenated Heterocyclic Compounds via Mizoroki-Heck Coupling reaction in Deep Eutectic Solvents* |
| 12:50 - 13:00 | **FP7** | **Dr. Alberto Perrotta** Institute of Nanotechnology, NANOTEC-CNR (Italy) *Development of nanoporous ZnO layers derived from molecular layer deposition (MLD) hybrid polymers* |
| 13:00 - 14:00 | **Lunch break (Independent)** | |
| **Afternoon Session** | | |
| **Chairperson:** Prof. Simone Mascotto, University of Hamburg | | |
| 14:00 - 14:30 | **KN4** | **Dr. Íñigo Bretos** Materials Science Institute of Madrid, ICMM-CSIC (Spain) *Low-temperature strategies to induce the crystallization of metal oxide thin films by wet chemical methods* |
| 14:30 - 14:50 | **OP13** | **Dr. Sebastiano Campis**i University of Milan (Italy) *Synthesis and functionalization of sustainable hydroxyapatite-based materials for multipurpose applications in environmental protection* |
| 14:50 - 15:10 | **OP14** | **Mr. Rafal Lysowski** Wroclaw University of Science and Technology (Poland) *Selected spinel-based oxygen carriers for CLC application* |
| 15:10 - 15:30 | **OP15** | **Prof. Mauro Carraro** University of Padua (Italy) Halloysite nanotubes as scaffold for the support of nano-catalysts |
| 15:30 - 15:50 | **OP16** | **Dr. Federico Olivieri** Institute for Polymer Composite and Biomaterials, IPCB- CNR (Italy) *Smart nanocarriers based on mesoporous silica nanoparticles for the tailored release of corrosion inhibitors* |
| 15:50 - 16:10 | **OP17** | **Prof. Roberto Scotti** University of Milano-Bicocca (Italy) *Zinc single sites anchored on silica as curing activators for rubber* |
| 16:10 - 16:20 | **FP8** | **Mrs. Debora Carrozza** University of Modena and Reggio Emilia (Italy) *Synthesis and characterization of large-pore mesoporous silica structures* |

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|---|---|---|
| 16:20 - 16:30 | **FP9** | **Dr. Lorenzo Degli Esposti** Institute of science and technology for ceramics, ISTEC-CNR (Italy) *Use of Amorphous Calcium Phosphate as Innovative Precursor for the Synthesis of Hydroxyapatite Biomaterials* |
| 16:30 - 16:40 | **FP10** | ***Mrs. Sevasti Matsia*** Aristotle University of Thessaloniki (Greece) *Polymeric microparticle synthesis as advanced materials in Chronic Obstructive Disease therapeutics* |
| 16:40 - 17:10 | **Poster Award Ceremony – Closing remarks** |  |

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## Abbreviations

**PI** – Plenary lecture
**KN** – Keynote lecture
**OP** – Oral presentation
**FP** – Flash presentation
**P** – Poster presentation

**Page**

### Plenary lectures

### Keynote lectures

### Oral presentations

**Flash Oral presentations**

## Poster presentations

# Plenary Lectures

# Halide Perovskite Nanocrystals: Their Synthesis, Chemical, Structural, and Surface Transformations

Liberato Manna

Department of Nanochemistry, Istituto Italiano di Tecnologia,
via Morego 30, 16163 Genova, Italy

Halide perovskite semiconductors can merge the highly efficient operational principles of conventional inorganic semiconductors with the low-temperature solution processability of emerging organic and hybrid materials, offering a promising route towards cheaply generating electricity as well as light. Perovskites not only show exceptional primary optoelectronic properties such as a direct bandgap, small exciton binding energy, low carrier recombination rates, ambipolar transport, and tunability of the bandgap covering a wavelength range from the near-infrared to the ultraviolet, but they are also very attractive for their ease of processability for mass production (e.g. printing from solution) and for the large availability of their chemical components. Following a surge of interest in this class of materials, research on halide perovskite nanocrystals as well has gathered momentum in the last years. In such a narrow time span, several properties/features of halide perovskite nanocrystals were investigated, among them electroluminescence, lasing, anion-exchange, as well as control of size and shape. Important developments include doping, synthesis of Pb-free perovskite nanocrystals, and investigations of their rich surface chemistry, combining a variety of experimental techniques and computational approaches. The present talk will highlight the research activities of our group on halide perovskite and perovskite-related nanocrystals, with a focus on synthesis, as well as structural, chemical, and surface transformations.

# Efficient Photon-harvesting Technologies for Water Splitting Reactions

Sanjay Mathur

Chair, Inorganic and Materials Chemistry
University of Cologne, Greinstrasse 6, D-50939 Cologne, Germany
E-mail: sanjay.mathur@uni-koeln.de

Metal oxide nanostructures with hetero-contacts and phase boundaries offer unique platform for designing materials architectures for energy harvesting applications. As viable alternative to water electrolysis, photoelectrochemical (PEC) water splitting has emerged as a competitive technology being capable of converting solar energy directly into chemical energy using stable and efficient photocatalysts for solar hydrogen production. Besides the size and surface effects, the modulation of electronic behaviour due to junction properties leads to modified surface states that promote selective decomposition of analytes and adsorbates. The growing possibilities of engineering nanostructures in various compositions (pure, doped, composites, heterostructures) and forms has intensified the research on the integration of different functional material units in a single architecture to obtain new photocatalytic materials. Even though the potential of hematite thin films for water splitting applications are widely accepted, researchers are still tackling the 'rust challenge'. We report here on the influence of external magnetic fields applied parallel or perpendicular to the substrate during plasma enhanced chemical vapor deposition of hematite (α-$Fe_2O_3$) nanostructures. Hematite films grown from iron precursors showed pronounced changes in crystallographic textures depending upon whether CVD was performed with or without external magnetic field.

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[1] Eunhwan Jung, Kestutis Budzinauskas, Senol Öz, Feray Ünlü, Henning Kuhn, Julian Wagner, David Grabowski, Benjamin Klingebiel, Marie Cherasse, Jingwei Dong, Pierfrancesco Aversa, Paola Vivo, Thomas Kirchartz, Tsutomu Miyasaka, Paul H. M. van Loosdrecht, Luca Perfetti, and Sanjay Mathur *ACS Energy Letters* **2020** *5* (3), 785-792.

[2] Schütz, M.; Lê, K.; Ilyas, S.; Mathur, S., *Langmuir* **2020**, 36 (6), 1552-1558.

[3] Möllmann, A.; Bialuschewski, D.; Fischer, T.; Tachibana, Y.; Mathur, S., In Advanced ceramics for energy conversion and storage, Guillon, O., Ed. Elsevier Ltd.: Amsterdam, **2020**; pp 207 - 273.

[4] Luo, L.; Zhou, K.; Lian, R.; Lu, Y.; Zhen, Y.; Wang, J.; Mathur, S. *Nano Energy* **2020**, 72, 104716.

[5] Straub, M.; Leduc, J.; Frank, M.; Raauf, A.; Lohrey, T.; Minasian, S.; Arnold, J.; Mathur, S. *Angewandte Chemie International Edition* 2019, 5805-5809.

[6] Stadler, D.; Mueller, D. N.; Brede, T.; Duchoň, T.; Fischer, T.; Sarkar, A.; Giesen, M.; Schneider, C. M.; Volkert, C. A.; Mathur, S. *The Journal of Physical Chemistry Letters* **2019**, 10 (20), 6253-6259.

[7] Leduc, J.; Gönüllü, Y.; Ruoko, T.; Fischer, T.; Mayrhofer, L.; Tkachenko, N. V.; Dong, C.; Held, A.; Moseler, M.; Mathur, S., *Advanced Functional Materials* **2019**, 29 (50), 1905005.

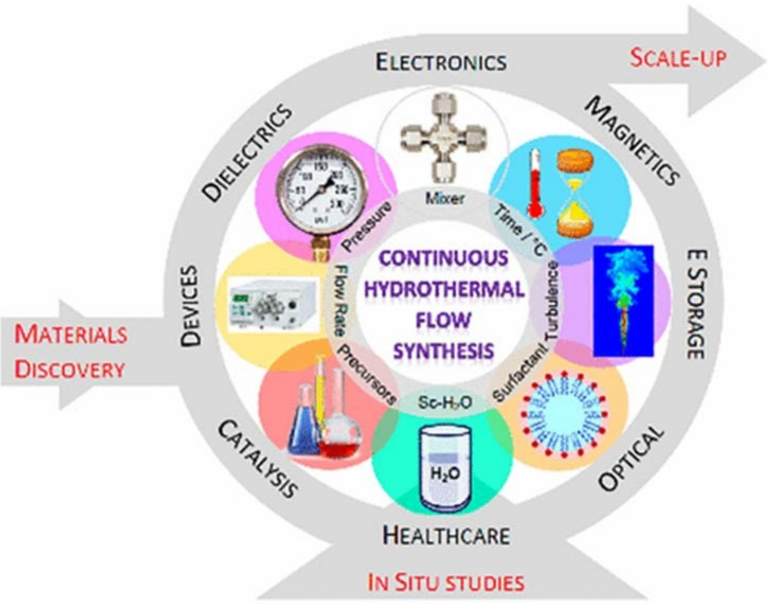
# Keynote Lectures

# Green Unconventional Supercritical Water Flow Routes to Energy Materials Discovery and Kg/h Scale-up

Jawwad A. Darr

Department of Chemistry, University College London, London, WC1H OAJ, UK
E-mail: j.a.darr@ucl.ac.uk

This talk will describe the collaborative endeavors of materials chemists and chemical engineers in the field of chemical and process engineering and nanomaterials discovery. A novel (unconventional) and green supercritical (sc-) continuous system will be described for making inorganic nanoparticles. Due to the exotic reaction conditions, this synthesis method enables the manufacture of nanomaterials that are difficult or impossible to make using more conventional synthesis techniques; directly giving highly crystalline doped nano-powders with very high surface areas (typically up to 300 m2g- 1). The process also allows rapid fabrication of nanomaterial libraries via a high throughput serial approach. The precise control of conditions in the flow system allows influence over product characteristics (e.g. size, shape, etc.) for use in a variety of applications from solid oxide fuel cell materials, battery materials, doped titanias (dielectrics and photocatalysts) and dispersible ceramics. The talk will begin with a discussion of some of the amazing properties of supercritical water as well as engineering principles for the continuous process (which allows smooth operation and efficient mixing) as well as guiding principles for scale-up to a pilot plant capable of Kg/h production of nanoparticles. A few case studies will be provided to show current and future applications of such energy materials, some of which could have early commercial potential.



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[1] See Continuous Hydrothermal Synthesis of Inorganic Nanoparticles: Applications and Future Directions. Darr et al Chem. Rev., 2017, 117 (17), 11125–11238

# Structural and Morphological X-ray Studies of Inorganic Nanomaterials

Cinzia Giannini

Institute of Crystallography, National Research Council,
via Amendola 122/O, Bari, 70126, Italy

In order to structurally and morphologically characterize novel materials, X-ray based techniques such as X-ray Diffraction – XRD, Small/Wide Angle X-ray Scattering - SAXS/WAXS, including the grazing incidence (GI) version - GISAXS/GIWAXS and Pair Distribution Function - PDF are typically used. The choice of the proper technique depends – as first - on the state of the materials, as they can be produced in powders (suitable for XRD and PDF), embedded in films and free-standing membranes (convenient for SAXS/WAXS), anchored on top of surfaces (proper for GISAXS/GIWAXS) or dispersed in liquids (to analyze via SAXS/WAXS). Additionally, micro and nano X-ray beams can be adopted to eventually explore the lateral heterogeneity of the materials or to map area of interest. As ultimate possibility coherent X-ray beams can be used.
An overview of the possibilities available in this field will be given [1,2,3,4], selecting specific examples of inorganic nanomaterials studied for different applications.

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[1] Altamura, D., Sibillano, T., Siliqi, D., De Caro, L. and Giannini, C. Assembled Nanostructured Architectures Studied By Grazing Incidence X-Ray Scattering (2012) Nanomater. nanotechnol., 2, Art. 16
[2] Giannini, C., Ladisa, M., Altamura, D., Siliqi, D., Sibillano, T. and De Caro, L. X-ray Diffraction: A Powerful Technique for the Multiple-Length-Scale Structural Analysis of Nanomaterials (2016) Crystals 6, 87
[3] Mino, L., Borfecchia, E., Segura-Ruiz, J., Giannini, C., Martinez-Criado, G., and Lamberti, C. Materials characterization by synchrotron x-ray microprobes and nanoprobes, (2018) Rev. Mod. Phys. 90, 025007
[4] Giannini, C., Holy, V., De Caro, L., Mino, L and Lamberti, C. Watching nanomaterials with X-Ray eyes: probing different length scales by combining scattering with spectroscopy (2020) Prog. Mat. Sci. 112 – 100667

# Self-regenerating supported metal nanoparticles for $CO_2$ conversion applications

Simone Mascotto

Institute of Inorganic and Applied Chemistry, University of Hamburg, 20146, Germany
E-mail: Simone.Mascotto@chemie.uni-hamburg.de

One of the nowadays biggest challenges is how to make use of $CO_2$ for the synthesis of higher value chemicals. With this respect $CO_2$ methanation and $CO_2$-mediated dehydrogenation of alkanes play an important role. Supported metal nanoparticles are fundamental to activate these reactions. However, during high-temperature and prolonged operation, these catalysts suffer from deactivation by sintering and surface coke poisoning. In the present paper, the synthesis of smart, regenerative supported metal nanoparticles obtained by cationic segregation from perovskite oxide supports is shown. High-temperature treatments under reducing atmosphere lead to reduction of metal dopants and the formation of strongly anchored nanoparticles. Upon oxidation, the exsolved metal nanoparticles dissolve back into the perovskite lattice as dopant (Fig. 1). The nanoparticles are then self-regenerated during a second reduction step. The same process applies also for bimetallic nanoparticles. We will show that by enhancing the porosity of the parental perovskite oxide we significantly improve the ionic transport and thereby the exsolution kinetics. This effect enables to achieve better control of size and distribution of exsolved Ni and bimetallic Fe-Ni nanoparticles. The combination of socketed, regenerating Ni nanoparticles within mesoporous perovskite supports lead to improved $CO_2$ conversion to methane with respect to non-porous and commercial catalysts. In case of bimetallic systems, the size decrease and the composition variation of Fe-Ni nanoparticles showed to increase ethane selectivity in the $CO_2$-mediated ethane dehydrogenation reaction.

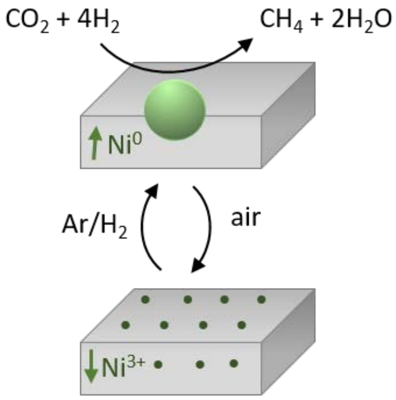

**Fig. 1: Representation of the exsolution process for the synthesis of regenerative anchored Ni nanoparticles**

# Low-temperature strategies to induce the crystallization of metal oxide thin films by wet chemical methods

Íñigo Bretos, Ricardo Jiménez, Jesús Ricote and M. Lourdes Calzada

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The versatility of wet chemical methods facilitates the exploration of novel crystallization pathways for metal oxide thin films and makes them fundamental in the development of low-temperature strategies for the preparation of advanced inorganic materials. The benefits obtained from decreasing the processing temperature (and hence the energy consumption) of the fabrication process span from minimizing the environmental impact to reducing the manufacturing cost of the product. More challenging is however the preparation of complex oxide layers at temperatures compatible with their direct integration into flexible systems using polymeric substrates (≤350 ºC). The high crystallization temperatures of the former materials (500-700 ºC) usually impede the development of electronic devices that take full advantage of the large variety of oxide functionalities available (electrical, magnetic and optical). Here, we present a number of strategies based on wet chemical methods for inducing the crystallization of metal oxide thin films at low temperatures.[1] The key mechanisms of these approaches are explained in relation to the specific step of the fabrication process that is promoted: the formation of a defect-free, highly densified amorphous metal– oxygen network or the actual crystallization of the metal oxide. Thus, low-temperature strategies such as (i) molecular design, (ii) heterogeneous photocatalysis, (iii) electronic photoactivation, (iv) combustion synthesis, or (v) seeding effect are particularly highlighted. Relevant examples derived from the direct growth of different oxide layers ($BiFeO_3$, $Pb(Zr,Ti)O_3$ or $Bi_2O_3$) on flexible polymeric substrates showing multiple functionalities (ferroelectricity, piezoelectricity, magnetism, photovoltaic effect or photocatalytic activity) will illustrate the most recent achievements reached in this field by our group.[2]

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# Oral Presentations

# Inkjet printing of thin chalcogenide semiconductor layers for solar cell applications

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A thin film solar cell based on $Cu(In,Ga)Se_2$ technology comprises six layers. The first n-type layer is known as the buffer and is often made of cadmium sulfide; where cadmium is toxic. Lower toxicity materials such as zinc oxysulfide and indium sulfide are investigated as alternative buffers. The standard buffer layer deposition techniques, namely chemical bath deposition and physical vapor deposition, are materially wasteful, in the sense that the layers deposited represent a small fraction of the actual material used. To eliminate this waste, we investigate inkjet printing and annealing as an alternative. We find compared to our standard chemical bath deposition that we can decrease the use of solvents and salts by a factor of 50 000 and 6500 respectively. We apply inkjet printing to the synthesis of $In_2S_3$ [1] and Zn(O,S) [2] buffer layers.
Indium and zinc chloride and thiourea were dissolved in a mixture of water, ethanol and propylene glycol to make the inks. These were inkjet printed onto the light absorbing layer to create the pn junction of the solar cell. The stacks were annealed in either nitrogen or air to synthesize either $In_2S_3$ or Zn(O,S) layers. The inks were formulated to jet as single drops and to have a low wetting angle on a sufficiently treated absorber layer.

Annealed $In_2S_3$ films had a S/In ratio of 1.4 & 1.3 as characterized by X-Ray photoelectron and electron dispersive spectroscopies (XPS, EDS) which is close to stoichiometric within the error of the measurements. XPS also showed residual C, N, O, and Cl within the layer. Grazing incidence X-Ray diffraction measurements showed crystal coherence lengths smaller than the Bohr exciton radius, leading to quantum confinement effects, namely larger band gaps. Tauc plots obtained from UV-Vis data confirmed higher band gaps than the bulk 2.5 eV value. A correlation between the band gap and the grain size was observed, depending on the annealing temperature, in-line with the Brus equation. Similar analyses have also been made for Zn(O,S).

Absorber layers with inkjet printed buffer layers were completed into full devices by the addition of i-ZnO, Al:ZnO and Ni/Al grids. Both $In_2S_3$ and Zn(O,S) showed higher light to electricity power conversion efficiencies than the CdS reference making them non-toxic, materially efficient, environmentally friendly alternatives.

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# Photoluminescence emission induced by localized states in halide-passivated colloidal two-dimensional $WS_2$ nanoflakes

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Engineering physicochemical properties of two-dimensional transition metal dichalcogenide (2D-TMD) materials by surface manipulation is essential to enabling their practical and large-scale application. This is especially challenging for colloidal 2D-TMDs that are plagued by the unintentional formation of structural defects during the synthetic procedure. However, the available methods to manage surface states of 2D-TMDs in solution phase are still limited, hampering the production of high-quality colloidal 2D-TMD inks. Here, we demonstrate an efficient solution-phase strategy to passivate surface defect states of colloidal WS2 nanoflakes with halide ligands, which results in the activation of their photoluminescence emission. Photophysical investigation and density functional theory calculations suggest that halide atoms enable the suppression of non-radiative recombination through the elimination of deep gap trap states and the introduction of localized states in the energy band structure from which excitons can efficiently recombine. Importantly, halide passivated WS2 nanoflakes retain colloidal stability and photoluminescence emission after several weeks of storage in ambient atmosphere, corroborating the potential of developed WS2 inks thereof.

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# Unveiling the impact of doping ions on aluminum oxide as automotive catalyst support

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In recent years more than ever, problems related to climate changes have become paramount for the whole planet. In particular air quality must be preserved, avoiding the introduction in the atmosphere of noxious gases, *e.g.* CO, $NO_x$. In this framework, the field of automotive catalysts plays a key role for exhaust gas abatement.

Alumina is an earth-abundant material that finds wide applicability as support for catalytically active nanoparticles to be stabilised against sintering. Alumina presents different crystallographic polymorphs, depending on structure and hydration degree.[1,2] The most common ones are $\alpha$-$Al_2O_3$ and $\gamma$-$Al_2O_3$, which are both employed due to enhanced catalytic activity endowed by thermodynamic stability and high specific surface area (SSA), respectively.[2,3]

The main topic of this work regards catalytic processes for exhaust gas abatement adopting $Al_2O_3$ as catalyst support for Precious Group Metal particles (PGMp), to achieve the oxidation of different exhaust gases, such as $NO_x$, CO and hydrocarbons.[4] In particular, this project aims at synthetising doped alumina by a sol-gel route, with the purpose of providing improved thermodynamic stability to $\gamma$-$Al_2O_3$ and of forming new anchoring sites for PGMp. After the optimisation of the synthesis of pure $\gamma$-$Al_2O_3$, doped alumina is prepared using varying amounts of zirconium, lanthanum and phosphate as doping ions. [5,6] The materials are characterised by XRD, BET, TEM, SEM-EDX for the determination of the crystal structure and to investigate the possible segregation of new phases due to the presence of doping ions, for the measurement of SSA, for the evaluation of the particles' morphology and for the quantification and distribution of the doping ions.

Eventually, to understand how the interaction between PGM and alumina varies with the presence of doping ions in the alumina structure, Pt-$Al_2O_3$ samples are prepared.

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# Geopolymer Based Catalysts and Oxygen Carriers for Application in Thermochemical Processes

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Thermochemical processes, such as hydrocarbon reforming or decomposition, oxy-combustion, solid fuels gasification, hot syngas cleaning and upgrading, etc., require the utilization of suitable catalysts or oxygen carrier in structured solid shape. The severe operation conditions, e.g. moved or fluidized beds, at temperature in the range 973-1273 K impose that the materials have excellent resistance to high temperature and mechanical stresses. Furthermore, in the view of a circular approach and sustainable economy the utilization of green and no-toxic raw materials is even more pursued.

Geopolymers are a class of synthetic inorganic polymers, produced at room temperature through a chemical activation process which involves the reaction of a solid alumino-silicate source with an aqueous alkali solution [1]. Geopolymers are ceramic materials in all respects, and as such boast excellent properties both in terms of chemical inertness, mechanical strength and high temperature resistance. They can be easily shaped to form monoliths, granules, disks, either dense or highly porous. Geopolymers have already been successfully developed to obtain nano-structured catalysts and oxygen carriers, through a one-step synthesis protocol [2].

The paper will report on recent progresses on utilization geopolymer based active materials in i) catalytic cleaning/upgrading of syngas; ii) oxy-fuel chemical-looping combustion, and iii) fluidized bed behavior. Catalytic cleaning of syngas is relevant for removing undesired heavy hydrocarbons (tar) before its utilization as fuel or reactant [3]. Oxy-fuel combustion via chemical-looping is a very efficient and clean technology, allowing generation of flue gas with high $CO_2$ concentration [4]. Fluidized bed technology is widely used for accomplishing processes requiring circulation of granular materials, e.g. catalyst, as well as high coefficients of heat and mass transfer.

The results of materials characterization and experimental tests carried out at laboratory scale will be presented and discussed, also in comparison with standard catalysts of the process industry, in the perspective of a green approach.

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# Nanostructures produced via Laser Ablation in Liquids

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Pulsed laser ablation in liquid (PLAL) or Laser Assisted Synthesis in Solution (LASiS) is getting an increasing interest for the production of various typologies of nanostructures because this technique needs a very simple set-up, it is possible to obtain high quality NPs, in terms of purity and size distribution, and it does not require stabilizers or chemical compounds for their growth and stabilization in solution. The basic mechanisms involved in the formation of NPs have been largely discussed in literature and although different hypothesis has been reported, what has been clearly demonstrated is that the PLAL techniques involves the following processes: Laser matter interaction [1], plasma induction and particle growth [2], the formation of the cavitation bubble and the releasing of nanostructure in solution [3]. In this work a detailed description of the chemical and physical processes involved in PLAL as well as the peculiar features of the produced NPs is discussed.

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# Bimetallic exsolution of Ni-Fe nanoparticles from perovskite oxides: an insight on mechanistic aspects through in-situ synchrotron measurements

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Bimetallic exsolution in perovskite oxides has recently developed increasing interest in heterogeneous catalysis for environmental and sustainable energy applications. This is related to the possibility of regenerating these materials through *in-situ* re-oxidation, and to the flexibility in tailoring catalytic properties given by the synergistic effects that lie behind the exsolution process of two or more metals. In this work, *in-situ* XANES and synchrotron XRD have been used for analysis on Ni-Fe doped, A-site deficient strontium titanates ($La_{0.4}Sr_{0.4}Ti_{0.60}Fe_{0.35}Ni_{0.05}O_3$), in order to investigate the processes of reduction and nucleation of metal nanoparticles throughout the exsolution process and the effect of the temperature on the kinetics of exsolution. This allowed to point out how the stages of reduction of the metal species (namely $Fe^0$ and $Ni^0$) and the nucleation/growth of the metal nanoparticles on the materials' surface constitute two separate yet interconnected processes. Moreover, the structural and catalytic properties of these materials can be modified by varying the exsolution conditions, such as temperature, treatment time and oxygen partial pressure. These assume major interest in many catalytic applications, in the light of the chance of regenerating metal nanoparticles when deactivated, by simply treating the materials at elevated temperatures under oxidizing atmosphere. In particular, we have studied the catalytic performance of the metal supported Ni-Fe nanoparticles with respect to dry ethane reforming and oxidative dehydrogenation of ethane (OED). The results demonstrated stable time-on-stream performances and good selectivity, and pointed out the possibility of acting on the exsolution operative parameters for tailoring the performances of the catalysts and their surface properties.

# Polymer-Assisted Perovskite Assembly

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Metal halide perovskites are among the most promising materials for next generation photovoltaics, combining a convenient solution processability at mild temperature and excellent power conversion efficiencies, as over 25% in lab-scale devices. [1,2] Nonetheless, finding a truly scalable manufacturing process and improving the durability of perovskite materials under operational conditions are the next technological challenges to be faced before perovskite solar cells can enter the market.

The inherent and main limitations interfering with perovskite solar cell large-scale production are related to a critical material deposition/reproducibility, as the film formation occurs throughout a complex self-assembly process driven by weak interactions.[3] Herein, we act on the perovskite material by using polymers as cooperative assembling component. The use of polymers with pendant hydroxyl/hydroxyethyl groups, which can interact with the perovskite precursors already in solution,[4] allowed to massively interfere with nucleation probabilities and growth rates of perovskite crystals, leading to the formation of compact and uniform film via a single straightforward coating step. We found that the organic polymeric nature and the non-covalent interactions between adjacent chains confers superior flexibility and moisture stability to the perovskite-polymer films, enabling the composite material to accommodate a strain, whilst maintaining transport properties suitable for devices, thus very attractive for flexible photovoltaics. A judicious polymer selection can in addition allow to modulate perovskite films transparency and improve its tolerance to thermal stress. [5]

Finally, we demonstrate that though the use of polymeric rheological modifier the viscosity of perovskite-polymer inks could be easily modulated and adapted to the requirements different up-scalable printing techniques. [6-9]

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# $CuO$-$CeO_2$-$TiO_2$ photocatalysts prepared *in situ* by Solution Combustion Synthesis for the efficient degradation of Methyl Blue and Nalidixic Acid under UV and Visible light

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The presence of pharmaceutical compounds in water systems and sediments is a major and worldwide environmental concern, which requires appropriate and eco-friendly technologies for effective degradation of such organic chemicals. Heterogeneous photo-catalysts have been widely investigated for water purification and $TiO_2$-based materials are among the most promising ones, although their effectiveness is limited to the ultraviolet region (< 380 nm), due to the large band gap energy (3.2 eV) for anatase. The combination of titania with other visible region-sensitive oxides is a viable strategy to enlarge the applicability of $TiO_2$-based photocatalysts. Ceria is well known for its redox pair $Ce^{3+}/Ce^{4+}$ which is advantageous for its application as photocatalyst. CuO has been also reported as a convenient promoter of the visible-light activity of $TiO_2$ catalysts.
The present work is an investigation of $CuO$-$CeO_2$-$TiO_2$ heterogeneous photocatalysts prepared *in situ* by Solution Combustion Synthesis (SCS) as effective systems for the degradation of Methyl blue and Nalidixic Acid under UV and Visible light, respectively, compared to commercial $TiO_2$ Aldrich, tested as a reference. Results of the structural, morphological, textural and redox analysis evidenced a significant synergistic effect played by the presence of both $CeO_2$ and CuO phases in contact with $TiO_2$.

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# Aerosol-Assisted Atmospheric Pressure Plasma Deposition of $TiO_2$/rGO nanocomposite coatings

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Among n-type semiconductors, $TiO_2$ is particularly valuable for different applications, such as electronic and optoelectronic devices, photocatalysis, photovoltaics and sensors. However, its wide band gap of 3.2 eV leads to a strong absorption only in the UV region and it is characterized by a fast electron-hole recombination rate during photocatalytic activity. Often, nanocomposites of $TiO_2$ with carbon nanomaterials, and in particular with rGO (reduced Graphene Oxide), are produced, in order to overcome all the limitations of $TiO_2$. Furthermore, the design and realization of $TiO_2$ nanostructured-based coatings represents a challenging task in many perspectives, though essential to make them suitable for environmental application.

In this scenario, we addressed the Aerosol Assisted Atmospheric Pressure Plasma Deposition (AA – APPD) of nanocomposite $TiO_2$/rGO thin films. Despite both, $TiO_2$ and graphene thin films have already been prepared by this technique, here for the first time the deposition of $TiO_2$/rGO nanocomposite films was investigated. In particular, different chemical compositions of the aerosol suspensions and the effect of carrier gas (He) flow rate were explored. Film chemical composition and morphology were characterized by means of XPS, Raman, FT-IR and SEM analyses. Eventually, nanocomposite coatings deposited on different substrates were tested for the photodegradation of methylene blue, and their photocatalytic activity was demonstrated and rationalized.

# Porphyrin functionalized ZnO/SiO$_2$ hybrid nanoparticles as scintillator agents

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ZnO nanoparticles (NPs) coupled with organic photosensitizers (PS, typically porphyrin) are potential candidate as scintillator agent for cancer treatment under X-ray, as they convert the X-ray into UV-Vis emission, promoting the PS excitation and the production of reactive oxygen species (ROS). Besides, its photostability and biocompatibility make ZnO suitable for in vivo applications. However, the efficient coupling of ZnO with PS is still a controversial issue, as it requires high ZnO luminescence yield, good overlapping of ZnO emission-PS absorption spectra, along with suitable ZnO-PS energy transfer.

In this perspective, the aim of this work is to design ZnO-porphyrin structures with high energy transfer efficiency for application in anti-cancer therapies and imaging that exploit ionizing radiations. Thus, the work focused on the development of porphyrin functionalized ZnO hybrid NPs anchored on SiO$_2$ NPs as carrier and on the investigation of their optical properties and ZnO-PS interaction, aiming at the understanding of the role of ZnO-PS proximity on their optical behavior.

The material synthesis was based first on the anchoring of ZnO NPs onto silica NPs, used as support and carrier; then, increasing amounts of PS (tetrakis(4-carboxyphenyl) porphyrin (TCPP) were covalently supported onto the surface of ZnO/SiO$_2$ NPs through a silane-grafting agent (3-aminopropyl)triethoxysilane, APTES) by using amino:TCPP molar ratios equal to 1:0,1, 1:0,25, 1:0,5 and 1:1. The structural and surface characterization confirmed the presence of amorphous ZnO NPs of 5-6 nm on SiO$_2$ surface, as well as the successful functionalization of ZnO/SiO$_2$ depending on the TCPP loading (0.3-3.0 wt% of TCPP over SiO$_2$). The Photoluminescence and Radioluminescence Analysis (PL, RL) revealed a high luminescence of ZnO NPs both under UV and X-ray irradiation. Besides, they enlighten the absence of non-radiative energy transfer between ZnO and TCPP, while a radiative one occurred, in which ZnO emitted photons are re-absorbed by TCPP. This energy transfer was not visible in a mechanical mixing of ZnO and TCCP, thus demonstrating that the optical interaction between ZnO and TCPP was partially achieved only upon functionalization.

In conclusion, this work paves the way to the deeper understanding of the correlation between the synthesis and the optical interactions of ZnO scintillator coupled with organic moieties and stimulate the further optimization of the structural and morphological features to improve their luminescence performances.

# Exsolution of Ni nanoparticles from nanostructured perovskite oxides for biogas reforming

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Perovskite-type oxides ($ABO_3$) systems were recently proposed for the in situ growth of metal supported nanoparticles as novel high performing catalysts in heterogeneous catalysis [1]. Perovskites possess the ability to easily incorporate catalytically active dopants forming $AB_{1-x}M_xO_{3-\delta}$ compositions. Subsequent exposition to reducing atmospheres ($Ar/H_2$) at high temperatures (≈ 900 °C) these metal dopants $M^{n+}$ are reduced and exsolved as highly dispersed nanoparticles strongly socketed in the perovskite oxide support. Nanostructuring represents a method to improve exsolution kinetics exploiting the smaller crystallite sizes and hence the shorter diffusion paths for charge carriers [2] [3]. In this way, faster nanoparticle growth at lower temperatures and higher catalytic reactivity are expected. Although nanoparticle exsolution is extensively studied, to the best of our knowledge, the effect of nanostructuring was poorly investigated so far. To study this concept the exsolution of Ni nanoparticles was examined for highly dense and nanoporous $La_{0.52}Sr_{0.28}Ti_{0.94}Ni_{0.06}O_3$ (LSTN), with specific surface area of 30 $m^2/g$. Reductions were performed from 900 °C down to 500 °C to thoroughly investigate the exsolution process. In comparison to sintered LSTN, exsolved Ni particles in nano-LSTN formed already at 500 °C. The early occurrence of the reduction process was demonstrated by $H_2$-TPR experiments, *in situ* electron microscopy, synchrotron XRD and X-ray absorption spectroscopy (XAS) studies. Nanostructured LSTN displayed nanoparticles of ca. 35 nm whereas in the sintered counterparts their size was ca. 30 nm. We found that the reduction process of Ni in nanostructured perovskites occured 200 °C earlier than in sintered materials without any loss of porosity during exsolution. Biogas dry reforming tests showed the superior catalytic performance of exsolved Ni from nanostructured LSTN. $CH_4$ and $CO_2$ were converted above 70 % and found 7 times and 2 times higher with respect to sintered systems and commercial $Ni/Al_2O_3$ catalysts, respectively.

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# Ferrate salts as stand-alone catalysts for chemical fixation of $CO_2$ into epoxides and aziridines: a theoretical perspective

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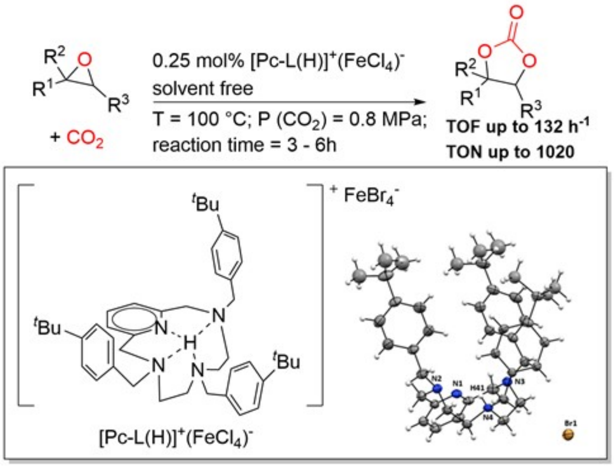
In recent years, the exponential increase of carbon dioxide ($CO_2$) emission in the atmosphere, as the terminal product of all the carbon-based process for energy production (i.e. burning fossil fuels), have become an alarming problem which threaten the whole environment [1] and the utilization of carbon dioxide as a feedstock for chemical production is becoming remarkably attractive [2].



Early results on the reaction of aziridines with $CO_2$ to yield oxazolidinones using ferrate catalysts are promising. DFT studies were performed to study the reaction mechanism. A plausible equilibrium between the ferrate $FeX_4^-$ and $FeX_3 + X^-$ in the neat epoxide could be responsible for the activity of this system, where the iron salt acts as a Lewis acid activating the epoxide and $X^-$ as a nucleophile for the ring opening reaction [3]. The straightforwardness of the synthesis and handling of these salts compared to their iron and ammonium precursors, the possibility to modify the cationic and the anionic part of these salts, added to their impressive reactivity, open up the possible use of these catalyst in the valorization of industrial flue gas.

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# Synthesis and functionalization of sustainable hydroxyapatite-based materials for multipurpose applications in environmental protection

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Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) is a bioavailable, multifunctional and sustainable material, which constitutes a valuable candidate for several applications in environmental remediation [1]. In the last years, our research group investigated the ion exchange and adsorption capacities of bare HAP materials, prepared through a green precipitation synthesis from aqueous solution of cheap and safe salt precursors, for application in water remediation [2]. Moreover, HAP surface properties can be also enhanced to boost performance or tailored to suit cutting-edge applications. Thus, metal-modified HAP samples as well as composite materials have been developed in our laboratories to obtain goal-oriented HAP-based materials, which will be herein presented. Hence, the precipitation of HAP in the presence of a biomass-derived carbonaceous material resulted in effective C/HAP composites, whose dual nature allowed one-step removal of organic/inorganic pollutants from water [3]. A similar synthetic approach was employed to produce chitosan/HAP composites with enhanced uptake capacity towards hexavalent chromium, a toxic water contaminant, which is scarcely retained by pure HAP. Alternatively, Cr(VI) removal has been addressed by reductive adsorption approach on tin-modified hydroxyapatite materials [4]. Specifically, Sn(II) or Sn(0) species have been immobilized at the HAP surface either by post-synthesis functionalization or one-pot co-precipitation. The introduction of tin species with reducing capacities allowed to convert Cr(VI) to Cr(III) at the HAP interface, even at neutral pH, with successive trapping of the formed Cr(III) at the HAP surface. When metal species having Lewis acid character and redox properties were deposited on the HAP surface by ion-exchange procedure, active and selective heterogenous catalysts were produced, showing promising results in several reactions for toxic air-pollutant abatement (i.e. reduction of $NO_x$, $N_2O$ decomposition). Lastly, multi-composites C/Cu/HAP demonstrated to be interesting electrocatalysts for the selective reduction of $CO_2$ (CO2RR) to formate as well as for microbial electromethanogenesis process.

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# Selected spinel-based oxygen carriers for CLC application

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Growing concern over climate change leads to a necessity of the developing, new and more environmental friendly technologies of energy production. One of the proposed technologies is Chemical Looping Combustion (CLC). During CLC process, fuel doesn't have direct contact with an atmospheric air. Which is reducing emission of thermal nitrogen oxides to almost zero, and, consequently, it is making sequestration of carbon dioxide from fumes much cheaper, in comparison to similar technologies like oxy-combustion. It is possible due to implementation of two reactor system (oxidizing and fuel reactor), with circulating in between them solid oxygen carrier (OC).

One of main issues that affect feasibility of whole technology is cost of oxygen carrier - a material that is used to transport oxygen into the fuel. To lower its cost different approaches have been proposed. One of them is to use mono-phase OCs based on metal oxides with promising properties. In presented research, spinel based oxygen carriers synthetized from iron and copper oxides. They were tested as suitable materials for application in CLC technology using Thermogravimetric analysis (TGA) and X-ray diffractometry (XRD).

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# Halloysite nanotubes as scaffold for the support of nano-catalysts

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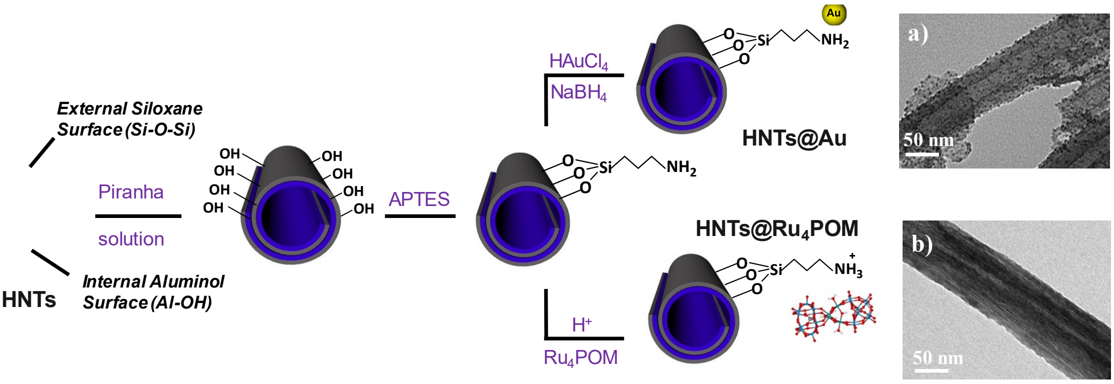
Halloysite nanotubes (HNTs) are aluminosilicates with formula $Al_2(OH)_4Si_2O_5{\cdot}nH_2O$ (n = 0 or 2) and tubular structures, with 20–200 nm external diameter, 5–50 nm cavity diameter, and 0.50–4.50 µm length. They are appealing for natural availability, low cost, high surface area. Moreover, both the exposed silica layer and the internal alumina layer can be functionalized, making them useful as nano-scaffolds or nano-containers. In this work, a pre-treatment with piranha solution has been optimized to increase both the surface area and the amount of exposed surface hydroxyl groups, so to foster the efficient grafting of organic pendants as 3-aminopropyl triethoxysilane (APTES). Two examples on the use of modified HNT will be presented: (i) the support of Au nanoparticles (NPs), for the reduction of 4-nitrophenol to 4-aminophenol by $NaBH_4$, and for the oxidation of furfural (converted into furoic acid) by $O_2$. The pre-treatment implements support efficiency (15.5 wt% higher loading), catalytic performance (>25% rate) and stability (up to 8 recycles) of Au NPs [1]; (ii) the grafting of a ruthenium substituted polyoxometalate ($Ru_4POM$), with the goal of using evolved $O_2$, resulting from the $Ru_4POM$-catalyzed $H_2O_2$ dismutation, as anti-fouling agent for water treatment membranes. To this aim, HNTs@$Ru_4POM$ are dispersed into polyether sulfone (PES), showing higher hydrophilicity, porosity and water permeability than the non-doped PES films [2].



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# Smart nanocarriers based on mesoporous silica nanoparticles for the tailored release of corrosion inhibitors

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Mesoporous silica nanoparticles (MSN) have been recently exploited as very promising nanoreservoirs/nanocarriers for the loading and the controlled release of anticorrosive agent for cultural heritage applications [1,2]. In this contribution, new results obtained on the synthesis of MSN and their engineering to maximize the loading and to tailor the stimuli-responsive release of corrosion inhibitors are reported. MSN were synthetized by a high-throughput synthesis and two different strategies were optimized to realize smart systems. In a first approach, after the optimization of the loading of MSN with benzotriazole (BTA), the loaded nanoparticles were treated with a silver salt to realize new MSN/BTA/Ag systems. These nanoparticles showed a pH-controlled BTA blocking/release mechanism that was dependent on the dynamic equilibrium of formation and dissolution of the BTA/Ag complex [3]. With a second approach, amino-functionalized MSN (MSN-$NH_2$) were reacted with benzoyl chloride (BC). With this method, the benzoyl groups were grafted onto MSN-$NH_2$ through formation of amide bonds, and the release of benzoic acid was controlled by pH changes. Both the engineered MSN were embedded in acrylic coatings that showed effective protection of metal substrates, potentially impacting on a wide range of applications.

*Acknowledgement.* This work has been supported by the Project RIPA-PAUN, financed by Regione Campania (POR FESR Campania 2014-2020, CUP B63D18000370007) and by the H2020 Project InnovaConcrete, financed by European Commission (G.A. n. 760858).

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# Zinc single sites anchored on silica as curing activators for rubber

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Sulphur vulcanization and the use of reinforcing fillers, such as silica nanoparticles ($SiO_2$ NPs), are used to obtain performant tires. Rate and efficiency of the industrial vulcanization process are enhanced by using activators (ZnO), accelerators (sulfenamides) and co-activators (fatty acids). [1] In this process ZnO plays a key role, promoting the formation of Zn (II)- sulfurating complexes during the first steps of the reaction, determining both the kinetic and the nature of the cross-linked products. However, the low affinity of ZnO towards the rubber entails its high consumption to achieve a good distribution in the matrix, leading to a non-negligible environmental impact. [2]

In this work, a possible alternative to the use of ZnO is proposed. The novel curing activator is based on Zn (II) single sites, directly anchored on filler surface, developed with the goal to increase the zinc availability and reactivity towards the polymer chains, thus reducing its amount in rubber materials. Zn (II) ions were anchored on the surface of $SiO_2$ NPs, through the coordination with different functional groups, to obtain double function fillers acting both as curing activators and reinforcing agents. Therefore, (3-aminopropyl) triethoxysilane (APTES), (3-Mercaptopropyl) trimethoxysilane, (N-[3-(Trimethoxysilyl) propyl] ethylenediamine) and a carboxyl-based silane, were chosen as functionalizing reactants to link, respectively, amino, thiol, etilendiamine and carboxyl ligands on the silica surface. The synthetic procedure includes the functionalization of silica particles by hydrolysis and condensation of the silane-grafting agents, followed by the reaction with a Zn (II) precursor. The chemical nature of Zn (II) single site-based activators was assessed by structural and morphological analyses, that demonstrated the formation of isolated zinc centers. The curing activators were used to vulcanize silica/isoprene nanocomposites (IR NCs), without using conventional activator ZnO. The results obtained demonstrated that the novel zinc single site-based activator promotes both higher vulcanization efficiency and good mechanical behavior, depending on the coordination of the surface Zn (II)-ligand complex, able to both stabilize Zn (II) centers and to further react with the curing agents, improving the kinetics of the process. These results are promising for the possible replacement of ZnO in the industrial production of tires.

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# Flash Oral Presentations

# Advanced Vanadium-Peroxido Materials in Sustainable Catalytic Systems

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Vanadium catalysts are nowadays a state-of-the-art field in research, mainly due to the importance of their structural, magnetic, optical properties, and potential applications in catalytic oxidation processes involving various organic compounds and their relevance in abiotic and biological systems. The mono and bis(peroxido)vanadium(V) compounds have been shown to transfer oxygen effectively, leading to the generation of valuable synthetic molecules, derived through oxidation with enhanced selectivity. The new synthetically derived, hydrolytically stable, and highly effective vanadium(V)- peroxido materials were characterized by elemental analysis, FT-IR, Raman, NMR spectroscopy in solution and the solid state, UV-Visible, cyclic voltammetry, thermal gravimetric analysis and (TGA), and X-ray crystallography. The physicochemical properties of the title materials were amply exemplified in their catalytic reactivity toward organic substrates through GC-MS-TIC and GC-FID methods [1-3], thereby emphasizing the importance of appropriately designed and synthetically isolated vanadium-peroxido species in catalytic reactivity at the abiotic and biological level with industrial interest.

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# Ag/Cu supported on $SiO_2$-$TiO_2$ oxides as potential antifouling systems: Characterization of chemical physical and rheological properties

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Marine biofouling is receiving a widespread concern from both the scientific community and the industrial parties owing to the environmental and economic impacts of shipping on aquatic ecosystem. The need to search viable solutions to tackle marine biofouling issues allowed the development of antifouling and anticorrosion coatings associated with the design of nanocomposite materials based on biocidal agents. The use of silica and titania as solid supports for Ag and Cu has been reported in the preparation of nanomaterials with antifouling and antimicrobial features. The choice of metal supported antifouling materials is based on their tunable surface properties combined with other intrinsic parameters that strongly depend on the metal loadings and preparation method. In the present work we propose a series of antimicrobial materials based on Ag- and Cu-active species on $SiO_2$ and $TiO_2$. The materials were easily prepared via the wetness-impregnation method of the metal precursors on the supports. Morphological and structural characterizations of the powder materials were performed. In parallel, coating films were prepared by mixing the above materials with a commercial polymeric matrix and deposited on metallic DH36 steel substrate for rheological properties investigation. Biological tests were carried out by monitoring the bacterial growth of Pseudoalteromonas sp., Alteromonas sp., Pseudomonas sp. through optical density (OD) measurements.

**Acknowledgments**: This work was supported by the Project: "SI-MARE" (Soluzioni Innovative per Mezzi navali ad Alto Risparmio Energetico" PO FESR 201412020, n. 08ME7219090182, CUP G48I18001090007).

# Innovative and green perspectives of Iron (III) Trimesate Metal Organic Frameworks via Mechanochemical and Sonochemical approaches

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Metal Organic Frameworks (MOFs) are porous coordination polymers consisting of organic-inorganic building units [1]. Among these structures, MOFs built on iron(III) and 1, 3, 5-benzenetricarboxylate (BTC or trimesate) have proven to be valid candidates to be applied in several fields, including catalysis, gas storage and separation, drug-delivery and protein immobilization [2]. This is mainly due to their high biocompatibility, low cost, redox behavior and stability in air, water and organic solvents [3]. We present here two green and innovative approaches for the synthesis of an iron(III) trimesate MOF at room temperature in a mild pH range, using either mechanochemical or sonochemical alternative methods. Traditional harsh acidic conditions were avoided, opening up novel perspectives for the application of this material as biocompatible support. pH effect in terms of microstructure, thermal stability and textural properties of the material was investigated. All samples showed similar microstructure and thermal behavior despite the use of different synthesis conditions. The material porosity has proven to be easily tunable varying the amount of base and, thus, the pH. Moreover, sonochemical synthesis led to the formation of a gel as the effect of cavitation [4]. The gel and monolithic states hold great promise, owing to providing a minimal mass transfer resistance and an increased gas adsorption capability, compared to powders [5]. This study pointed out how efficiently the synthesis of an iron(III) trimesate MOF could be tailored to biocompatible and green conditions, paving the way for numerous novel applications of this material.

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# Continuous Hydrothermal Flow Synthesis of Therapeutic Magnetic Nanoparticles

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Early detection and diagnosis of illness is an essential key to success in modern medical innovations and advancements. The controlled manufacturing of nanoparticles for healthcare applications (such as imaging techniques or cancer therapies), allows us to control properties such as toxicity, biocompatibility and bioaccumulation, as well as imaging properties in vivo.[1] Recently, there has been increased interest in developing routes to multifunctional nanoparticles based on magnetite ($Fe_3O_4$)[2] that can show enhanced performance for clinical applications, primarily medical imaging and hyperthermia. The development of such multifunctional materials is often lengthy and encounters many concerns including manufacturing of nanoparticles and lack of understanding the effects of dopants on the final properties.[1]

This presentation will showcase a material discovery approach[3] that allows structure-property-composition relationships to be developed in this field; the synthesis and optimization of multifunctional magnetite nanoparticles for potential use in niche healthcare applications will be discussed. This talk will cover the relationship between the phase purity of the iron oxide for a range of reaction parameters including choice of reagent, and number of dopants and additives.

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# Optimisation of a green synthesis of zinc oxide nanoparticles exploiting an algae-mediated biogenic approach

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In recent years, particular attention has been paid on the optimisation of synthetic pathways compliant with the principles of Green Chemistry for obtaining inorganic nanomaterials with relevant functional properties. For the synthesis of inorganic nanomaterials, biology provides exciting opportunities and solutions. A synthetic approach supported by the exploitation of the possibilities offered by nature is more cost-effective and environmentally friendly when compared to classical chemical and physical synthetic routes. [1,2] Within this framework, the current work focuses on a one-pot approach for the green production of zinc oxide nanoparticles using microalgae and microalgae's extract. Microalgae are microorganisms of choice in biotechnology thanks to their wide range of potential bio-applications responding to an economic, circular and eco-sustainable perspective. [3] Concerning zinc oxide, this inorganic system has attracted significant attention due to its wide range of applications, such as in electronics, optics and since this product is generally recognised as safe (GRAS) by the US Food and Drug Administration. Zinc oxide nanoparticles also find applications in biomedical systems and as an antimicrobial e.g., in food packaging. [2] Therefore, in order to investigate and evaluate the role of microalgae in the synthesis of this inorganic system, a rational approach through the systematic exploration of the experimental parameters landscape was applied (temperature, volume ratio between microalgae extract and $Zn^{2+}$ solution, microalgae species, molar ratio between $Zn^{2+}$ solution and NaOH). The micro- and nanostructures synthesised were characterised through different analytical tools from the structural, morphological and functional point of view. In view of applications of zinc oxide, antimicrobial tests were carried out to investigate the antimicrobial activities of zinc oxide nanoparticles synthesised through biogenic synthesis compared to zinc oxide nanoparticles synthesised without microalgae.

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# Synthesis of Functionalized Oxygenated Heterocyclic Compounds via Mizoroki-Heck Coupling reaction in Deep Eutectic Solvents

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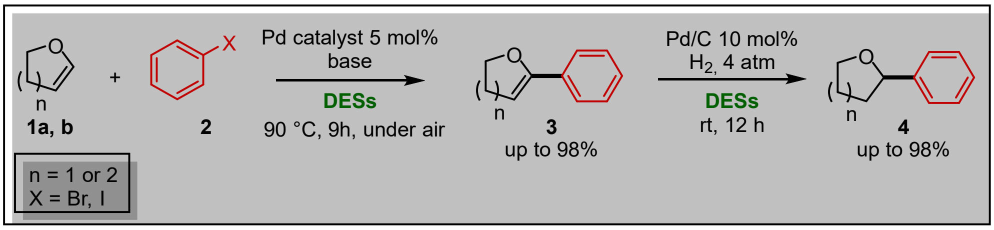
Oxygenated heterocyclic compounds are common structural motifs that are widely distributed across bioactive natural compounds.[1] Palladium-catalyzed Mizoroki-Heck (MH) cross-coupling processes have been proven to be powerful and useful tools for the functionalization of heterocycles containing oxygen, sulfur or nitrogen atoms, however often carried out in toxic and volatile organic solvents.[2] To the best of our knowledge, there are only a few reports on MH couplings run in environmentally friendly Deep Eutectic Solvents (DESs). Building upon previous findings from our research group on the use of unconventional reaction media such as DESs and water for catalytic cross-coupling reactions,[4–7] in this communication we report that 2,3-dihydropyrans and 2,3-dihydrofurans **1a,b** undergo regioselective Pd-catalyzed cross-coupling reactions with (hetero)aryl bromides and iodides **2**, under mild hydrous conditions in DESs, to afford adducts **3** in yields up to 98% (Scheme 1). The latter, in turn, have been successfully reduced in the same eutectic mixture to afford valuable 2-arylated saturated heterocycles **4** in yields up to 98% (Scheme 1).



**Scheme 1.** Mizoroki-Heck Coupling reactions in Deep Eutectic Solvents and functionalization thereof.

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# Development of nanoporous ZnO layers derived from molecular layer deposition (MLD) hybrid polymers

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Functional organic and inorganic thin films offer innovative solutions for a plethora of technological applications: organic electronics, smart (bio) devices, membrane technology, photocatalysis, sensors and drug delivery systems. The applicability of such thin films strongly depends on the versatility of the synthetic method in tailoring the chemical-physical properties of the materials. In this perspective, functional porous materials are gaining a fundamental role in nano-technology in a broad variety of fields, from catalysis to permeation membranes, from (bio)sensors to batteries. The implementation of simple methodologies for the engineering of controlled porosity and its characterization in thin films is not trivial, due to the intrinsic lack of control in pore content for the classical thin film fabrication methods.

In this contribution, the study of the "latent" porosity in hybrid polymeric thin films will be presented. The synthesis of nanoporous ZnO thin films is demonstrated through annealing of hybrid Zn-based polymers (zincone) obtained by molecular layer deposition (MLD). [1] Often referred as the organic version of atomic layer deposition, MLD allows the delivery of pure organic and/or hybrid polymers, with nm-level thickness control and excellent conformality. By controlling the organic content in the MLD polymers, [2] nanoporous ZnO thin films were obtained by calcination of the zincone layers. The removal of the carbon linkers, development of controlled and tunable nanoporosity, and formation and growth of ZnO crystallites were followed *in-situ* during calcination by spectroscopic ellipsometry, X-ray diffraction (XRD) and reflectivity (XRR). The combination of the *in-situ* methods allowed the identification of temperature windows for the formation of pores and ZnO crystallization. Mesoporous ZnO layers were delivered with controllable porosity in the range 13-25%, with pore size distribution between 3 and 6 nm as measured with ellipsometric porosimetry.

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# Synthesis and characterization of large-pore mesoporous silica structures

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Cancer is a leading cause of death worldwide, with 10 million deaths every year. The use of nanosized carriers seems appealing owing to their capacity to encapsulate drugs within their structure [1]. The synthesis of silica-based materials with porous structures, suitable for the confinement of theranostic substances and their delivery, has attracted a lot of interest in the last years. Mesoporous silica nanoparticles have been widely applied as carriers for cancer treatment, thanks to the possible loading, inside the structure, of interesting anticancer molecules [1]. Silica structures are interesting due to their biocompatibility and biosafety. Also bioactivity [2] can be achieved if $Ca^{2+}$ is included in the structure. Mesoporous silica with different porous structures can be synthesized using different templates (porous-genic agents) and starting by TEOS (tetraethyl orthosilicate) as a precursor of silica structure.

With respect to the classical way of synthesis [3], in which are obtained structures with mesopores in the range of 2-5 nm, a new way was followed. In this study, we have concentrated on the synthesis of large pores meso-structures, with the purpose of loading inside pores bigger molecules (compared to classic ones) interesting from a biological point of view (i.e. P53 plasmid). The synthesis were conducted in a large excess of the template, at high temperature and high pressure [4]. This synthesis pathway allows to obtain structures with mesopores in the range of 20-40 nm (figure 1).

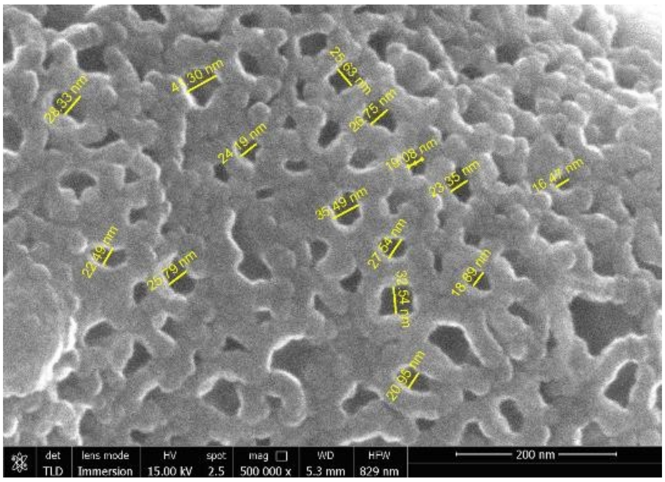

**Figure 1 – Large mesopores silica microparticles (LPMS)**

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# Use of Amorphous Calcium Phosphate as Innovative Precursor for the Synthesis of Hydroxyapatite Biomaterials

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Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) is a calcium phosphate phase widely used in medicine both in the form of particles as well as three-dimensional massive bioceramics or porous scaffolds thanks to is excellent biocompatibility, non-toxicity, and capacity to deliver bioactive ions and molecules. In this regard there is a high interest in drug-loaded HA bioceramics functionalized with antitumor drugs for filling the defects caused by surgical removal of bone tumor, regenerating bone tissue, as well as providing a continuous release of antineoplastic drugs. Therefore, there is a strong need to produce HA materials with tailored properties for specific applications, which in turn has prompt a great research work on controlling HA formation and crystallization. In our work we have used amorphous calcium phosphate (ACP, $Ca_x(PO_4)_y{\cdot}nH_2O$) stabilized by citrate and carbonate ions as precursor phase for unconventional preparation of HA. We have discovered that the thermal treatment our citrate-stabilized ACP uniquely yields ion-doped, biomimetic hydroxyapatite as pure product instead of other calcium phosphate phases yielded by classic ACP materials [1]. The perspective is to produce and sinter massive HA bioceramics for medical application though thermal treatment of citrate-ACP, allowing to obtain dense materials that at the same time preserve a high bioactivity. In this way, the bioactivity of the material would allow the functionalization with antitumor drugs while the thermal consolidation would provide good mechanical properties.

Acknowledgements. This work was supported by the Italian Ministry of Health (Bando Ricerca Finalizzata 2016, no. GR-2016-02364704).

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# Polymeric microparticle synthesis as advanced materials in Chronic Obstructive Disease therapeutics

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Chronic Obstructive Pulmonary Disease (COPD) is a disease that affects human lungs due to narrowing of the airways and destruction of lung tissue. COPD is known as the third leading cause of death on the planet and will be the fifth global burden worldwide by 2020 [1,2,3]. The purpose of this study is to design and synthesize biodegradable and bioavailable microparticles with a size range of 2-5 μm. In recent years, numerous studies have been conducted with biodegradable polymers, such as poly(ε-caprolactone) (PCL), poly(lactic acid) (PLA), poly(lactic-co-glycolic) acid (PLGA) and natural polysaccharides, such as chitosan, as micro-carriers [4,5]. PCL is a biodegradable polyester that decomposes gradually in water, providing a sustainable and controlled release. The structure and solubility resistance of PCL offer protection of the pharmaceutical agent until its release. In order to form the desired microparticles, oil in water (O/W) emulsions are produced using a series of stabilizers, such as Tween 80, Span 60, and whey protein isolate (WPI). The morphology and size distribution are studied using FT-IR, confocal microscopy, Mastersizer 3000, and TEM. UV-Visible spectroscopy was used for the investigation of drug release studies. Both particle size distribution measurements and particle observations under microscope show a size range of <5μm and a release of COPD drugs over 7 min.

## Acknowledgments

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# Poster Presentations

# Continuous and Scalable Production of Advanced Energy Materials

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The development of materials with specific, tailored functional properties continues to drive key technological advances, for example in energy materials. However, translating the synthesis of such materials from the gram scale in the lab to the kilogram scale is a critical technical challenge to realize their use in an industrial and/or commercial settings. Typically, lab-based synthesis routes of nanoceramic particles are not directly scalable, thus requiring an alternate route. This means that the gram scale materials discovery products and their scaled-up counterparts are rarely similar. Moreover, reducing the carbon footprint of these production methods is also key as many materials require long durations (≥ 8 h) at elevated temperatures (≥ 800 °C).

At UCL, we have developed a Continuous Hydrothermal Flow Synthesis (CHFS) assisted approach to (i) materials' discovery and (ii) scale-up of advanced ceramic and nanoceramic materials. CHFS is a directly scalable process utilizing supercritical water (450 °C, 240 bar) capable of producing many different smaller samples concurrently for materials' discovery (~2-20 g), up to large batches for scale up (> 5 Kg), in flow. In materials' discovery mode >50 samples can be produced in a few hours, allowing the intimate study of phase diagrams and structure property relationships (**Figure 1**).

CHFS can be used to produce either final nanoceramic products, or chemically homogenous precursors for further chemical or thermal treatment. Towards the latter, UCL have also developed a scalable post-processing methodology for high-throughput heat treatment (~400 g $h^{-1}$) of CHFS products. This has led to critical advances in materials processing for conventional Li-ion and solid-state battery materials.

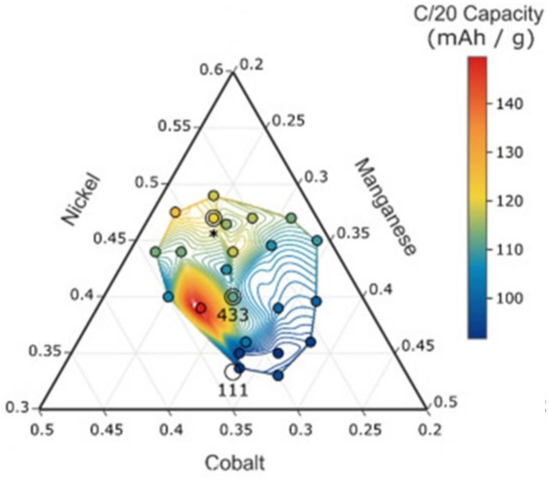

**Figure 1:** Ternary plot of composition versus gravimetric capacity for high-throughput NMC [1].

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# Rice husk derived carbon aerogels for supercapacitor applications

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Carbon aerogels (CAs) have gathered attention since their first fabrication in 1980s thanks to outstanding physical and chemical properties like low density, high conductivity, chemical stability, high specific surface and a 3D porous structure. These properties derive from the aerogel microstructure, which is a network of interconnected particles, and make CAs promising materials for many different applications, e.g., as adsorbents and supports for catalysis, electrodes for rechargeable batteries and supercapacitors. In particular, the latter are especially relevant devices in electrochemistry due to their high energy density, power density, and long life. [1]

CAs can be obtained from different precursors such as organic monomers, biomasses, polymers or carbon nanostructures like graphene or nanotubes. Regardless of the starting material, they are usually prepared in three steps, i.e. gelation, drying and carbonization. [2]

We are working on the possibility to build a light, stable and highly conductive CAs-based supercapacitor electrode made of cellulose purified from rice husk (RH).

RH is an agricultural waste that represents a green and virtuous source of carbon, being inexpensive, abundant, and eco-friendly. It is mostly made of cellulose (≈38%wt), lignin (≈22% wt), hemicellulose (≈18% wt), silica (≈20 wt% wt) and inorganic components. Due to its nontoxic nature and its good biodegradability, the use of cellulose to prepare CAs has already been reported. [1,3]

The process hereby presented involves a two-step pretreatment, respectively with NaOH and with $NaClO_2$ in acetic acid, aimed at the removal of silica, inorganic impurities and other carbonaceous components, i.e. lignin and hemicellulose. In order to form a gel, the purified cellulose thus obtained is dissolved in a solution of NaOH, urea and water at 0°C, then the gel is aged and regenerated with distilled water, freeze dried at -50°C for four hours and lastly carbonized in inert atmosphere.

Preliminary results obtained by testing our material as electrode pave the way to the application of rice husk cellulose derived CAs in supercapacitors and to different electrochemical devices.

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[3] Fuel 2010, 89, 913-933

# Pt-loaded, Se-doped Hydroxyapatite Nanoparticles with Potential Application against Bone Tumors and Metastases

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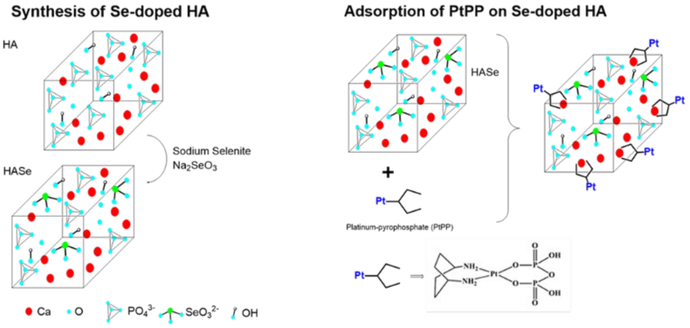
Treatment of primary bone malignancies comprises surgery, radiotherapy, chemotherapy, and analgesics. Bone metastases are the result of the progression of some tumors to bone. Since systemic antitumor chemotherapy can lead to severe side-effects, a strategy to overcome these drawbacks consists in delivering cytostatic drugs from locally implanted bone substitute materials. Among bone-filler materials, hydroxyapatite (HA) is well known for its biocompatibility and capability to load a wide variety of therapeutic agents. Moreover, a combination therapy with two or more drugs could offer the opportunity to synergistically improve the curative effect and overcome shortcomings of traditional chemotherapy.

Since platinum(II) compounds are well known antitumor drugs (*i.e.* cisplatin, carboplatin, and oxaliplatin), we have developed platinum-loaded, selenium-doped HA nanoparticles. A series of Se-doped HA nanoparticles with different Se concentration has been synthesized and characterized and then loaded with [Pt(dihydrogenpyrophosphate)(*cis*-1,4-DACH)] (DACH = diaminocyclohexane), a hydroxyapatite-binding antitumor Pt(II)-complex. The chemotherapeutic activity of the Pt-loaded, Se-doped hydroxyapatite nanoparticles has been tested *in vitro* against human prostate or breast cancer cells co-cultured with human mesenchymal stem cells[1].



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# Novel Mn-Based Metal Organic Framework Derived Metal Oxide And Their Application In Electrocatalytic ORR Process

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The hydrogen fuel cell offers immense potential for supplementing depleting renewal sources of energy best for its high calorific values as well as benign by product in the form of $H_2O$. The challenge lies with the sluggish oxygen reduction reactions (ORR) at the cathode thereby hindering its growth. With reference to kinetic values, platinum is best known catalyst for ORR, however its less abundance, high cost and corrosive nature warrants the development of low-cost catalyst. In an effort to develop efficient catalytic system for ORR, we synthesize porous $Mn_2O_3$ through carbonization of $[Mn_2(DOT)(H_2O)_2]_n$ (Mn-SKU-1) and $[Mn(H_2DOT)(BPY)]n$ (Mn-SKU-2) (DOT= 2,5-dihydroxyterethalate; BPY= 4, 4' bipyridine) metal organic frameworks (MOFs). These $Mn_2O_3$ derived from MOFs show high surface area and efficient catalytic activity for the ORR with onset at 0.85 V *vs* RHE (0.1 M KOH). Rotating disc electrode (RDE) and Rotating ring disc electrode (RRDE) experiments indicates nearly 4 electron reduction of $O_2$ to $H_2O$ with less than 5% $H_2O_2$.

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# Green-Graphene from agro-food waste: a sustainable chemical production technology

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In the view of Energy Transition, the intermittent nature of solar and other renewable energy sources requires the development of energy storage technologies not only able to provide high efficiency, but also being formed by environmentally friendly and low cost components. Several experimental works have demonstrated the potential of graphene as electrode material for devices like supercapacitors and batteries. However, synthesis of graphene by chemical vapor deposition (CVD) is not suitable for low-cost and large-scale production. On the other side, micromechanical exfoliation of graphite is a scalable synthesis methodology, but it involves hazardous and toxic reagents as well as graphite that is a critical raw material.

In this preliminary study, we propose a sustainable technique for the large-scale production of graphene by hydrothermal carbonization of natural sources like plant wastes from agriculture, reforestation actions, food waste, etc. that are usually discarded or delivered to land fills. Specifically, we set about exploring a Plasma-Enhanced Pyrolysis (PEP) process with focus to decrease graphene synthesis temperature as well as to provide both chemical surface functionalization and doping by heteroatoms. The electrical and structural properties of the as-grown *Green-Graphene* are presented.

# Low-temperature crystallization of solution-processed functional metal oxide thin films via hydroxyl free radicals

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Metal oxide thin films play an important role in our modern society, with applications that keep expanding, such as thin film transistors, sensors, actuators, ferroelectrics, superconductors, transparent electrodes or photovoltaics.

Among the methods used to fabricate high quality metal oxide thin films, Chemical Solution Deposition (CSD) is preferred over vacuum techniques, because of their low-cost, scalability and high deposition rate. The preparation of metal oxide thin films from solution methods usually involves the use of metal alkoxides, modified metal alkoxides and/or metal complexes as chemical reagents, in which the metal cation (M) is bonded to an alkoxide group (O – R) and/or to an organic ligand. Understanding and manipulating the chemistry behind the solution reactions provide opportunities to reduce the processing temperature in these films. Therefore, many researchers have recently attempted to develop novel low-temperature thin film solution processes, particularly for amorphous metal oxide semiconductor, but also, more recently, for high-performance crystalline metal oxides. Some of these works already show the significance that photochemistry has gained in the field of the low-temperature processing of metal oxide thin films.

In this work, we propose a photochemical strategy to generate very reactive $OH^{\cdot}$ radicals in the atmosphere in which solution deposited films are UV-irradiated. These radicals are able to react with the film material, triggering the hydrolysis and condensation reactions, and enhancing the formation of the amorphous metal oxide and its further crystallization at a low temperature. We demonstrate this hypothesis for ferroelectric oxide thin films, a type of inorganic materials that provide a wide range of functional properties of interest in multifunctional electronic devices.

This low-temperature solution processing method assisted by hydroxyl free radicals is applicable to the fabrication of thin films of all of the amorphous and crystalline metal oxide compositions. This fact provides new opportunities for the integration of high-performance functional oxides into the devices that are to come.

This work is part of the Spanish Project PID2019-104732RB-I00 funded by MCIN/AEI/10.13039/501100011033. I. B. acknowledges Grant RYC-2016-20047 funded by MCIN/AEI/10.13039/501100011033. A. Y. R. acknowledges the financial support of CAM, PEJ-2019-AI/IND-13396.

# Surface functionalization of 2D black phosphorus for catalysis and sensor applications.

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Since its discovery in 2014, exfoliated black phosphorus (2D BP) has attracted the interest of the scientific community thanks to its peculiar and relevant physico-chemical properties, being a natural semiconductor with a layer-dependent band gap, a high carrier mobility and a non-planar anisotropic structure.

The study of the functionalization of 2D BP with transition metal nanoparticles is of great relevance since it contributes to improve its ambient stability[1] and additionally opens a wide scenario of application going from heterogeneous catalysis to microelectronic devices. In our group, nickel[2] and palladium[3] nanoparticles were grown on 2D BP nanoflakes and the resultant nanohybrids behaved as highly selective catalysts in hydrogenation reactions. Additionally, FET (field effect transistors) were built by thin film deposition of the nanocomposite and showed superior sensing performance to ppb level for environmentally toxic gas.[4]

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# Hydrothermal Synthesis of New Iridium Pyrochlores

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Iridates with various crystal structures have previously been synthesised using mild, one-step hydrothermal synthesis under basic conditions at relatively low temperatures (<250 °C) without the need to purify the product.[1] These materials have application as electrocatalysts in the oxygen evolution reaction (OER) under acidic conditions [2] and may also have interesting magnetic properties.[3] The $A_2B_2O_7$ pyrochlore structure is known for various different A and B cations and several novel examples have been prepared using hydrothermal conditions, some of which cannot be accessed using traditional high-temperature synthesis methods.[4] In this work we have investigated the preparation of new compositions of iridate pyrochlore

The materials were synthesised hydrothermally at 240 °C for 4 days using $IrCl_3{\cdot}4H_2O$, $CaO_2$ and $KO_2$ in 10 M KOH solution. The synthesis of $(Ca,Na)_{2-x}Ir_2O_6{\cdot}H_2O$ and $(Ca)_{2-x}(Ir_{2-x},Nb_x)O_6{\cdot}H_2O$, a new composition of the pyrochlore with up to 20% Nb in the B-site by using $Nb_2O_5{\cdot}H_2O$ as the source of Nb, was successful. When replacing above 20% of the Ir by Nb, the product contains $KNbO_3$ and two pyrochlore phases. Lattice parameters from Pawley refinements against powder data show an increase in unit cell volume when Nb is in the B site. TEM images show the Ca, Ir and Nb are well dispersed within the materials, and XRF was used to perform bulk chemical analysis, giving Ca:Ir:Nb ratios as expected. The TEM shows the samples to contain small crystallites, around 10 nm in size. The pyrochlore materials retained their structure after an acid test using 1 M $H_2SO_4$ and no impurities were observed however the XRD patterns show changes in peak intensities and shifts in peak positions, which is consistent with elemental analysis from XRF that shows significant losses of Ca from the structure.

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# "Customized" phenols to introduce specific moieties in Metal Phenolic Networks

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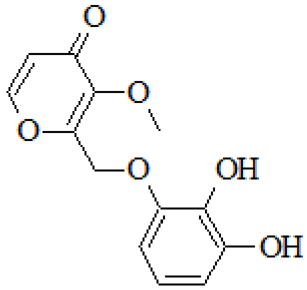
Metal-phenolic networks MPNs are supramolecular network structures consisting of metal ions coordinated with phenolic ligands. Recently, MPNs have attracted increasing attention for the engineering of multi-functional platforms because of their easy fabrication processes, attractive physicochemical properties and biocompatibility. One of the significant advantages of MPNs is that they adhere to several substrates, regardless of the size, shape and chemical composition, so.acting as coating materials for surface modification. [1] The multi-step mixing is an approach widely used to fabricate MPNs: it does not require special equipment and devices, the most common solvent is water and the reaction is carried out at room temperature. [2] Herein, the multistep assembly strategy was used to cover polystyrene substrates with MPN films obtained by using some common polyphenols (pyrogallol, caffeic acid, and L-DOPA), known for their ability to polymerize cross-linked by Fe(III). These materials have been widely characterized by many different spectroscopic techniques. In addition, a new maltol derivative (Scheme 1) was tested for its ability to grow a MPN for the first time. Modification of the phenolic ligands structure could represent a valid approach to design and prepare multi-functional MPNs.



Scheme 1

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# Screening of Pd and Ni supported catalysts for the production of renewable diesel

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Renewable diesel is a mixture of hydrocarbons, obtainable from deoxygenations reactions of bio-derivable fatty acids or triglycerides, and it represents a good candidate to substitute diesel from fossil fuel. In this work, the production of renewable diesel from a mixture of fatty acids, mainly palmitic (50.8% wt) and oleic (43.8% wt) acids, was investigated. Ni and Pd catalysts supported on different supports ($Al_2O_3$, $CeO_2$, $TiO_2$), with active metal loading equal to 2% and 5% wt for Pd and Ni, respectively, were synthesized by the wetness impregnation method and were tested for deoxygenation reactions, comparing their performances with that of a commercial 10% Pd/C catalyst, already proven to be efficient in the catalysis of such reactions. Higher conversions were evaluated for Pd catalysts with respect to Nickel catalysts: for the latter a maximum hydrocarbon yield of 10.0% wt was determined for Ni5%/ $CeO_2$. For Pd catalysts higher conversions (24.6-57.4% wt) and higher hydrocarbon yields (11.6-36.0% wt) were evaluated, with the highest values evaluated for the catalyst Pd2%/$TiO_2$. The detected hydrocarbons were mostly $C_{15}$ and $C_{17}$, suggesting that decarbonylation and decarboxylation were the predominant mechanisms; the main by-products were long-chain alcohols, obtained by the reduction of fatty acids, waxes, obtained from the esterification of these alcohols with unreacted fatty acids, and ketones, probably deriving from the dehydration of two acid molecules with anhydride formation and subsequent decarboxylation. With almost the same weight ratio between the active metal and fatty acids, a greater catalytic activity of Pd/C compared to Pd2%/$Al_2O_3$ and Pd2%/$CeO_2$ catalysts was observed, attributable to the fact that the absorption of long-chain fatty acids on carbon is more favoured than metal oxides. The interaction of fatty acids on carbon-based supports generally occurs through the alkyl chain; on the other hand, supports based on transition metal oxides can present both acidic and basic functionalities on the surface, generating electrostatic interactions with the carboxylic functionality of fatty acids, slowing down the subsequent decarboxylation process by the active metal species. With the use of Pd2%/$TiO_2$, higher yields in hydrocarbons were observed with respect to Pd/C, attributable to a greater dispersion of the metal center as well as to the interaction between the two metal centers, leading to an increase in the catalytic capacity of the Pd in the decarboxylation reaction. Modest yields in hydrocarbons have been obtained using the various catalysts, by using reaction conditions that were milder than those reported in the literature, in terms of pressure and catalyst amount. A further enhancement in the yield could be obtained by improving these conditions, making the use of Pd/$TiO_2$ promising for the production of renewable diesel.

***Acknowledgments****: This research was performed in the framework of the "Energy for Taranto- Technology And pRocesses for the Abatement of pollutaNts and the remediation of conTaminated sites with raw materials recovery and production of energy tOtally green (TARANTO)" project, funded by the Ministry of Education, University and Research, grant number ARS01_00637.*

# Study of the Antimicrobial Inactivation Assisted by Photocatalytic Mesoporous $TiO_2$ Nanoparticles

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Photocatalytic $TiO_2$ nanoparticles (NPs) are receiving a great deal of attention owing to their potential applications in environmental remediation. In particular, $TiO_2$ based nanomaterials are among the most studied materials in the field of photocatalytic antimicrobial applications, due to their ability in disinfection/inactivation of harmful pathogens (bacteria, fungi, and virus) [1, 2, 3]. Indeed, $TiO_2$ based antimicrobial nanomaterials can be effectively applied in water and air remediation, self-cleaning applications, cultural heritage protection, disinfection of biomaterials, and food packaging. The antimicrobial activity of this class of materials can be ascribed to their ability in photogenerating, under band-gap irradiation, reactive oxygen species (ROS), that can kill microorganisms in different matrices.

On these bases, an *in vitro* study was conducted to investigate the potential antimicrobial activity of mesoporous $TiO_2$ ($mTiO_2$) nanoparticles (NPs) synthesized by means of an original approach [4]. The inhibition activity was assessed against different microorganisms, namely *Escherichia coli*, *Enterococcus hirae*, and *Candida albicans*, used as model organisms, to evaluate any possible effect of their structural differences. The antimicrobial activity of the nanostructures was tested in an aqueous medium, under different experimental conditions, to single out the photocatalytic effect on the microbial inhibition process, using $TiO_2$ P25 (Evonik) as a benchmark catalyst. Furthermore, the process was monitored at increasing time (30, 45 and 60 min) by using plate count method. The antimicrobial activity was observed under UV irradiation. In particular, $mTiO_2$ showed enhanced inhibition performance on *C. albicans*, while *E. coli* and *E. hirae* were inhibited to a larger extent by $TiO_2$ P25.

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# Decorating $TiO_2$ Nanocrystals Seeds with PbS Quantum Dots

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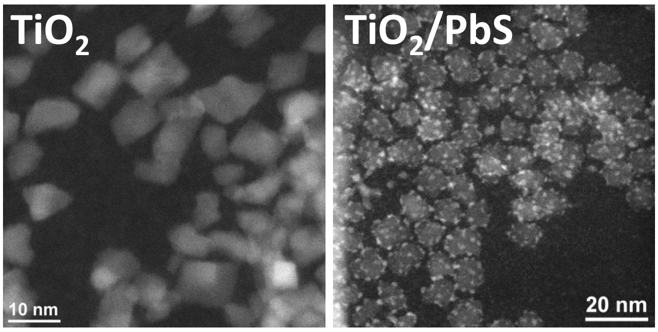
$TiO_2$ nanocrystals (NCs) have a well-known strategic role in environmental photo-catalysis and photo-electrochemical solar energy conversion. However, because of the wide band gap, this material can absorb almost only the ultraviolet region of the solar spectrum, *i.e.* less than the 5% of the total energy reaching Earth. Several approaches were proposed in the last decades in order to extend $TiO_2$ NCs photoactivity in a wider spectral range. A nano-chemical strategy has been investigated for this purpose. To enhance $TiO_2$ NCs photoactivity, sensitization with small lead sulfide (PbS) nanocrystals, which show peculiar size-dependent optical absorption in the near-infrared range [1], has been systematically studied. A seeded growth method combined with a hot-injection strategy has been ingeniously set up to prepare $TiO_2$/PbS hybrid structures under controlled experimental conditions, suitably defined to limit homogenous nucleation and favour heterogeneous nucleation [2].



We present structural, morphologic and spectroscopic evidence supporting the formation of small dots of PbS decorating the oleylamine surface capped $TiO_2$ nanocrystals under temperature control, offering useful insights for the design of new advanced inorganic materials with potential application in solar cell field for more efficient solar light harvesting and improved light conversion.

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# Biomass-Derived Carbon-Supported Calcium Oxide Nanostructures: Efficient and Eco-Friendly Catalysts for the Biodiesel Production from Waste Cooking Oils

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The development of new processes for the conversion of waste oils into biodiesel is one of the main challenges that must be addressed to make the biodiesel production more profitable and sustainable [1]. Calcium oxide is one of the most widely used catalysts due to its high catalytic activity and low cost, however leaching within the reaction medium, represent one of the most important reasons for its deactivation. To address this issue, the research has been focused on the improvement of catalytic performance of calcium oxide by anchoring it onto cheap inorganic or organic support. Carbon-based materials are considered as ideal supports due to their low cost, thermal stability and high surface area. In addition, these materials are eco-friendly, biodegradable and can be directly produced from waste biomass, thus reducing the environmental impact of biodiesel production.

In this work, nanostructured calcium oxides supported onto biochar obtained from the pyrolysis of avocado seeds were synthetized, fully characterized and tested as catalysts for the biodiesel production from waste cooking oils. The effect of calcium loaded on the structure and the catalytic activity was investigated. Elemental analysis, XRD, SEM, FTIR, BET, acid and basic sites were used for the characterization of carbon-based calcium oxides. Supported catalysts efficiently promoted the transesterification of oil with methanol, but compared to calcium oxide, they can be easily recovered and reusable for several reaction cycles without any loss of activity. Overall reaction kinetics has been studied with a pseudo-second order model with an activation energy of 39.9 kJ $mol^{-1}$. Thermodynamic parameters were also determined. Finally, a Box–Behnken factorial design of experiments was used to evaluate the influence of process variables and optimize the reaction conditions. By carrying out the reaction at 99.5 °C for 5 h with 7.3 wt% of catalyst and a molar ratio of methanol to oil of 15.6, a FAME content over 96% was obtained. Even starting from waste cooking oil, the final biodiesel was complied with the main EN14214 specifications.

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# Hybrid nanocomposites based on Reduced Graphene Oxide decorated with $TiO_2$ Nanocrystals for photocatalysis and antimicrobial applications

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Thanks to the large surface area, high chemical reactivity and excellent charge acceptor properties of the basal plane, graphene (G) derivatives are interesting scaffolds for chemically anchoring a high density of $TiO_2$ nanocrystals (NCs), thus resulting in nanocomposites with interesting photocatalytic and antimicrobial properties [1-2]. In this work, novel hybrid nanocomposites based on High Porous Reduced Graphene Oxide (HPRGO) and $TiO_2$ nanorods (NRs) have been synthesized, by means of an *in situ* colloidal route. HPRGO has been functionalized, by a non-covalent approach, with 1-pyrenil carboxylic acid (PCA), which features carboxylic groups acting as coordinating sites for NRs heteronucleation and growth, both assisted by oleic acid surfactant. The nanocomposites have been investigated by means of TEM, XPS, XRD, Raman and UV-Vis spectroscopy. The $TiO_2$ NRs, anchored onto HPRGO basal plane, are in anatase phase and have mean length and width of $20.0 \pm 1.7$ nm and $2.9 \pm 0.2$ nm, respectively. The photocatalytic and biocidal properties of the nanocomposites have been investigated and compared to those of bare PCA-HPRGO, $TiO_2$ NRs and commercial $TiO_2$ P25, by monitoring the degradation of methyl red (MR) under UV-light irradiation, of nalidixic acid (NA) under visible light irradiation, and the inactivation of *Escherichia coli* (*E. coli*) under both illumination conditions. The resulting UV-light induced MR photodegradation rate has resulted 4 times faster when assisted by PCA-HPRGO/$TiO_2$ NRs with respect to the $TiO_2$ NRs, whilst a negligible photodegradation of NA under Vis-light has been found. The antimicrobial tests under UV-light assess a biocidal activity of PCA-HPRGO/$TiO_2$ NRs due to ROS generation, whilst experiments in the dark have highlighted the occurrence of an intrinsic antimicrobial effect, induced by oxidative stress due to oxygen-containing functional groups of the G basal plane defects.

The authors acknowledge the projects: TRANSISTOR funded by INAIL (Bando BRIC 2019 ID:33), Italian PON (2014-2020) ECOTEC (ARS 01_00951), 'Multi-stacked intercalating hybrid PbS quantum dot film/graphene architectures for enhanced photodetectors' (Prot. MAE0065807, MAE00691402020-06-26) funded by MAECI and the TOOL bilateral CNR-MHESR (Tunisia) project funded by CNR.

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# Large-Scale MOCVD Deposition of Nanostructured $TiO_2$ on Stainless Steel Woven: A Systematic Investigation of Photoactivity as a Function of Film Thickness

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Heterogeneous photocatalysis is considered as one of the most appealing Advanced Oxidation Processes (AOPs) for the treatment of organic pollutants in water. However, its application into industrial practice is still very limited because of both the complexity of large-scale production of catalysts and the problems involved in handling the powder-based photocatalysts in the industrial plants. Here, the Metal Organic Chemical Vapor Deposition (MOCVD) process is used to prepare large-scale supported catalysts. Nanostructured $TiO_2$ thin film photocatalysts were deposited on a stainless-steel mesh substrate and the film thickness, the morphological features, and the crystallographic properties of the different portions of the sample were correlated to the position in the reactor chamber and the reaction conditions. The photocatalytic activity was evaluated according to the international standard test ISO 10678:2010 based on methylene blue degradation. A good photocatalytic activity was demonstrated, being essentially constant (PMB over 40 $\mu mol \cdot m^{-2} \cdot h^{-1}$) throughout the film, except for the portion of sample placed at the very end of the reactor chamber, where the $TiO_2$ film is too thin to react properly. It was assessed that a minimum film thickness of 250–300 nm is necessary to reach the maximum photocatalytic performance.

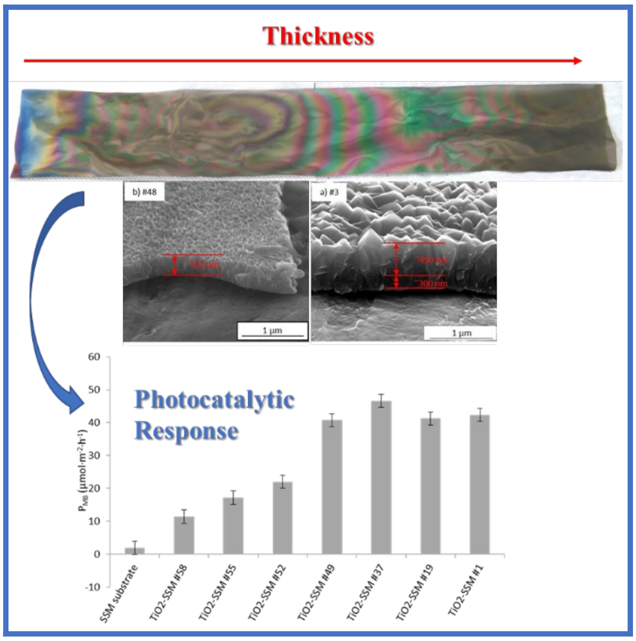

Figure 1. SEM morphology and photocatalytic properties as function of $TiO_2$ film thickness.

# Biocompatible encapsulating $TiO_2$ thin films deposited via Atomic Layer Deposition for neuronal interfaces

Naida El Habra[a], Alessia Famengo[a], Giacomo Sagrini[b], Patrizia Canton[b], Stefano Boldrini[a], Alberto Ferrario[a], Alessandro Galenda[a], Marta Maria Natile[a], Alessandro Leparulo[c], Marta Maschietto[c], Stefano Vassanelli[a,c]

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The development of smart implantable medical devices, focused to neuro-stimulation and/or recording with high resolution and long-term neuronal activity, are gaining a powerful importance in Neuroscience, aiming to a deep study of cerebral functions and treatment of pathological brain disorders. In the wider framework of bioelectronics, the present work tackles the urgent need of miniaturized interfaces between living and artificial systems, consisting of highly biocompatible materials for applications in smart biosensors for neurodegenerative disease treatments. Specifically, materials based on dielectric nanostructured $TiO_2$ thin films, conformally grown and highly surface encapsulating, are deposited via Atomic Layer Deposition (ALD). To evaluate the biomedical potential applications, neuron *in-vitro* biocompatibility tests of $TiO_2$ thin films are explored by cultivating neurons dissociated from rat hippocampi and monitoring their development and morphology in culture. The results show the deposited $TiO_2$ thin films are highly biocompatible: neurons present a homogeneous and stable development and morphology over time, in comparison to neurons cultivated on standard substrates. An in-depth study of the physical-chemical, surface activation, and biocompatibility properties of downscaled $TiO_2$ ALD-deposited films is investigated.

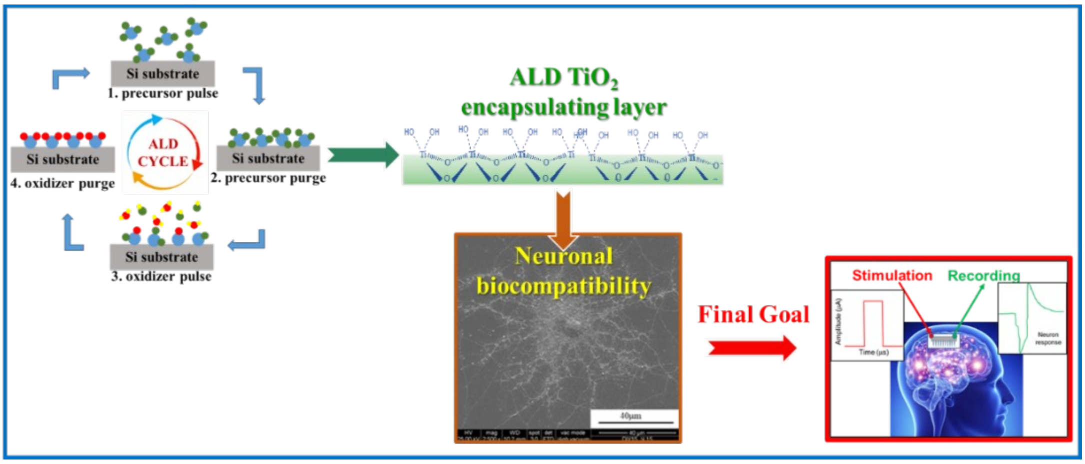

**Figure 1.** Schematic representation of the encapsulation process.

# A New Metastable Nanocrystalline Polymorphic Form of Diclofenac Acid by Manual Grinding.

Guido Ennas[a], Francesco Lai[b], Francesca Marongiu[b] and Alessandra Scano[b]

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2-(2-[(2,6-dichlorophenyl)amino]phenyl)acetic acid (DCF), also known as diclofenac acid (figure 1), is a molecule belonging to the category of nonsteroidal anti-inflammatory drugs (NSAIDs), which has analgesic, antipyretic and anti-inflammatory activity [1]. Two monocline polymorphic forms of DSC are well known: HD1 (space group $P2_1/c$) and HD2 (space group $C2/c$) [2]. In both forms, the molecules present centrosymmetric dimers linked by hydrogen bonds between the oxygen atoms of the carboxyl group. Of particular interest are the changes in the crystalline structure of polymorphs after the grinding process. In fact, such changes are usually strictly connected with solubility and dissolution rate, with the biological properties and the shelf life as well, which cannot be predicted from the properties of the parent drug [3].
X-ray Powder Diffraction, Fourier Transform Infrared Spectroscopy and Differential Scanning Calorimeter were used to study the effect of the manual grinding in an agate mortar of the diclofenac acid polymorphs HD1 and HD2. In particular, we have tried to highlight how the HD2 form is more sensitive than the HD1 to the grinding process to achieve a nanometric crystal size. HD1 shows no change, while in the case of the HD2, changes in the molecular conformation and the formation of a new metastable form of the polymorph are observed after grinding.

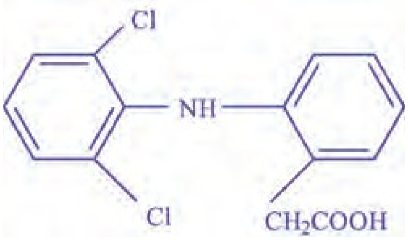

**Figure 1.** 2-(2-[(2,6-dichlorophenyl)amino]phenyl)acetic acid (DCF).

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# Hybrid Nanocellulose/$TiO_2$ materials for biomedical applications

Alessia Famengo[a], Naida El Habra[a], Andrea Riccioni[b], Elisabetta Schievano[b] , Tommaso Carofiglio[b]

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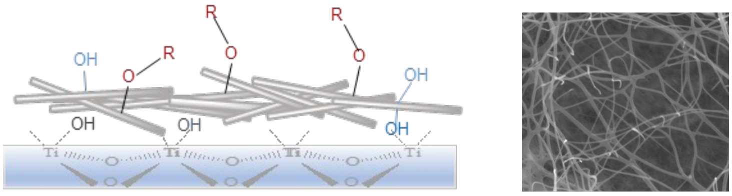
The functionalization of inorganic surfaces such as Si or metal oxides ($SiO_2$, $TiO_2$, $Nb_2O_5$) has since long been considered a key step for the design of biocompatible materials promoting specific cell growth with non-fouling properties. Particularly prone to bioconjugation because of the high –OH content of its sugar backbone, cellulose possesses an excellent biocompatibility, large availability from sustainable sources, and very low toxicity. In this work, bio-cellulose with nanoscale dimensions, i.e. Crystalline Nanocellulose (CNC) was chemically modified and processed in order to deposit CNC-based layers onto $TiO_2$ thin films. CNC hydrogels were chemically characterized via $^{13}C$ Solid State Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy (MAS-NMR), Thermogravimetric Analysis (TGA), Infrared Spectroscopy (FT-IR) and Zeta Potential to check the presence of COOH functional groups while the morphology of the NCC-based thin films was investigated via Scanning Electron Microscopy (SEM).



**Activated CNC on $TiO_2$ surfaces**

# Controlled synthesis and characterization of 0-1-2-3 dimensional $SnO_2$ nanocrystals

Mariangela Giancaspro[a,b], Marica Tancredi[a], Teresa Sibillano[c], Cinzia Giannini[c], Antonella Milella[a,d], Rachele Castaldo[e], Gennaro Gentile[e], Marino Lavorgna[f], Antonino Madonia[b], Annamaria Panniello[b], Maria Lucia Curri[a,b], Marinella Striccoli[b], and Elisabetta Fanizza[a,b]

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In recent years, tin dioxide ($SnO_2$) has been considered a promising low-cost functional metal oxide material for application in the field of energy conversion, environmental remediation, and sensors.[1] Physical-chemical properties of this semiconductor oxide strongly depend on morphology, structure and surface characteristics and can be modulated by purposely selecting the synthetic route. Although various synthetic strategies, often based on colloidal chemistry, have been employed to prepare $SnO_2$ nanocrystals (NCs) with different geometry and size, the mechanism underlying the NC formation and the growth kinetic are still not fully understood. In this regard, this work is focused on the synthesis of $SnO_2$ NCs via two synthetic approaches, precipitation and hydrothermal methods, aiming at establishing the reaction condition suitable to provide 0D quantum dots, 1D nanorods, 2D nanosheets, to 3D hierarchical nanostructures. The role played by the synthetic methods, the nature of base (NaOH or $NH_4OH$) and the reaction pH and temperature on the structure, morphology and optical properties has been systematically investigated thus significantly contributing to the rational understanding of the growth mechanism. The comprehensive characterization of the obtained nanostructures enable the identification of the most appropriate synthetic approach to achieve the NCs with the most suited properties for their different technological applications

*Acknowledgement.* The work has been supported by PON R&I 2014-2020 project code ARS01_00951 “ECOTEC” and ARS01_00519 “BEST-4U” the National Projects.

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# Novel synthetic pathway for antimicrobial hybrid nanocomposites based on Reduced Graphene Oxide decorated with Ag Nanoparticles

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Hybrid nanocomposites based on graphene (G) and inorganic nanoparticles (NPs) have attracted increasing interest for technology applications due to the multiple 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 [2]. On the other hand, colloidal inorganic NPs are characterized by original size and shape dependent properties and a surface coating layer that endows them for an interesting surface chemical reactivity, which can be further engineered. In this work, novel hybrid nanocomposites based on Ag NPs decorated Reduced Graphene Oxide (RGO) flakes have been synthesized by a facile *in situ* colloidal approach in aqueous solutions. Initially, RGO has been exfoliated and functionalized with the aminoacidic histidine (His), a biocompatible aromatic linker capable to bind RGO via π-π interactions and the Ag NPs by means of coordination bonds. The Ag NPs have been synthesized onto the His-RGO sheets from aqueous solutions by reduction of silver nitrate ($AgNO_3$) with trisodium citrate ($C_6H_5O_7Na_3$) and sodium borohydride ($NaBH_4$). An exfoliating step has been performed on the RGO sheets in His solutions at different pH subsequently the Ag NPs have been synthesized at different pH, RGO:$AgNO_3$ w/w and $AgNO_3$:$C_6H_5O_7Na_3$ and $NaBH_4$:$C_6H_5O_7Na_3$ molar ratio. An investigation of the spectroscopic and morphologic characteristics of the prepared nanocomposites has been performed by means of UV-Vis absorption and Raman spectroscopy, TEM and SEM-EDS in order to identify the most suited conditions for optimizing the coating density of the sheets with Ag NPs. The obtained His-RGO/Au NPs nanocomposites show a good colloidal stability in water and reveal an effective exfoliation of the His-RGO sheets, that result coated by spherical Ag NPs ca. 24 ± 4 nm in size and exhibit a LSPR absorption at 366 nm, thus resulting promising for antimicrobial and optoelectronic applications.

The authors acknowledge TRANSISTOR funded by INAIL (Bando BRIC 2019 ID:33), PON Ricerca e Innovazione (2014-2020) ECOTEC (ARS 01_00951), 'Multi-stacked intercalating hybrid PbS quantum dot film/graphene architectures for enhanced photodetectors' (Prot. MAE0065807, MAE00691402020-06-26) funded by MAECI and TOOL bilateral CNR-MHESR project funded by CNR.

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# Aminopropylsilica-based materials containing tris(catecholato)silicate moiety from hydrolysis of 3-ammoniumpropylbis(catecholato)silicate

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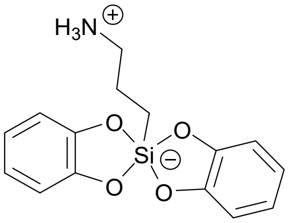
The chemistry of catechol and silicon is very intriguing. As an example, the structure of the simple bis(catecholato)silane has been debated since 1951 [1] and only in 2021 a detailed discussion about its structural features has been reported [2]. Here we describe the hydrolysis of 3-ammoniumpropylbis(catecholato)silicate **1** giving two different silica- based materials containing different amount of the tris(catecholato)silicate moiety [3]. The latter moiety is formed via transformation of the pentacoordinated silicon compound to hexacoordinated silicon compound with the concomitant Si-C bond cleavage. As far as we know, this transformation has not been described before and, given the importance of silica-based organic-inorganic hybrid materials, it could add further knowledge to silicon chemistry.



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# Silicon/carbon composite anodes from rice husk for lithium-ion batteries: optimizing the Si/C ratio to enhance battery performances and durability

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Rice husks (RHs), the outer covering of rice kernels, is an abundant agricultural byproduct that can be reused, among other applications, as anode materials for lithium-ion batteries (LIBs). RHs can be a source of both carbon (from the organic constituents like cellulose, hemi-cellulose, and lignin), and silicon, as RHs are naturally rich of hydrated silica (~ 20% wt). [1] As anode material for LIBs, Si has a theoretical capacity ten folds that of standard graphite electrodes (~ 3500 mAh/g *vs*. 372 mAh/g), but it is subjected to huge volumetric expansion upon lithiation (> 300% for bulk Si) which leads to high mechanical instability and thus a very short battery life cycle. Compositing Si with C is an effective route towards mechanical stability while also increasing the anode conductivity. [2]

Our main scope is to obtain Si/C composite anodes for LIBs with an optimized Si/C ratio in order to enhance the battery performances and life cycle. The raw RH undergoes three different reactions to obtain the composite material: an acidic pre-treatment, a carbonization process, and a low temperature magnesiothermic reduction (MgR).

Different acidic pre-treatments ($HNO_3$, $H_2SO_4$) have been performed at reflux with varying reaction times (1h, 2h and 4h) and acid concentration (16 N, 8 N and 4 N) to assess their effects on the final Si/C ratio and on the composite structure. Preliminary results show that $HNO_3$, also having a strong oxidizing activity against C, gives the highest Si/C ratios.

Carbonization at ~800°C in argon atmosphere allowed for the reduction of residual organic components to carbon.

For the MgR, we mixed the Mg powder with a eutectic mixture of $AlCl_3$ and NaCl, which has been proved to allow for low temperature MgR (as low as 200°C) [3], thus leading to a double advantage: saving energy and reducing the risk of undesirable side reactions.

The obtained materials have been characterized (*e.g.*, by scanning electron microscope energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy and Brunauer–Emmett–Teller surface analysis) and electrochemically tested in a half-cell configuration.

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# Solar-driven photocatalytic removal of sulfonamides from the aquatic environment - Comparison of the efficiency of selected photocatalysts

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Titanium dioxide ($TiO_2$) is the most common photocatalyst used for the micropollutants degradation, including pharmaceuticals, from the environmental matrices. Zinc oxide (ZnO) is recently mentioned to be an alternative to $TiO_2$ for environmental applications. However, there is still a lack of information on its operation efficiency, especially in more complex matrices. This study aimed to compare the efficiency of $TiO_2$-P25 and ZnO in the removal of selected veterinary sulfonamides (SAs), namely: sulfadiazine (SD), sulfamethoxazole (SMX), and sulfamethazine (SMZ) spiked in distilled water (DW), river water (RW), and municipal wastewater effluent (MWWE).

SAs were low-degraded by the photolysis in all studied matrices, their removal efficiency did not exceed 42%, 50%, and 38% in DW, RW, and MWWE, respectively. The complete removal of SAs from DW was observed after 20 min in $TiO_2$-P25-based photocatalysis and after 30 min in the ZnO-based photocatalysis. However, in the case of the environmental matrices, the degradation of SAs was lower than in DW. After 90 min of the $TiO_2$-P25-based photocatalysis, the removal efficiency did not exceed 48% and 38% in RW and MWWE, respectively. The ZnO-based photocatalysis was more efficient in the degradation of the target SAs, and removal efficiency was up to 89% and 75% in RW and MWWE, respectively. Doubling the photocatalyst dose increased the efficiency of removal of target SAs up to 61% and 98% in RW, and up to 81% and 99% in MWWE for $TiO_2$-P25 and ZnO respectively. The removal of the studied SAs decreased in the following order: SMT > SD > SMX.

$TiO_2$-P25 has been found the most efficient photocatalyst to remove target antibiotics from DW. However, in the case of the environmental matrices (RW, MWWE) more efficient photocatalyst in the degradation of studied SAs was ZnO. Due to its lower cost than $TiO_2$-P25 and high removal rate obtained for the environmental matrices, ZnO is a promising photocatalyst and could be used as an alternative to $TiO_2$-P25 for environmental purposes.

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# Oxygen carriers as examples of advanced inorganic materials-synthesis and structural analysis

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Chemical looping combustion is a novel, low-emissive technology of energy production.
Due to application of two fluidized bed reactor system (air and fuel reactor) with called oxygen carrier (OC) circulating in-between. Since fuel is not in direct contact with atmospheric air, formation of nitrogen oxides in combustion process is reduced almost to zero. Oxygen carrier is a material composed from one or several metal oxides suitable for releasing and receiving oxygen in certain conditions like temperature or oxygen partial pressure change. Since price of OC is an important economic factor for applying that technology in practice, it is necessary to produce these materials at low possible cost. Very promising route is solid state synthesis of OC from metal oxygen precursor(s) by mechanical mixing and calcination in high temperatures. It more cheaper and environmental friendly in compare to other methods e.g. sol-gel synthesis.
Furthermore, solid state synthesis allows to obtain both multicomponent OC containing different mixed metal oxides or single component oxygen carriers (for example spinel or perovskite type). Synthetized materials were examined using X-ray diffractometry, while Rietveld refinement was applied to determine crystal structure and composition.

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# Green synthesis of multifunctional MIL-100 for $CO_2$ cycloaddition to epoxides

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MIL-100 is a widely used Metal-Organic Frameworks (MOFs) obtained via reaction of trivalent metal ions (e.g. $Fe^{3+}$, $Cr^{3+}$ or $Al^{3+}$) and trimesic acid. It has large pores (of 25 and 29 Å), a well-developed specific surface area (of ca. 2000 $m^2/g$) and high thermal resistance (up to 623 K). Due to these features, MIL-100 exhibits high catalytic activity in many reactions [1,2], for example in cycloaddition of $CO_2$ to epoxides resulting in cyclic carbonates, that are used, e.g., in the pharmaceutical and chemical industries [3]. However, the applicability of unmodified MIL-100 in the $CO_2$ conversion is limited due to the lack of the active sites having basic character.
The synthesis of MIL-100 is usually carried out at high temperature (160 °C). In this work, we report the successful, green synthesis of modified MIL-100(-$NH_2$), that was conducted in an aqueous solution at room temperature. The obtained material was subjected to detailed physicochemical characterization including XRD, $N_2$ and $CO_2$ sorption, SEM(EDS), TEM, XPS, FTIR, and TGA. Its catalytic performance in the $CO_2$ cycloaddition to epoxides was also determined.

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# Plasmo-chemical method for deposition of photocatalytic nanocomposite coatings for environmental applications.

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Photocatalysis is known among the advanced oxidation processes (AOP) to generate in water reactive oxygen species (ROS), such as $OH\cdot$ and $O_2\cdot^-$ radicals, that can degrade the organic pollutants [1]. $TiO_2$ is the most used catalyst for this application given its low toxicity, low cost, high chemical stability and high efficiency [2].

This work presents the deposition of photocatalytic nanocomposite coatings formed by $TiO_2$ nanoparticles (NPs) embedded in a nanometric layer of organic matrix. The deposition has been performed by aerosol assisted atmospheric pressure plasma fed with He and a suspension of $TiO_2$ nanoparticles in a mixture of hexamethyldisiloxane (HMDSO) and isopropyl alcohol (IPA). This type of approach has been already used to deposit $TiO_2$-based coatings, however their actual photocatalytic activity has been rarely documented [3-6]. Here a stainless-steel mesh has been used as a support, being particularly suitable for its integration in water treatment reactors.

The photocatalytic activity of the coatings obtained under different experimental conditions, namely deposition time and possible post deposition plasma treatment has been tested under UV light for the degradation in water of methylene blue (MB), used as model molecule for organic pollutants. Deposition time of 3min ($TiO_2$-3m) and 20min ($TiO_2$-20m) resulted in +22±3% and +39±3% MB degradation after 90min irradiation if compared to photolysis alone. The possible effect on photocatalytic performance of an $O_2$ plasma post-deposition (-P) on the obtained coating has been also investigated. Interestingly, an increase in the photocatalytic rate has been observed in both cases, reaching +35±3% and +49±4% (compared with photolysis) for $TiO_2$-3m-P and $TiO_2$-3m-P, respectively. The photocatalytic activity of the coatings has been found stable over at least 5 cycles of use, making these coatings very promising for water treatment applications.

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# Morphological changes in metal mixed oxygen carries examined using SEM-EDS method

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Chemical Looping Combustion (CLC) is a new, emerging technology of fuel combustion. During CLC process oxidation of fuels occurs without contact with an atmospheric air. In this process, material called oxygen carrier (OC) is used to transport oxygen between fuel and air reactor.

Various materials as OCs for CLC process are used, most common systems contain for example iron and manganese oxides etc. In addition various inert oxides (e.g. $ZrO_2$ , $TiO_2$, or $Al_2O_3$) are used as a support material. One of the main features of OC, besides its ability to transport oxygen, is its durability. OC should be durable enough to resist many cycles of oxidation and reduction inside CLC installation.

Scanning electron spectroscopy (SEM) combined with Energy-dispersive X-ray spectroscopy (EDS) is one of the methods used for examining materials in material science. Using combined SEM-EDS method it is possible to investigate changes in structure of OC after its reaction with fuel. Featured Fe-Mn-Zr OCs were characterized using that method. Changes in chemical composition were also confirmed using X-ray diffractometry (XRD).

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# Synthetic Approaches for Bright Red-Emitting Carbon Nanoparticles

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Light-emitting carbon nanoparticles, or carbon dots (CDs), are renown in the research community because of their significant visible-light absorption capabilities, intense emission bands, low toxicity, and bio-compatibility [1]; all these properties make CDs extremely appealing for a wide range of applications in fields such as optoelectronic, sensing, bioimaging, nanomedicine, and photocatalysis.

Despite the efforts to understand the origin of their photoluminescence and some recent hints for their blue- and green-emission, the mechanisms allowing CDs to emit, especially in the red region, still needs to be elucidated in full [2]: in particular, the reported syntheses leading to red-emitting CDs are mostly based on trial-and-error approaches. As such, the obtained carbon nanoparticles often display low fluorescence quantum yields. Red-emitting carbon dots, nonetheless, are regarded as viable safe substitutes for either rare or toxic semiconductor-based nanoparticles, mainly for nanomedicine and bio-imaging applications. Managing to enhance and control the optical properties of CDs is thus considered a fundamental step towards reliable alternatives to these dangerous and polluting materials.

Here we present some novel approaches towards brightly red-emitting CDs. In particular, we have developed purification and post-synthetic procedures allowing for higher reaction yields, enhanced emission intensities, and better control of the optical properties of the obtained carbon nanoparticles. The prepared CDs display high intensity emission bands peaking at wavelengths longer than 600nm, making such innovative materials potentially useful for light emission devices based on safe and biocompatible carbon dots.

The Italian MIUR PRIN 2017 Candl2 Project Prot. n. 2017W75RAE is gratefully acknowledged.

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# Novel $^{19}$F-MRI tracer based on Solid Lipid Nanoparticles Encapsulating Superfluorinated Molecular Probes

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Novel synthesis approaches of ever more performing contrast agents have been recently developed in order to address the pressing need of improving molecular imaging and cell tracking performance of $^{19}$F-Magnetic Resonance Imaging (MRI), a non-invasive tool for early disease diagnosis and treatment monitoring.[1] Multibranched fluorinated residues encompass a new generation of superfluorinated tracers which allow the achievement of good-resolution images in $^{19}$F-MRI.[2] For in vivo applications, they need to be formulated in tailored delivery nanocarriers, in order to overcome their low water solubility and obtain injectable preparations. The class of nanovectors proposed to tackle such an issue is represented by solid lipid nanoparticles (SLNs), composed of crystalline and physiological fatty acids, useful for delivery of therapeutic and/or diagnostic agents, as they are characterized by high drug loading efficiency, ability to protect the cargo from degradation and metabolic inactivation and high degree of biocompatibility at both cellular and systemic level.[3] Here, a novel approach has been developed for formulating new tracers based on SLNs, encapsulating the multibranched superfluorinated imaging probe PERFECTA.[5] The latter is a tracer suitable for in vivo cell imaging by $^{19}$F-MRI, due to its spectral properties, relaxation times, and sensitivity.[4] Herein, formulations of SLNs have been prepared by an oil-phase evaporation-induced self-assembly strategy by tuning the lipids weight ratio. SLNs with high colloidal stability in water, regular morphology, narrow size distribution and controlled surface charge, have been achieved. The encapsulation of PERFECTA has been integrated in the preparation protocol of the SLNs. A comprehensive morphological and spectroscopic characterization of the SLNs, as bare and loaded by PERFECTA, has been performed. The results demonstrate the formation of negatively charged nanostructures with a regular spherical morphology, hydrodynamic diameter of ca. 200 nm, effectively encapsulating the tracer with retention of morphology and of the typical intense $^{19}$F-NMR signal of the tracer, resulting hence a promising contrast agent for $^{19}$F-MRI.

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# Optical traceable PEG-Liposomes as suitable nanodelivery systems of MCC950, inhibitor of the NLRP3 inflammasome activation

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Nanotechnology holds an innovative role in medicine as it allows to fabricate multifunctional and high-performance nanoplatforms for targeted diagnosis and therapy of numerous pathologies. Purposely designed liposomes (LPs) have been demonstrated to be suitable to deliver to specific sites bioactive compounds such as drugs and nanoparticles (NPs)[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 tools in visual monitoring of biological processes and analysis of drug releasing kinetics[2]. Hence, polyethylene glycol (PEG)-LPs co-loaded with MCC950, a NLR pyrin domain-containing 3 (NLRP3) inflammasome activation inhibitor, and luminescent CDs[3] have been prepared to obtain optical traceable nanovectors for the treatment of the NLRP3 inflammasome. LPs have been prepared by means of a micro-emulsion approach[1] and characterized in terms of morphology, colloidal stability, optical properties and drug encapsulation efficiency. Furthermore, the nanoformulations have been in vitro tested, to investigate on their effect on cell viability, hepatic uptake and also on their ability to alleviate the activation of the NLRP3 inflammasome.

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# Highly Fluorescent Carbon Nanoparticles Synthesized in Open Reactor as Efficient pH-Responsive Materials

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Fluorescent carbon nanoparticles, usually named Carbon Dots (CDs), are novel members of the family of nanomaterials. Such nanoparticles, typically 1 – 10 nm sized and composed of carbon structures, have attracted increasing attention in the recent years due to their photoluminescence (PL) properties [1]. Many recent studies have aimed at developing synthetic routes for CDs with PL across the whole visible range. Such syntheses generally involve thermal carbonization of opportunely selected organic molecules an can be carried out employing different heating methods [2]. In this work, CDs are synthesized trough a thermal treatment of resorcinol (1,3-hydroxybenzene) at 180°C in ethylene glycol in an open reactor [3]. Such synthetic strategy promotes water evaporation, that forms as secondary product and also allows to monitor the evolution of CDs fluorescence during the synthesis. The CDs spectroscopic properties mainly consist of two emission bands: one in the green, originated by highly fluorescent polycyclic aromatic hydrocarbons (PAHs) within CDs and the other in the blue, attributed to CDs surface states emission. The rate of the carbonization process could be increased by introducing NaOH and $H_2SO_4$ as catalysts in the reaction solution. Variations of the spectroscopic properties of the CDs under exposure to prolonged UV irradiation revealed that PAHs in CDs have a high photobleaching resistance. Finally, we demonstrate a marked and interesting quenching/enhancing effect of the CDs emission in the presence of acidic or basic compounds in the surrounding environment of CDs, which suggests a profitable use of such CDs in on/off sensors or stimulus-responding devices.

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# Synthesis of sodium ion-exchanged functionalized UiO-66 MOFs

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Metal-organic frameworks (MOFs) have highly tuneable structures in terms of pore structure and surface chemistry, which allows for them to be tailored for specific applications such as energy storage. UiO-66 is one of the most stable MOFs, being constructed from zirconium oxide clusters and benzene-1,4-dicarboxylate ligands (BDC). The BDC ligands of UiO-66 can be modified with various functional groups such as carboxylic acid and sulfonic acid groups. [1] In recent work by Lu et al. functionalised UiO-66 materials were shown to be used to make artificial channels for ion-selective transport. [2] By selecting the appropriate organic modifications to the ligands, the MOF would be able to store and transport sodium ions. This ion-conductive property has the potential for use in Na-ion solid-state batteries.

This work aims to optimise the synthesis technique to make crystalline UiO-66-$(COONa)_2$ and to characterise the resulting material using powder X-ray diffraction, thermogravimetric analysis, IR spectroscopy and scanning electron microscopy. After synthesis of UiO-66-$(COOH)_2$ the aim was to develop a synthetic approach to exchange the carboxylic acid protons with sodium to make UiO-66-$(COONa)_2$. We have used X-ray fluorescence spectroscopy to determine the relative percentage of sodium incorporated into the MOF and IR spectroscopy to detect the removal of -COOH groups.

We synthesised and characterised UiO-66-$(COOH)_2$ using a hydrothermal synthesis technique under aqueous conditions that formed crystals of undefined morphology and low crystallinity. We then modified this synthesis technique using formic acid as a modulator in water, resulting in more crystalline UiO-66-$(COOH)_2$ with the typical octahedral morphology of UiO-66. We investigated different approaches to exchanging the carboxylic proton with sodium using various sodium salts, bases and solvents. The optimal conditions we developed for UiO-66-$(COONa)_2$ synthesis were to stir the MOF in DMSO with NaOH under nitrogen for 16 hours at 80 ºC.

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# Novel Coordination Polymers Based on Carboxylate And 4,4'-Trimethylenedipyridine Ligands for the Removal Of Heavy Metal And 2,4,6-Trichlorophenol from Water

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The reaction of $Zn(NO_3)_2.6H_2O$ with 4,4'-Trimethylenedipyridine (tmdp) and corresponding carboxylate ligands: 3,3-Thiodipropionic acid (tdpa), 4-Hydroxybenzoic acid (hba) and 4-Biphenylcarboxylic acid (biphen) gave three novel Zn(II) coordination polymers $[Zn(tdpa)(tmdp)]_n0.2n(H_2O)$(**1**), $[Zn(nba)_2(tmdp)]_n$ (**2**) and $[Zn(biphen)_2(tmdp)]_n$ (**3**) respectively by stirring the reactants in appropriate solvents with/without the application of heat. The compounds were characterized using FT-IR, CHN Analysis, TGA, PXRD and single-crystal X-ray diffraction. Crystallographic results showed that the porous 2D networks of **1** are linked by the oxygen atoms of tdpa in one direction and the nitrogen atoms of tmdp in another direction; and contains water molecules in its voids. Compounds **2** and **3** are one-dimensional coordination polymers with the zinc(II) carboxylate units bridged through the spacer N-donor ligand. The phase purity was confirmed by comparing the simulated and experimental X-ray powder diffraction patterns. Porosity in 2 is created with the packing of the polymer chains. Compounds **1** and **2** were investigated for the removal of $Pb^{2+}$ and 2,4,6-Trichlorophenol from water with adsorption capacities of 666 mg/g and 207.8 mg/g respectively.

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# Solvothermal Synthesis of Multiferroic Bismuth Ferrite Nanoparticles and the Influence of Annealing Temperature on Structural, Optical and Magnetic Properties

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Multiferroic materials now appear promising as energy harvesting materials for photovoltaic applications. Ideally, the semi-conductors used for photovoltaic and photocatalytic conversions should: a) present a band gap small enough to absorb the entire solar spectrum and b) prevent the recombination of electrons and holes. Intrinsic multiferroic materials can currently fulfill these two roles because the presence of new electronic levels in the band gap near the Fermi level, due to the presence of transition metals, allowing the capture of solar photons of lower energy; moreover, the internal electric fields associated with ferroelectric properties cause the displacement of electrons and holes in opposite directions. Hence, this type of material exhibits a spontaneous electric polarization, which can be reversed by the application of an external electric field. The multiferroic perovskite bismuth ferrite (BiFeO3 or BFO) presents valuable high stability, narrow band gap and large ferroelectric polarization what make it suitable for photovoltaic applications. In this study, highly crystalline BFO nanoparticles have been synthetized by solvothermal technique. As produced amorphous BFO nanoparticles were annealed at different temperatures and timing. The effects on structural, optical and magnetic properties of annealing temperature were investigated by XRD, SEM, TEM, diffuse UV-Vis spectroscopy and VSM. Our results confirmed a perovskite structure and high purity of the BFO phase. We observed a homogenous morphology, and the particle size was estimated to be smaller than 60 nm. A significant reduction in bandgap energy 2.06 eV could be attributed to the competing effects of coulombic interactions, oxygen defects and microstrain. M-H loop confirmed the BFO nanoparticles exhibit magnetic ordering at room temperature demonstrating the suppression of the cycloid spin structure of BFO. The magnetic measurements exhibited ferromagnetic behavior with high remnant magnetization values.

# The crystallisation and characterisation of basic magnesium chloride salts studied *in situ* using a laboratory SAXS/WAXS instrument.

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We demonstrate a method for monitoring the *in situ* crystallisation of basic magnesium chloride salts $Mg_{x+y}(OH)_{2x}Cl_{2y}\cdot zH_2O$. The salts were synthesised using a mixture of $MgCl_2$ aqueous solution and nano-sized MgO. The reagent mixture was transferred to a disc-shaped reaction cell for *in situ* monitoring using a SAXS/WAXS instrument. The reaction cell consists of a circular metal washer with internal diameter of 4 mm and thickness 1 mm sealed, each side using Kapton® tape. Although the synthesis of basic magnesium chloride salts has been reported,[1-2] by monitoring their synthesis using simultaneous SAXS and WAXS we are able to obtain time resolved data showing the phase evolution of the material and particle size.

Temperatures between 25-120 °C were investigated and were found to be an influential factor in the formation of basic magnesium chloride phase, with $Mg_3Cl(OH)_5\cdot 4H_2O$ being favoured at lower temperatures and $Mg_5Cl(OH)_5\cdot 2H_2O$ - at higher temperatures.

Using the *in situ* WAXS data, a two-phase Rietveld refinement was carried out to quantify the progress of the reaction over time. The extracted phase fraction allows the decay of the MgO starting material and growth of product phase(s) to be observed directly over a period of several hours. Avrami kinetics were fitted to the data from which we suggest that there are two competing mechanistic processes in the formation of $Mg_3Cl(OH)_5\cdot 4H_2O$. This was then compared to the SAXS data, analysed using combined sphere and Porod gradient model. With SAXS being sensitive to particle size below 160 nm, we observe a reduction in the volume fraction of the primary MgO particles during the initial stages of the reaction and, at later stages of the reaction, the emergence of larger crystalline material. Considering the SAXS and WAXS data we observed an offset between the consumption of crystalline MgO in the WAXS and reduction in the sphere volume fraction in the SAXS. We suggest this is due to the formation of an amorphous $Mg(OH)_2$ intermediate during the synthesis of $Mg_3Cl(OH)_5\cdot 4H_2O$.

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# Engineering Upconverting Nanocrystals for FRET

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Lanthanide-doped upconverting nanocrystals (UCNCs) have an exceptional capability to generate visible luminescence emission under near-infrared (NIR) photoexcitation. This feature, which enables spectral elimination of the background autofluorescence, along with high photostability and non-toxicity, provides them unique advantages as Förster resonance energy transfer (FRET) donors in biosensing, bioimaging and light activated therapy applications.[1] Despite multiple advantages, the use of UCNCs as FRET donors is still quite complicated because each single NC can contain multiple donors at different distances from the acceptor molecules on the UCNC surface.

Seeking to build an efficient FRET-UCNC system, we have prepared different core-shell compositional architectures of UCNCs functionalized with dye-labelled single-stranded DNA. Advanced modelling is fundamental to understand energy dynamics in UCNCs[2] and a new semi-analytical model[3-4] has been developed with aim to better rationalize the FRET-based biosensing experiments and predict the optimal UCNC architecture.

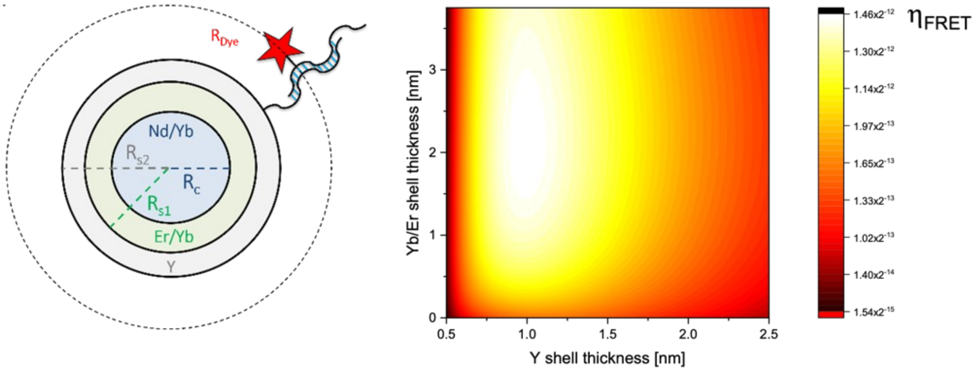

Figure 1. Left: Schematic of the UCNP-DNA system. Right: FRET efficiency as a function of the inert (Y) and active (Yb/Er) shell thicknesses.

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# Sequential Biotransformation and Metal-catalyzed Reactions in Unconventional Media for the Synthesis of Pharmaceutically Relevant Molecules

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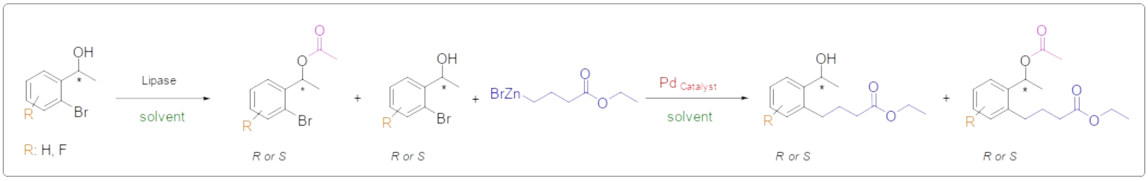
Increasing environmentally awareness has pressured companies to become more proactive in addressing public concerns related to environmental effect of products during use and as waste, and to drive the field of synthetic chemistry towards more green practice.[1] In this context, the use of renewable feedstocks of more environmentally responsible solvents like the so-called Deep Eutectic Solvents (DESs) is seen by many as an important strategy towards sustainable development.[1,2] Previous findings from our research group have shown that DESs behave  as effective ligands and catalysts in several metal-[3] and biocatalyzed[4] transformations, also aimed at synthesizing heterocyclic compounds.[5] In this communication, we report two sequential transformations based on a kinetic resolution of racemic secondary alcohols and biotransformation, followed by a Negishi cross-coupling reaction an route to pharmaceutically relevant compounds concerning anti-Alzheimer’s drug[6]. (**Scheme 1**).



**Scheme 1.** Combination of bio- and metal-catalyzed reactions

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# Design of core@shell nanostructures for biomedical applications

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Core@shell nanostructures consisting of non-porous silica core and a mesoporous silica shell represent versatile generation of nanomaterials with tailorable properties, well-defined morphologies and integration of multi-functionality into a single nanostructure useful for applications in wide variety of different fields from catalysis, adsorption, separation, sensing to biomedicine[1]. Non-porous silica cores can be exploited to incorporate different functional materials such as organic molecules, molecular complex or nanoparticles (NPs) with fluorescent, magnetic or plasmonic properties and be further coated with a mesoporous silica shell[2]. Mesoporous silica shell (MSS), characterized by high surface area, good colloidal stability in an aqueous environment, high degree of biocompatibility and loading capacity, can be growth with high control on its structures, thickness and pore size. Since their first development, different mesophases have been synthesized ranging from hexagonal ordered, worm-like disordered, stellate, dendritic and central-radial pores structures, whose design aims at increasing pore size improving the loading efficiency of large macromolecules and NPs. Here, a systematic study has been performed to fabricate core@shell nanostructures consisting of non-porous silica core of about 30 nm used as seeds for the growth of MSS with tunable and well-defined geometry. Monophasic and biphasic soft-template approaches have been explored to define the mesoporous structures, using cetyltrimethylammoniumbromide (CTAB), as cationic surfactant, tetraethyl orthosilicate (TEOS) as silica precursors and alkaline conditions. The effect of experimental parameters, such as CTAB and TEOS concentration, type of base and organic solvent, on the structure of the resulting mesophase has been investigated by a comprehensive morphological, structural and optical characterization, that has demonstrated as texture and pore size of the mesostructures can be modulated according to the preparative method and conditions.

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# New Green Tandem Protocol Combining Organolithium Oxidation and Organolithium Chemistry to Obtain Chemoselective Tertiary Alcohols

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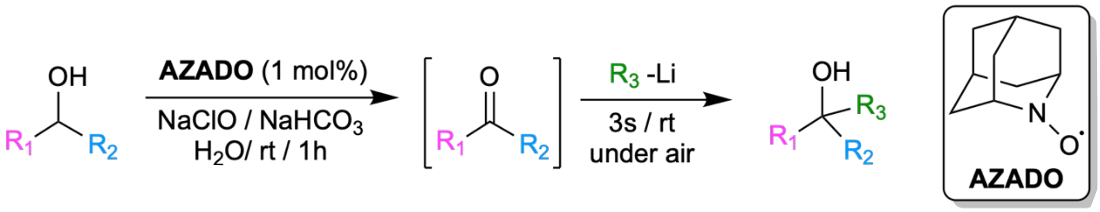
Water is the quintessential solvent used in mother nature for biological processes [1], so the use as a solvent into organic synthesis constitutes one of the greatest advances within the so-called *green chemistry* and the fulfillment of most of their important twelve Principles [2]. Besides is abundant, non-toxic, cost-effective, non-flammable, renewable, and non-volatile and it has already shown an enormous potential as a versatile reaction medium [3]. Putting synthetic procedures in the spotlight, eliminating the need of isolation and purification of reaction intermediates, one-pot tandem processes are highly useful and efficient green approaches to produce organic high added value molecules [4].

Breaking new ground in this evolving field, in this communication we present for the first time a *one-pot* tandem process combining organocatalysis and organolithium chemistry in water as a new methodology to prepare highly substituted tertiary alcohols. [5] Reactions were carried out in aqueous media, under air and at room temperature (a trio of conditions that are typically forbidden in polar organometallic chemistry).



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# Supercritical $CO_2$-assisted introduction of Cu into Zr-MOFs

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Over the recent years, metal-organic frameworks (MOFs) have gained a significant attention from the academia, mainly thanks to their superior textural features and the possibilities for introducing a wide range of modifications resulting in the improvement of the physicochemical, adsorptive and catalytic properties of those materials. Adding functionality to MOFs, e.g., by combining them with other materials, such as metal nanoparticles (NPs), is usually beneficial for their catalytic activity. The NPs can be introduced to the already synthesized MOFs via impregnation using different metals salts dissolved in various solvents. However, this facile method of NPs@MOF preparation exhibits some serious drawbacks such as accumulation of the deposited active phase, thus, its poor dispersion resulting in reduced interaction with MOF. By employing a supercritical $CO_2$ (sc-$CO_2$) one may eliminate these flaws. Thanks to low viscosity, high diffusion coefficient and a zero surface tension, the sc-$CO_2$ allows deep penetration and even distribution of the metal nanoparticles in the MOF.

In this work we deal with a sc-$CO_2$ assisted impregnation of two popular, zirconium based MOFs – UiO-66 and MOF-808, using copper salts to obtain CuNPs/MOF catalysts for the reactions of $CO_2$ conversion. In our study, as an environment we used sc-$CO_2$ alone and with a co-solvent. Adopted procedures allowed to limit the use of volatile organic compounds during both the impregnation and the purification stages of the process. By employing X-ray diffraction, scanning and transmission electron microscopy, $N_2$ sorption, and thermogravimetric analysis it was found out that the obtained CuNPs/MOF composites showed crystalline structure, developed specific surface area, good porosity, and sufficient thermal stability. Most importantly, the uniform distribution of CuNPs was achieved.

*The financial support from the National Science Centre (project no. 2019/35/D/ST5/03440 "Metal-organic frameworks for catalytic conversion of $CO_2$") is gratefully acknowledged.*

# Analysis of the influence of activator type on the synthesis and performance of based on metakaolin geopolymers

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The alkaline hydraulic cement, whit low calcium also called geopolymer, has been studied worldwide as an alternative binder to Portland cement, due to its eco-efficiency (low energy consumption required and low $CO_2$ emissions in its production). The syntrense of this ligand is generally performed from alkaline activation (using alkali metal/alkaline earth cations) of a precursor rich in aluminum silicate. However, in recent years new research has demonstrated that geopolymers can also be activated by phosphoric acid. Therefore, this work evaluated the mechanical and microstructural performance, as well as the activation efficiency of aluminosilicate hydrate materials, based on metakaolin, mechanochemically activated by the one part mix method by three types of alkalis (NaOH, KOH and $Na_2SiO_3$) and by the two part method by phosphoric acid ($H_3PO_4$). For this analysis, the characterization of the precursor was carried out, the synthesis was studied, the occurrence of geopolymerization was evaluated by means of XRD and FTIR tests and the mechanical performance of the material obtained. The results show that, if geopolymerization occurred in all samples, there was a significant variation in mechanical performance between the alkali-activated and acid-activated samples, according to the age of curing and hardening of the samples.

# Bio-based strategies for enhancing supercapacitors' energy density

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Among the electrochemical energy storage devices, supercapacitors present superior eco-friendliness and safety, long life, and high charge/discharge rates. The main limit of supercapacitors is their relatively low energy density due to the capacitive mechanism of charge storage. To improve energy densities and expand supercapacitor applications, several concepts mainly based on adding faradaic contributions to the capacitive storage have been proposed. [1] An interesting approach is the use of natural antioxidants as redox additives to the electrolyte and/or to the electrode material. [2]

The use of agri-food ligno-cellulosic wastes as raw materials for hierarchical porous carbon as electroactive component for supercapacitors has been proved effective, and among various bio-based sources, coffee residues and waste have been shown to be quite promising. [3] Thus, to fully exploit the value of a single natural source, we explored and demonstrated the possibility of using coffee extracts and brewed coffee directly as redox electrolyte for bio-based supercapacitors with improved energy density thanks to the faradaic contributions of abundant chlorogenic acids. Furthermore, the proof-of-concept device was fabricated with a current collector based on a novel metal-free carbon-biopolymer composite and using a bio-based binder for the porous carbon material, to preserve both bio-derivation and potential bio-degradability. Our preliminary findings demonstrate the feasibility of using complex natural extracts of polyphenols as redox active electrolytes for advanced bio-based energy storage devices.

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# Synthesis and catalytic applications of metal oxocluster-based hybrid nanoparticles

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The design and the catalytic applications of novel oxocluster-based hybrid nanoparticles is the focus of the present work. The synthetized hybrid materials are characterized by the covalent incorporation of structurally well-defined oxoclusters of group 4 metals ($Zr_4O_2(OMc)_{12}$ [1], $Ti_6O_4(O^iPr)_8(OMc)_8$ [2], $Ti_4O_2(O^iPr)_6(OMc)_6$ [2], $Ti_4Zr_4O_6(OBu)_4(OMc)_{16}$ [3], $Ti_2Zr_4O_4(OBu)_2(OMc)_{14}$ [3]) (OMc: methacrylate) in an organic matrix based on polymethylmethacrylate. The presence of polymerizable groups (C=C) in the oxocluster structure allowed the formation of strong chemical bonds between the organic and the inorganic counterparts protecting the guest species (oxocluster) towards hydrolysis and avoiding possible leaching and/or migration phenomena. The free radical copolymerization between the oxocluster and methyl methacrylate was carried out in the confined space of miniemulsion droplets, allowing the control of the size distribution of the resulting hybrid particles. The polymerization was carried out under UV light using a proper photoinitiator. Hybrid organic-inorganic nanoparticles were obtained with a spherical morphology and dimensions similar to those reported in a previous study[4]. The obtained hybrid nanoparticles were tested as heterogeneous catalysts for the oxidation of methyl p-tolyl sulphide, benzyl alcohol and cyclooctene. $H_2O_2$ was selected as oxidizing agent since the already known activation of this molecule by Zr oxoclusters[5]. The higher values of conversion were obtained with the monometallic oxocluster-based hybrids, in particular with those based on $Ti_4O_2(O^iPr)_6(OMc)_6$. After the catalytic trials, the catalysts were separated from the reaction mixture to assess the retention of the oxocluster structures, particularly prone to undergo hydrolysis. The absence of species related to the hydrolysis of the oxoclusters was confirmed by IR and Raman analysis, confirming the successful incorporation of the oxoclusters in the polymer and demonstrating the role of the polymer matrix in their stabilization.

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# Hybrid nanocomposite based on Au nanoparticles densely coated nanographene oxide towards theranostic applications

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Hybrid nanocomposites based on nano-graphene oxide (NGO) and colloidal Au nanoparticles (NPs) are attractive nanomaterials for diagnostics, therapeutics and drug delivery[1] applications thanks to high surface area and absorption in near infrared (NIR) region of NGO and localized surface plasmon resonance absorption in the visible/NIR spectral regions and a prompt surface functionalization of AuNPs. Although the typical synthetic route relays on a sustainable colloidal *in situ* approach with chloroauric acid and sodium citrate, the synthetic mechanism has not been elucidated so far, and the achieved nanostructures show a poor control of the Au NPs morphology and a low coating density of the flakes[2], thus limiting the potential for applications.

This work aims to overcome these issues studying the reaction mechanism by investigating the effect of precursors molar ratio, reaction temperature, pH and reactants injection sequence. The as synthesized NGO/Au NPs structures showed high stability in aqueous solution, dense coating with spherical in shape Au NPs, and an intense absorption peak at 533 nm. An *in vitro* study has been performed on normal epithelial (HCEC-1CT) and metastatic gastric cancer (N-87) cell lines to evaluate the effect on cell viability of the synthesized nanostructures. Photothermal activity has been evaluated under laser irradiation in the visible and NIR spectral regions. The novel NGO/Au NPs-PEG hybrid nanoplatforms represent promising candidates with a relevant potential for their use in imaging, drug delivery and photothermal therapy.

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# High Power, High-Rate Lithium-Ion Battery Wadsley-Roth structure Anodes

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In recent years, greenhouse gas emissions and global energy consumption have been increasing at an alarming rate leading to ozone depletion, rising sea levels and threats to biodiversity.[1] As such, the development of green, renewable energy systems such as solar and wind that can replace fossil fuel based energy is paramount. However, solar and wind suffer from inherent limitations of environmental intermittency so energy storage (batteries, supercapacitors) must be used to store this energy for later use while also being used extensively in electric transportation and portable electronics.[2] With the aid of recent ongoing experimental results, this poster presentation will examine the use of Continuous Hydrothermal Flow Synthesis (CHFS) methods towards the manufacture of anode materials for lithium-ion batteries based on Wadsley-Roth structure doped Niobium Oxides.[3] Wadsley-Roth Oxides are of great interest for fast $Li^+$ storage due to their unique 3D multilane open tunnel structures with an abundance of Li insertion sites that offer facile $Li^+$ diffusion paths.[4] This, coupled with a moderate lithiation potential enables high theoretical/practical capacities, long-term cyclability, and high safety.

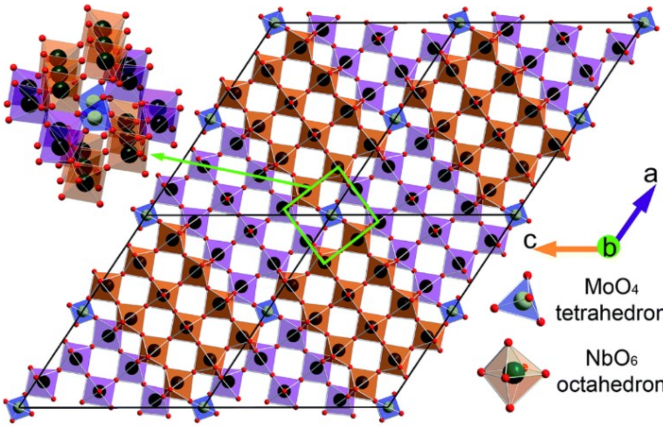

**Figure 1:** Wadsley-Roth crystal structure of $MoNb_{12}O_{33}$ (ref. 4).

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# Bottom up Synthesis of Sodium-Ion Battery Cathode Materials

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Sodium-Ion Batteries (SIBs) are considered likely substitutes for lithium-ion batteries (LIBs) owing to their comparable performance and great prospects for sustainability due to the greater availability of Na over Li. However, numerous challenges are yet to be addressed before marking them as potential candidates for practical applications. Different structures of sodium-based layered oxides (P2, O3) exist that depend on the number of distinctive oxide layer stacking and the surrounding $Na^+$ environment [1]. The optimum heat treatment synthesis conditions for high performance, greatly depend on many process variables. In this poster, the authours will showcase the optimized synthesis of direct routes to SIBs cathodic materials that are made from sustainable elements. A few case studies will be provided to show current and future applications of such energy materials, some of which can have potential commercial potential.

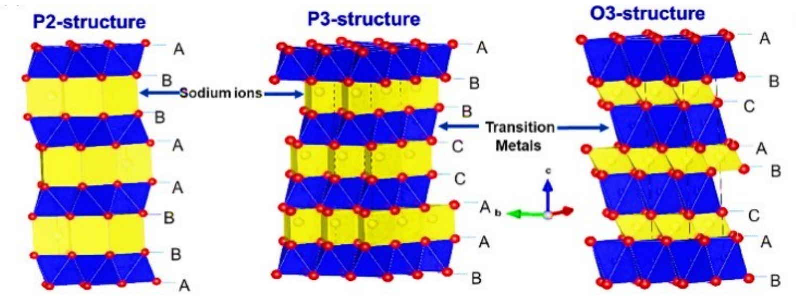

**Figure 1.** Sodium diffusion mechanism in P (Prismatic) and O (Octahedral) sites.

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# Nanostructured Materials for Innovative and Sustainable Production of Hydrogen

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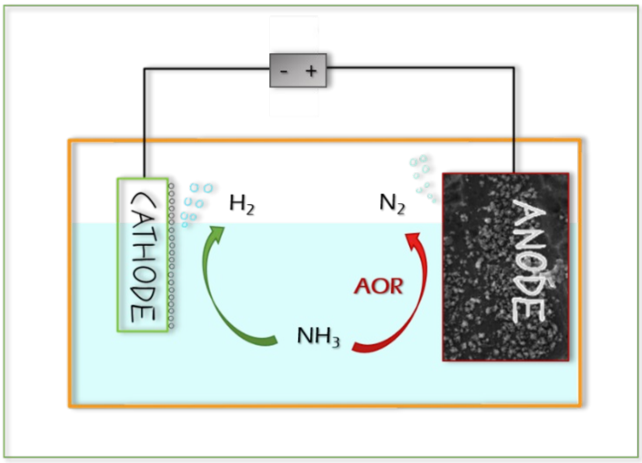
Shifting towards a Circular concept of Economy necessarily include a sustainable energy production, which is one of the most urgent tasks of our century. In this perspective, sewage sludge (SS) can be a source of valuable chemicals, including some interesting energy vectors [1]. The significant concentration of ammonia in SS [2] is appealing for this purpose: its oxidation does not produce any carbon containing species and it has much lower energy demand compared to hydroxyl oxidation in water splitting [3]. In this work, we investigated a composite system based on platinum nanostructures grown on nickel foam (NF) for the electrochemical ammonia oxidation reaction (AOR). NF was selected as a support due to its good electrochemical properties, mechanical stability and high specific surface area. Platinum, which is recognized as one of the most effective catalysts for AOR, was deposited on NFs via galvanic displacement or pulsed electrodeposition, also in presence of a proper templating agent. Our aim was to obtain nanostructures with a high surface area to mass ratio in order to minimize Pt loading on the electrocatalyst. Preliminary results highlighted the correlation between the morphological features of the electrocatalysts and the electrochemical active surface area (ESCA).



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# $TiO_2$ nanoparticles in the field of Cultural Heritage: Case study of the sarcophagus of Sparano from Bari

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Over the last few years, coatings based on $TiO_2$ nanoparticles (NPs) raised significant attention in the field of Cultural Heritage for their ability to limit the formation of black crusts[1] and saline efflorescence[2], confer hydrophobic properties to surfaces[3], and prevent biodeterioration[4] thanks to their photocatalytic and self-cleaning properties. The aim of our work was to develop, characterize and apply an original $TiO_2$-based coating made of rod-shaped nanocrystals, as a protective coating for limestone artifacts. $TiO_2$ NPs were obtained by means of colloidal synthesis, and coated with a shell of oleic acid molecules that make them dispersible in organic solvents[5]. The goal was to identify the most suited conditions for the application of the coating on the sarcophagus of Sparano from Bari on the occasion of its restoration, considering also the specific requirements for protective products to be applied for stone conservation. The self-cleaning and photocatalytic properties of this formulation have been compared with those of a reference product, the commercial Degussa $TiO_2$ P25.

Samples of the same lithotype of the sarcophagus (limestone from Bari) were subjected to treatment simulating the restoration procedure carried out on the sarcophagus, in order to evaluate the compatibility between the coating and a treated surface. Subsequently, the $TiO_2$ NRs and P25 formulations were directly applied on the samples surface by brush with a Japanese paper sheet interposed. A comprehensive set of experiments was performed in order to assess the self-cleaning, hydrophobic, and photocatalytic properties of the $TiO_2$ NRs-based coating, in order to optimize the performances and still preserving the aesthetic characteristics of the stone. The resulting coating was thoroughly investigated by means of complementary spectroscopy and microscopy techniques. Finally, its photocatalytic behavior under sunlight was assessed. The results demonstrated the effectiveness of $TiO_2$ NRs-based coating that proved to be a promising candidate for the preventive conservation of stone cultural heritage, thus prompting its application on the restored surface of the sarcophagus.

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