

2nd ENERCHEM SCHOOL

CHEMISTRY FOR THE ENERGY TRANSITION



Florence 13-17 February 2023
 "Centro Studi Cisl"
 Via della Piazzuola, 71 Firenze


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The second Italian school on renewable energies organized by the Interdivisional Group on the Chemistry of Renewable Energies (ENERCHEM) of the Italian Chemical Society

Centro Studi CISL, via della Piazzuola 71, Firenze

Scientific Programme

MONDAY, 13 FEBRUARY 2023

12:00-14:00 REGISTRATION

14:00-14:30 OPENING

Chairperson: Ilenia Rossetti

14:30-16:00 L1 – **Marc Robert** "Electrochemical and light-driven molecular catalysis. Principles, fundamental aspects, applications to CO₂ and N₂ reduction"

16:00-16:30 COFFEE BREAK

Chairperson: Massimo Innocenti

16:30-17:00 **Claudia Vivalda** "The National Energy Technology Cluster - Role and activities and its Energy Technology Roadmap"

17:00-18:30 OL1 – **Sara Garcia Ballesteros** "Green ammonia electrosynthesis in aqueous electrolyte: a preliminary study"

OL2 – **Costanza Tedesco** "Experimental strategy to enhance the photocatalytic activity of Cs₂AgBiCl₆ lead-free double perovskite derivative by g-C₃N₄ composite"

OL3 – **Lorenzo Rizzato** "N₂ solar activation: ammonia as hydrogen vector for energy storage"

OL4 – **Anna Mangini** "The Sun2rise Li-N₂ cell concept in the landscape of Li-mediated N₂ reduction reaction strategies for ammonia production"

OL5 – **Matteo Tommasi** "Photoreduction of CO₂ to liquid products with innovative photocatalysts"

OL6 – **Olimpia Tammaro** "High CO₂ photoreduction performance achieved with ceria-based photocatalysts"

18:30-19:30 POSTER SESSION

20:00 DINNER

TUESDAY, 14 FEBRUARY 2023

Chairperson: Lorenzo Zani

09:00-10:30 L2 – **Marina Freitag** " Diffuse light harvesting to structured information with molecular photovoltaics"

10:30-11:00 COFFEE BREAK

11:00-12:30 L3 – **Elisabetta Di Bartolomeo** " Materials for solid oxide cells (SOCs)"

12:30-14:00 LUNCH

Chairperson: Andrea Pucci

14:00-15:30 L4 – **Hyunwoong Park** "Photocatalysis: Principle and Applications"

Chairperson: Riccardo Basosi

- 15:30-16:15** T1 – **Silvia Gross** "MSCA: features, rules and my experience as MSCA reviewer: how to write a successful proposal"
- 16:15-16:45** COFFEE BREAK
- 16:45-17:30** T2 – **Francesco Basile** "Climate energy and mobility research opportunity and perspective in the Horizon Europe framework"

"

Chairperson: Marta Da Pian

- 17:30-18:15** OI7 – **Maria Varsalona** "Effect of dopamine on photosynthetic growth of both Rhodobacter sphaeroides R26 mutant and 2.4.1 wild type"
- OI8 – **Nicolò Rossetti** "Confined single nickel atoms in low condensed carbon nitride as efficient oxygen evolution catalyst "
- OI9 – **Alberto Picchi** "Luminescent solar concentrators based on poly(methyl methacrylate) from recycled sources"
- 20:00** SOCIAL DINNER

WEDNESDAY, 15 FEBRUARY 2023

Chairperson: Maria Assunta Navarra

- 09:00-10:30** L5 – **Stefania Specchia** "Sustainable electrocatalysts for PEMFC/AEMFC"
- 10:30-11:00** COFFEE BREAK
- 11:00-12:30** L6 – **Eliana Quartarone** " Critical raw materials in strategic energy technologies "
- 12:30-14:00** LUNCH

Chairperson: Alessandra Sanson

- 14:00-15:30** L7 – **Gianluca Chiarello** "Photo(thermo)catalytic hydrogen production for solar energy conversion and storage "

Chairperson: Matteo Bonomo

- 15:30-16:15** J1 – **Francesco Tassinari** "The Chiral Induced Spin Selectivity effect and its application to renewable energy technologies"
- 16:15-16:45** COFFEE BREAK

- 16:45-17:30** J2 – **Daniele Franchi** "Dye-Sensitized Solar Cells: exploring new designs of organic dyes to enhance optical properties"
- 17:30-18:15** J3 – **Chiara Liliana Boldrini** "Eco-friendly deep eutectic solvent electrolyte solutions for dye-sensitized solar cells"

Chairperson: Andrea Ienco

- 18:15-19:00** T3 – **Alessio Dessì** "Not just a matter of science! Tips and clues to improve your communication skills"

- 19:30** DINNER

Chairpersons: Alessio Dessì, Ottavia Bettucci

- 20:30-22:30** **ENERSHORT**
Ottavia Bettucci "Science on wall: STREETSCIENCE. Stories and curiosities about light through street art!"
Enershort presentations, 3 min each

THURSDAY, 16 FEBRUARY 2023

Chairperson: Adalgisa Sinicropi

- 09:00-10:30** L8 – **Teresa Gatti** "Photovoltaic energy harvesting: from the basics to new trends and future opportunities"
- 10:30-11:00** COFFEE BREAK
- 11:00-12:30** L9 – **Alessandro Abboto** " Hydrogen: a clean and renewable fuel for the energy transition "
- 12:30-14:00** LUNCH

Chairperson: Paola Manini

- 14:00-15:30** L10 – **Jae-Joon Lee** "Evolution of Sensitization-based Photovoltaic Cells "
- 15:30-16:15** **Lucio Cinà** "From steady-state to dynamic tests: a must in hybrid organic-inorganic devices"
OL10 – **Andrea Osti** "Ni-LaMnO₃ nanocomposites as novel PGM-free catalysts for CH₄ combustion: effect of synthetic method in catalytic performances"
OL11 – **Giacomo Provinciali** "TiO₂-based heterojunction with 2D black phosphorus for efficient H₂ production"
- 16:15-16:45** COFFEE BREAK
- 16:45-17:30** OL12 – **Filippo Antonio Vernile** "Corrosion of Al alloys tanks in bio ethanol blended gasoline fuel"
OL13 – **Asya Mazzucco** "Experimental and theoretical studies of the LiBH₄-LiI pseudo-binary system and LiBH₄-LiI-LiBr pseudo-ternary system for solid-state electrolytes applications"

OL14 – **Rossella Infantino** “Enhanced light harvesting efficiency by Förster Resonance Energy Transfer (FRET) in Dye-Sensitized Solar Cells (DSSCs)”

17:30-18:30 POSTER SESSION

19:30-21:00 APERITIVO CAFFE’ SCIENZA

21:00-22:00 CAFFE’ SCIENZA: Tutti i colori dell’Idrogeno
Chairperson: **Gianna Reginato**
Experts: **Alessandro Abbotto; Alessandro Lavacchi**

FRIDAY, 17 FEBRUARY 2023

Chairperson: Elena Selli

09:00-10:30 L11 – **Kevin Sivula** "Solar fuel production via photoelectrochemistry at direct semiconductor/electrolyte interfaces"

10:30-11:00 COFFEE BREAK

11:00-11:05 JUNIOR ENERCHEM AWARD ANNOUNCEMENT

11:05-12:35 L12 – **Federico Bella** "Electrochemical nitrogen reduction: ammonia as a solar fuel"

12:35 CLOSING

L= Lecture ; J= Junior Lecture; T= Tutorial lecture; O= Oral communication

ELECTROCHEMICAL AND LIGHT-DRIVEN MOLECULAR CATALYSIS.

PRINCIPLES, FUNDAMENTAL ASPECTS, APPLICATIONS TO CO₂ AND N₂ REDUCTION

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Reduction of small molecules such as carbon dioxide and dinitrogen has as main objective the production of useful organic compounds and fuels - *renewable fuels* - in which solar energy would be stored. Molecular catalysts can be employed to reach this goal, either in photochemical or electrochemical (or combined) contexts. They may in particular provide excellent selectivity thanks to easy tuning of the electronic properties at the metal and of the ligand second and third coordination sphere. Hybridization of these catalysts with conductive or semi-conductive materials may lead to enhance stability and new catalytic properties, as well as inclusion of molecular catalysts in devices for applications. This approach bridges between homogeneous and heterogeneous, and it raises new fundamental questions.

The catalytic processes involved in CO₂ or N₂ activation have in common to couple electron and proton transfers to bond breaking and bond making reactions. A fundamental understanding of these elementary processes is a pre-requisite to advance understanding mechanisms and designing efficient catalysts. Appropriate experimental tools, combining notably electrochemistry and spectroscopy, are also necessary. Starting from a description of fundamental reactivity aspects, I will then discuss some of our recent results related to CO₂ and N₂ reduction.

References

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DIFFUSE LIGHT TO STRUCTURED INFORMATION WITH DYE-SENSITISED SOLAR CELLS

Marina Freitag*^a

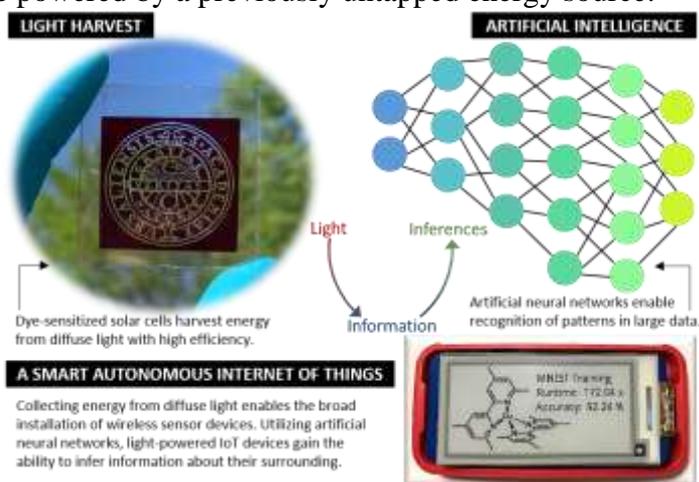
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By 2025 about 75 billion IoT devices will be installed, of which the majority will reside indoors. It is therefore crucial to find an energy source that yields high efficiencies in this environment.^{1,2} At high efficiencies under ambient light, while being more environmentally friendly, sustainable to produce and to recycle. Dye-sensitized solar cells (DSCs) are known for efficient conversion of ambient light. Fast charge separation in a variety of organic dyes and tuneable energy levels in Cu^{II/I} redox systems combined with negligible recombination processes allow DSCs to maintain a high photovoltage under ambient light.¹

We tailored dye-sensitized photovoltaic cells based on a copper (II/I) coordination complexes hole transport material for power generation under ambient lighting with an unprecedented conversion efficiency of PCE 38 %, at 1000 lux from a fluorescent lamp using a novel co-sensitization strategy² and electrolyte modifications.

Under 1000 lux lighting, 64 cm² photovoltaic area gives 152 J or 4.41 10²⁰ photons sufficient energy for training and testing of an artificial neural network in less than 24 hours. Ambient light harvesters enable a new generation of self-powered and "smart" IoT device to be powered by a previously untapped energy source.²



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MATERIALS FOR SOLID OXIDE CELLS

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In the current scenario of innovative energy systems, solid oxide cells (SOCs) are widely recognized as promising devices, thanks to their high conversion efficiency in both power-to-fuel and fuel-to-power modes. Solid Oxide Cells in Electrolyzer mode (SOEC) derive valuable chemicals from excess energy while in Fuel Cell mode (SOFC) fuel is converted back into power. A reversible cell (r-SOC) can interchangeably operate either as SOFC or SOEC. A crucial aspect for the scale-up is the development of multi-functional compounds that can work as either air or fuel electrodes. Conventional materials used for high-temperature SOFCs, such as Ni-containing anodic cermets (Ni-YSZ) and Co-based perovskite cathodes ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$, LSCF, $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$, BSCF), suffer from compatibility issues if coupled with a highly performing $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM) electrolyte. Thus, perovskite-type mixed conductors have been extensively studied as potential electrodes for all-perovskite devices.

A further step toward the cell reversibility would be the use of the same material at both fuel and air electrodes: the material synthesis, the deposition, the sintering of the electrodes will become simpler. The use of this symmetrical configuration would not only decrease the fabrication costs, but also alleviate thermochemical compatibility issues between the electrode and the electrolyte and would allow to switch between oxidizing and reducing atmospheres at both electrode sides, thus conferring a very high flexibility [1-3]. The key property of electrodes in reversible symmetric SOCs (r-SSOCs) is the structure stability/reversibility in both oxidizing and reducing atmosphere, which is the precondition for a symmetric electrode. Other features can be mentioned such as: high electronic-ionic conductivity and mechanical stability, chemical and thermal compatibility with the electrolyte and other cell components, electro-catalytic activity towards oxygen reduction and evolution, as well as fuel oxidation and $\text{CO}_2/\text{H}_2\text{O}$ reduction. In reducing conditions (fuel electrode), perovskite oxides can lead to the formation of new, active composite materials after the *ex-solution* of metal nanoparticles, resulting in “atmosphere-adaptive” oxide materials: changing the structural properties (phase and composition), with a concurrent change (improvement) in the electrochemical activity. A brief background on the relationship between defects and transport properties in solid state ionics, a description of SOFC state-of-the-art materials and an overview on recent developments of materials for symmetric r-SSOCs will be presented.

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PRINCIPLES AND APPLICATION OF PHOTOCATALYSIS

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Photocatalysis based on semiconductor materials is being actively investigated as a core technology in solar light harvesting and utilizing processes. The basic process is driven by the photoinduced charge transfers (CTs) occurring on the irradiated semiconductor surface with initiating various redox reactions that are utilized for environmental remediation and solar energy storage. The former reaction is usually initiated by a single electron transfer under aerated conditions to generate reactive oxygen species whereas the latter proceeds via two or more electron transfers in the absence of molecular oxygen. Most of the former reaction systems are thermochemically spontaneous ($\Delta G^\circ < 0$) and lead to the mineralization of organic pollutants whereas the latter is an energy uphill process ($\Delta G^\circ > 0$) and often needs co-catalysts to facilitate the multi-electron transfer processes. The mechanisms and kinetics of interfacial/interparticle CTs are influenced by the bulk and surface properties of semiconductor. While various surface modification techniques have been developed so far, their effects are very diverse and even contradictory in some cases. Better understanding of how the modification influences the photoinduced CT events in semiconductors is required, particularly for designing hybrid photocatalysts with controlled CTs, which is sought-after for practical applications of photocatalysis. Some outstanding questions related with CTs on semiconductor photocatalysts are as follows: 1) How can the recombination of charge pairs be minimized? 2) How can the single-electron transfer and the multi-electron transfer processes be controlled? 3) What determines the pathways of hole (or electron) transfer reactions leading to the generation of reactive radical species such as hydroxyl radical, superoxide, or singlet oxygen? Is it possible to control this selectively and if so, how? 4) How can visible light photons be utilized to induce CT in semiconductor photocatalysis? With these in mind, this lecture discusses the photoinduced CTs occurring on semiconductor photocatalysts modified with various methods developed by this research group and addresses the above questions.

SUSTAINABLE ELECTROCATALYSTS FOR PEMFC/AEMFC

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This century is facing a big challenge in terms of emissions reduction and clean energy source development. Kyoto Protocol first (1997), Paris Agreement later (2015), and the actual Glasgow Climate Conference (COP26) in 2021 have established benchmarks for the new decade to drastically reduce emissions and the global temperature increase, that cannot be satisfied by relying on fossil fuels. In parallel, problems with waste accumulation are rising, and a way of recycling the vast amount of biological wastes from industry could lead to a new circular economy that would turn waste into wealth. In fact, over 140 billion metric tons of biomass waste are produced every year, mostly carbon-containing materials that could be used in different fields by undertaking cheap and sustainable processes for the synthesis of materials with industrial value. Porous carbon materials can be obtained either from animal or vegetal waste, even bacteria or human sources.

Polymer electrolyte membrane fuel cells (PEMFCs) are devices that can convert chemical energy into electric energy. The main problem with this technology is the slow reaction at the cathode, namely the oxygen reduction reaction (ORR). Currently, the best materials for the ORR electrocatalysis are platinum-based in acidic environment, but thanks to a different mechanism in alkaline environment, carbon materials could compete for anion exchange membrane fuel cells (AEMFCs) in alkaline environment and also for direct alcohol fuel cells (DAFCs). And even biomass-derived carbon materials could be promising. The technology is still hindered by high requirements, expensive electrocatalysts, and competition with other energy conversion devices. Therefore, the possibility to recycle waste to prepare new electrocatalysts could be of high interest for this field of research.

The focus of this lecture is on the latest developments on Pt-free electrocatalysts for PEMFC and AEMFC, with a specific focus on carbon-based materials derived from waste biomass. To be appealing for industrial applications, durable low-cost and stable electrocatalysts are a must, a requirement hardly met by platinum-based electrocatalysts, which suffer corrosion and particles aggregation. First, we will introduce the challenge of efficient ORR performance, then analyze the best results obtained with biomass-derived materials, comparing not only the electrochemical parameters but also the approaches used.

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CRITICAL RAW MATERIALS IN STRATEGIC ENERGY TECHNOLOGIES

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The lecture will deal with a systematic overview of the supply chain dependencies of raw and processed materials across strategic energy technologies. These materials are the basis for the realization of all industrial value chains and of a climate-neutral and digital economy, ultimately contributing to societal well-being. Some of the raw materials, assessed as critical raw materials (CRMs), are essential pre-requisites for the development of key-sectors such as the renewable energy and the electric mobility.

EU industry is largely dependent on imports for many raw materials and in some cases is highly exposed to vulnerabilities along the supply chain. Following the global energy transition, the consumption of metallic raw materials necessary for the manufacture of wind turbines, PV panels, batteries and hydrogen production and storage, and other systems will drastically increase. The shift to e-mobility will require batteries, fuel cells and lightweight traction motors not only for cars but also for e-bikes, scooters and heavy-duty transport.

In this perspective, special focus will be devoted to the case of Lithium Ion Batteries (LIB) that are full of CRMs and are expected to dominate the market for the next few decades, from the current 0.5 TWh to about 2.5 TWh in 2030. This will lead to great difficulties in the procurement of critical raw materials and in the management of end-of-life systems. From a circular economy perspective, it is therefore necessary to identify reuse and recycling strategies that make the market demand fully sustainable. The industrial evolution of the sector in this circular economy perspective cannot ignore an accurate redesign of the battery system, starting from the single cell to arrive at the hierarchical structure of the modules.

The most advanced recycling methods will be analyzed from the point of view of economic and environmental sustainability, and the problems underlying the efficient reuse of battery packs from electric vehicles will be critically discussed. The sustainable technologies for the CRM recover and reuse in the Li batteries field, currently developed at the UNIPV-UNIMIB facility R2BATT, will be also finally presented.

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PHOTO(THERMO)CATALYTIC HYDROGEN PRODUCTION FOR SOLAR ENERGY CONVERSION AND STORAGE

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Hydrogen economy represents a possible solution to maintain the world energy demand, meanwhile pursuing the target of zero carbon emission from fossil fuels exploitation in agreement with the Paris climate change conference (COP21). In this contest, photocatalytic hydrogen production has been widely investigated as an environmentally-friendly method for solar energy conversion and storage. Photocatalytic reactions on semiconductors are initiated by the absorption of a photon with energy equal to, or greater than, the bandgap with the consequent formation of an electron-hole pair. The so produced charge carriers can induce the reduction of electron acceptor species (e.g., H^+ yielding H_2) and the oxidation of electron donor species (e.g., H_2O yielding O_2 or organic compounds to CO_2), both adsorbed on the semiconductor surface. Photocatalysis may be expected to be a temperature-independent process because temperature has little effect on photon absorption. However, temperature still influences the kinetics and the mechanism of reactions. In recent years, there is a growing recognition of a possible photo-thermal synergistic effect leading to process intensification [1]. This effect can be exploited to improve solar energy conversion because solar light can act as a combined source of photons and heat (especially the low energy IR portion). In this talk, the principles of photo(thermo)catalysis will be presented together with some selected case histories. Particular emphasis will be devoted to in-situ spectroscopy techniques (in-situ infrared [2] and X-ray absorption spectroscopies [3]) under dynamic conditions to unravel the surface mechanism of reaction.

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PHOTOVOLTAIC ENERGY HARVESTING: FROM THE BASICS TO NEW TRENDS AND FUTURE OPPORTUNITIES

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In this lecture, I aim to provide the student with some initial general concepts of photovoltaic (PV) energy conversion, moving from the description of the production process and working mechanism of first-generation silicon-based solar panels, followed by a description of the standard characterization methods for these devices.[1]

I will then continue by discussing current trends in last generation PV, with special emphasis on technologies based on metal halide perovskites (the so-called perovskite solar cells, PSCs).[2] For PSCs, I will present the current and future market perspectives, ranging from their potential for integration in solar modules and in tandem architectures up to their potential for representing a valuable low-cost solution to power the Internet of Things (IoT). Finally, I will give some indications on how PV and energy storage can be integrated, in order to ensure an efficient conversion and accumulation of solar energy.

References

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HYDROGEN: A CLEAN AND RENEWABLE FUEL FOR THE ENERGY TRANSITION

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Hydrogen is the most abundant element in the universe, of which it accounts for three-quarters of all matter. However, on earth, hydrogen is not present in its molecular form H_2 except in traces, but it is always found combined in molecules, including water, ammonia and hydrocarbons, substances related to many hydrogen-based applications. Hydrogen is an extremely versatile "material". It can be used as a raw material, as a fuel, and as an energy carrier and storage. In recent years, it has attracted the attention of the scientific, political, and economic world for its main feature: unlike traditional fuels, hydrogen does not generate CO_2 by combustion but just water.

Environmental and climate crisis has led, in recent years, to important international decisions and programs. Within these plans, hydrogen has been assigned a key role, outlined in the European "Hydrogen Strategy", launched on 8 July 2020. With this plan, the EU aims to promote the production of clean hydrogen in its multiple uses, in order to contribute to the reduction of climate-changing emissions. Recent geopolitical tensions and emergencies related to energy sources have further brought to the forefront the role of this energy vector, for which important investments have been dedicated by the NextGenerationEU plan and by the industrial world.

The emerging uses of hydrogen, which stimulate current interest, are associated to the property of hydrogen to react with oxygen in an electrochemical device - the fuel cell - producing electricity and, as the only by-product, water. Applications include use as a fuel, as an energy carrier and as an energy reservoir (power-to-gas). The sectors involved are many and varied, from transport to heavy industry and the residential sector.

The presentation will focus attention on the present and future use of hydrogen in the transport sector, which alone is responsible for a quarter of all emissions. Use as a fuel requires energy density and cost considerations. The main uses (some of which are already underway), the main problems and developments foreseen in the coming years will be presented, thus outlining a key role for the hydrogen energy carrier in our sustainable future society.[1]

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EVOLUTION OF SENSITIZATION-BASED PHOTOVOLTAIC CELLS FOR DIVERSE APPLICATIONS

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The recent development and the research directions of the sensitization-based photovoltaic cells (DSPV) will be presented. Since the first emergence of the dye-sensitized solar cells, lots of efforts have been paid for the commercialization of them while the highest attainable efficiency was still limited by far lower than that of the recently reported perovskite type solar cells.[1] Recently, significant progress was reported to enhance the transparency of dye-sensitized solar cells (DSSCs) with various color schemes so that they can be applied to the indoor-type photoenergy conversion/recycling system under very low light intensity condition as well as the conventional BIPV type applications.[1,2] The current efforts are mostly focused on the diversification of dyes for various colors, development of the highly transparent electrode materials for both photoanode and counter electrode, designing of the highly stable and transparent semi-liquid electrolytes.[1-3] The recent achievements were designed to make the large area module size up to 100 cm² with the overall transmittance of 30% and efficiencies of 6, 5, 4 %, for red, green, and blue colored, respectively.

These progresses expanded the application of DSPV to various areas including the development of DSPV-based artificial light cells (ALCs) for harvesting indoor-type low-intensity illumination for many self-powered IoT devices in conjunction with the development of the novel IoT-integrated smart lighting system for complete wireless interconnection as well as charging themselves.[4,5] Similarly, DSPV system can be extended to develop a self-powered electrochemical biosensor for many smart wearable health care systems. Another very challenging extension of this photovoltaic system is dye-sensitized photoelectrochemical energy conversion (DSPEC), which is designed to obtain some value-added fuels and chemicals very effectively and eco-friendly by electrochemical and photoelectrochemical degradation of many waste materials with a large molecular weight such as lignin and different types of micro plastics. [6,7]..

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DIRECT SOLAR-TO-FUEL ENERGY CONVERSION USING SEMICONDUCTOR PHOTOELECTROCHEMISTRY

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The development of robust and inexpensive semiconducting materials that operate at high efficiency are needed to make the direct solar-to-fuel energy conversion by photoelectrochemical (PEC) cells economically viable. In this presentation the strategy of PEC solar fuel production is introduced in a general way. Our laboratory's progress in the development new light absorbing materials and co-catalysts will be discussed along with the application toward overall solar water splitting tandem cells for H₂ production. Specifically, this talk will highlight recent results with the ternary oxides, 2D transition metal dichalcogenides, and organic (π -conjugated) semiconductors as solution-processed photoelectrodes. Aspects of solar light harvesting, material nanostructure, electrocatalysis kinetics, and charge-carrier separation/transport are discussed.

ELECTROCHEMICAL NITROGEN REDUCTION: A SUSTAINABLE WAY TO PRODUCE AMMONIA AND FERTILIZERS

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Solar energy driven processes with H_2O , CO_2 and N_2 as basic feedstocks can produce “solar fuels” that could substitute their fossil-based counterparts. These renewable fuels could reasonably play a key role in future energy systems, *e.g.* as a storage medium in the power sector, as an energy carrier in the transport sector, as fundamental building blocks for the chemical industry.

While H_2 is the most likely and realistic candidate for electricity storage in solar fuels, research on the electrochemical conversion of CO_2 and N_2 into C-based fuels and NH_3 has intrigued electrochemists for decades and is currently undergoing a notable renaissance. In contrast to H_2 production by H_2O electrolysis, CO_2 and N_2 electrocatalytic reduction processes are still far from a mature technology. Significant hurdles regarding reaction selectivity, energy efficiency and overall conversion rate need to be overcome if these processes have to become a viable option for storing renewable electricity and permit the ecological transition, for which Italy has recently created a new Ministry.

Among these technologies, electrochemical nitrogen reduction (E-NRR) has emerged as a challenging strategy for the replacement of the Haber-Bosch process for NH_3 and fertilizers production worldwide. Even if many E-NRR electrocatalysts and electrolytes have been proposed, major challenges are still related to the low activity and selectivity, and the competitive hydrogen evolution reaction (HER) dominates (the majority of electrons and protons goes toward H_2 evolution instead of reducing N_2 to NH_3). The present lecture will be focused on fundamentals of E-NRR, as well as most significant materials and chemical approaches developed in the last 5 years.

This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No. 948769, project title: SuN₂rise).

GREEN AMMONIA ELECTROSYNTHESIS IN AQUEOUS ELECTROLYTE: A PRELIMINARY STUDY

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Due to a potential energy crisis and the continuously increasing environmental problems, research has focused on ammonia (NH₃) as a promising alternative renewable energy carrier and storage intermediate for global use in the future is gaining momentum.^{1–3} Electrochemical nitrogen (N₂) reduction reaction (E-NRR) is a suitable technology widely recognised as an alternative option to the extremely energetically demanding Haber-Bosch process (HBP). The main challenges of E-NRR in aqueous electrolytes is the optimization of the system to suppress the process competing hydrogen evolution reaction (HER). At present, most of works employ a H-type cell, however the

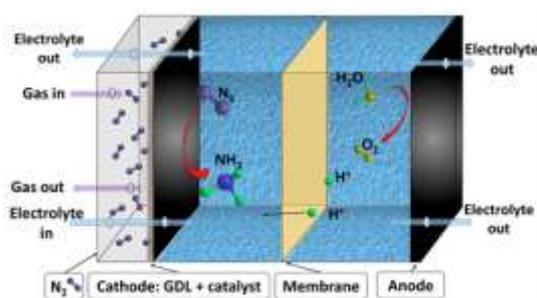


Fig. 2 Scheme of the flow cell equipped with a gas-diffusion electrode.

flow cell reactor with a gas-diffusion electrode (FC-GDE) shows clear advantages as it reduces mass transfer limitations due to low N₂ solubility and allows efficient and quick NH₃ remove.

The aim of the present work is to gain further insight into the activity and stability of a commercial molybdenum disulfide catalyst (MoS₂) combined with different formulated electrolytes (LiSO₄, LiClO₄ and K₂SO₄ at different concentration and pH). All the experiments have been

performed in a FC-GDE (Fig. 1) on which the catalyst is immobilized through air-brushing technique. Promising results have been obtained when employing Li⁺ as a cation in the electrolyte since it can promote MoS₂ NRR activity thanks to the modification of the crystalline structure after Li⁺ ions intercalation.⁴ The studied catalyst/electrolyte combination made it possible to obtain Faradaic efficiencies between 5 and 10%, and 85-301 μmol g⁻¹ h⁻¹ yield at -0.6 V vs. RHE. With these promising results, further experiments are being carried out to find the optimum electrolyte concentration and pH, potential and gas and liquid flow rate.

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EXPERIMENTAL STRATEGY TO ENHANCE THE PHOTOCATALYTIC ACTIVITY OF CS₂AGBiCl₆ LEAD-FREE DOUBLE PEROVSKITE DERIVATIVE BY G-C₃N₄ COMPOSITE

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The implementation of heterojunction based on metal halide perovskite (MHPs) is a promising route to obtain innovative photocatalysts to run relevant solar-driven reactions. Solar-driven photocatalysis by MHPs is emerging as a positive field to promote several significant reactions taking advantage of the superior optical properties of these novel semiconductor materials. However, the toxicity of lead, present in the most studied perovskites and, chemical instability issues prevent the lead halide perovskites wide practical application. Replacing two Pb²⁺ ($2\text{Pb}^{2+} \rightarrow \text{M}^+ + \text{M}^{3+}$) with one monovalent ion ($\text{M}^+ = \text{Au}^+, \text{Ag}^+, \text{Cu}^+$) and one trivalent ion ($\text{M}^{3+} = \text{Bi}^{3+}, \text{In}^{3+}, \text{Sb}^{3+}$) represents a simple strategy for the synthesis of lead-free perovskites that are quite stable in the air. Among these alternatives, Cs₂AgBiCl₆ has been widely investigated for its suitable band-gap, superior stability against moisture and high defect states. In this work, an experimental study on the synergic coupling between a lead-free double perovskite derivative Cs₂AgBiCl₆ and g-C₃N₄ thermally modified is presented. Three heterojunction systems with variable grain size and composition have been investigated for photocatalytic water splitting application towards green H₂ evolution and for nitrogen photo-fixation towards green NH₃ production in different reaction environment, in order to evaluate the role of the sacrificial electron donor. Interesting results have been achieved in both experiments series, reaching 2109 HER for hydrogen photogeneration in isopropanol aqueous solution (10% v/v) and more than 0.05 mmol/g/h of NH₃ for nitrogen photo-fixation. In view of this finding, is it possible to affirm that this novel class of perovskites represents a promising candidate for solar-driven photocatalytic reactions.¹⁻⁵

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N₂ SOLAR ACTIVATION: AMMONIA AS HYDROGEN VECTOR FOR ENERGY STORAGE

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In recent years, several studies focused their attention on alternative fuels in order to achieve a sustainable way to store and transform energy. In this regard, ammonia could be a good candidate for a circular energy transformation cycle. N₂ activation can be obtained by different mechanisms depending on catalyst and reaction conditions. In Haber-Bosch process the high temperature and pressure are necessary to activate nitrogen by dissociative mechanism¹. Less harsh conditions can be attempted favouring the associative N₂ reduction mechanism by means of a catalyst and using alternative forms of energy to activate the catalytic pathway. To effectively achieve chemical energy storage, energy vectors such as photons and electrons could be suitable choices over heat, as for their sustainability and efficiency. Layered Double Hydroxide Nanosheets (LDH) materials can act as a good photocatalyst as for its interesting properties: the spacing between layers can favour N₂ adsorption, while the high surface area can provide a significant number of catalytic sites².

In this work, [M^a(II)M^b(II)]_xM(III)_{1-x}(OH)₂ LDHs, in which M^a(II) and M^b(II) are, respectively, Ni and Cu, while M(III) are Cr and Al, were synthesised using an easy, reproducible, and sustainable procedure. The materials characterization showed a brucite – like structure, in accordance with literature data; BET surface area analysis resulted in high surface area and good porosity. A heterogeneous photocatalytic test was conducted illuminating an aqueous dispersion containing the sample with a commercial LED light at RT; the results obtained showed that Cr – containing LDHs seem to work better than Al – containing ones, based on the NH₃ production rate over surface area ratio. In addition, the insertion of Ni in the catalyst seem to enhance nitrogen activation, probably due to the insertion of new energy levels in the band structure and to the good Ni – H₂O interaction, which could help the effective N – H bond formation during the catalytic reaction.

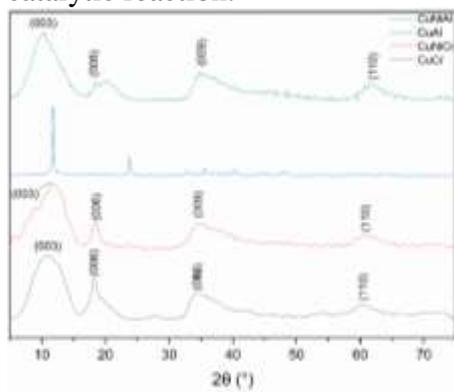


Fig. 1 - XRD patterns of different LDHs

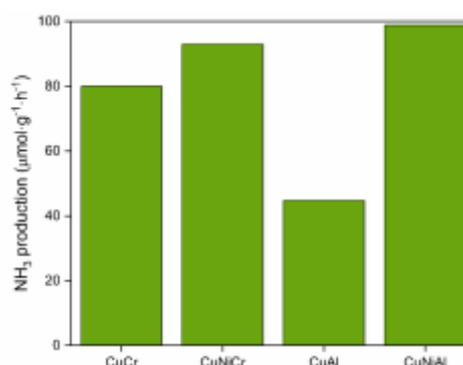


Fig. 2 – NH₃ production rate after 1 h of illumination at RT

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THE SUN₂RISE LI-N₂ CELL CONCEPT IN THE LANDSCAPE OF LI-MEDIATED N₂ REDUCTION REACTION STRATEGIES FOR AMMONIA PRODUCTION

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Operating in severe conditions (at least 450 °C and, in particular, 200 atm), the Haber-Bosh (HB) process is responsible of around 1.44% of the global greenhouse gas emissions. To find a renewable-driven and delocalized electrochemical process complementary to HB for NH₃ production could be a key solution for our society that is facing climate change crisis and is demographically growing.

The Li mediated (Li-m) pathway represents the most promising solution: thanks to the unique reducing power of this alkali metal, electrochemical cell with Li salt in aprotic environment achieves the highest Faradaic efficiency (FE) in the N₂ reduction reaction (NRR) research field. Different systems have been evaluated in literature for Li-m NRR, both in a continuous process in presence of a proton donor as ethanol [1] and in a step-by-step system, to conduct Li nitridation in absence of H⁺ and avoid the competitive hydrogen evolution reaction (HER).

In comparison with Li-m NRR continuous systems, the step-by-step technology could alternate H₂O presence, as proton donor, with the electrochemical reaction. The system degradation, the proton donor consumption and HER could be avoided. Moreover, the Li-N₂ reaction in a completely aprotic environment could maximize Li exploitation. This technology could enhance scalability, since the Li reduction, essential for its recirculation, is the more energy requiring step [2].

The promising Li-N₂ cells have been recently tested both for ammonia production and as energy storage devices, in similarity with metallic Li-gaseous batteries (e.g. Li-O₂ devices); even if this technology is still in its infancy, a proof-of-concept of Li₃N formation has been verified [3] and our laboratory is currently addressing this challenge within the SuN₂rise project.

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PHOTOREDUCTION OF CO₂ TO LIQUID PRODUCTS WITH INNOVATIVE PHOTOCATALYSTS

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Emission of CO₂ caused by the use of fossil fuels has been widely considered as the anthropogenic primary contributor to the climate change. Lately, photocatalysis and in particular CO₂ photoreduction (PR) has gained more and more attention [1] as a way to store solar energy. CO₂ is used as reagent to produce different kind of liquid products, such as formic acid and methanol, in mild condition (80°C) in aqueous solution [2]. An innovative high pressure photoreactor allows to perform the reaction in aqueous phase up to 20 bar which increase the CO₂ solubility and subsequently also the activity of the process.

At first, the influence of different hole scavengers on the productivity has been investigated. TiO₂ is cheap, non-toxic to humans, abundant and for these reasons it has been used as a reference [3]. Ammonia did not show any activity. P25 performances when using alcohols, vary greatly depending on the HS used. 2-propanol showed a HCOOH and a H₂ productivity of 2401 mmol/kg_{cat} h and 1478 mmol/kg_{cat} h respectively, with the additional production of acetic acid.

Then, different catalyst has been synthesized and tested to increase the productivity of the process. BaTiO₃, CuO nanoparticles were synthesized by solvothermal process, ZnO by precipitation method and the CuO NPs have been deposited through impregnation. Pure WO₃ and a composite of WO₃/TiO₂ have been synthesized through FSP. Bare BaTiO₃ and 40% WO₃/60% TiO₂ showed the best performances with productivity of 36.9 mol/kg_{cat}h and 36.5 mol/kg_{cat}h respectively, which are outstanding results compared to the ones reported in literature.

Lastly, glass tiles support has been designed, optimized and realized in stainless-steel through the use of 3D-printing technology. The latter allow to fit 12 slides coated with the desired catalyst in the reactor. The deposition procedure has been standardized, modification with Ag has been also performed and the obtained glass tiles have been tested towards the CO₂ PR, showing good performance compared to P25 in form of powder. The deposited catalyst avoids the problem of the separation of titania from the liquid mixture and represents a starting point for the recycle and reuse of the photocatalysts.

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HIGH CO₂ PHOTOREDUCTION PERFORMANCE ACHIEVED WITH CERIA-BASED PHOTOCATALYSTS

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The massive presence of CO₂ in the atmosphere represents a global challenge for industry and academia to combat climate change that is affecting the environment with implications for human life. One promising approach to reduce the concentration of CO₂ is photoconversion reactions. In these reactions, CO₂, after being adsorbed onto an appropriate substrate, reacts with the reactive species generated when the substrate (photocatalyst) is illuminated with an appropriate light source (UV or visible light) [1].

The present research aims to design a high-performance catalyst capable of enhancing CO₂ conversion under UV or visible light irradiation. In this scenario, cerium oxide (ceria) emerges as a promising candidate, due to the easy conversion between Ce(III) and Ce(IV) states which generates a strong catalytic potential without any structural modification of the fluorite structure. Furthermore, exploiting the doping with other metals is possible to tune the light absorption range. Among the heteroatom dopants, Fe³⁺ is a promising candidate as it can create defect states in the band gap or introduce energy levels in it.

Fe-doped Ceria nanoparticles (NPs) have been synthesized by reverse microemulsion method conducted at room temperature. This approach involves the formation of an inner aqueous core, containing cerium and dopant precursors simultaneously, where a controlled nanoprecipitation takes place. The aqueous core stage acts as a nanoreactor, favoring the effective inclusion of heteroatoms in larger quantities. The adopted one-pot reverse micelle strategy allowed the preparation of mesoporous catalyst with a high nominal molar percentage of 2.5, 5, 7.5 and 10%.

The set of prepared catalysts have been characterized by several techniques and their photocatalytic activity has been tested at 8 bar and compared with TiO₂-P25 as benchmark commercial catalyst. For all the prepared samples the activity was higher than the benchmark P25. In particular the productivity of formic acid and the conversion of the hole scavenger both increased with Fe content. For instance, the catalysts with 2.5% and 5% of Fe showed a productivity of formic acid respectively of 22.1 mol/kg_{cat} h and 26.8 mol/kg_{cat} h of formic acid, respectively, vs. ca. 14 for P25.

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EFFECT OF DOPAMINE ON PHOTOSYNTHETIC GROWTH OF BOTH *RHODOBACTER SPHAEROIDES* R26 MUTANT AND 2.4.1 WILD TYPE

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Rhodobacter (R.) sphaeroides R26 is a purple non-sulfur microorganism belonging to the class of anoxygenic photosynthetic bacteria (APB), chosen as model system to study bioremediation and optoelectronic applications. R26 is the mutant of wild type *sphaeroides* 2.4.1: it is carotenoidless and easily to handling respect of the photosynthetic apparatus and the extraction of reaction center (RC). RC is the photochemical core of the anoxygenic photosynthesis in bacteria, specialized on the generation of an electron-hole couple after the solar light harvesting by bacterial antennae systems. Dopamine (DA) is a neurotransmitter which polymerize into polydopamine (PDA), a variegated polymer melanin-like and thus, as natural melanin, provides adhesive properties and biocompatibility useful to enhance and improving the extracellular electron transfer from the bacterial photosynthetic apparatus to an electrode. Adaptation of photosynthetic microorganisms to increasing concentrations of DA allows to firstly investigate the effect of the monomer on the cellular activity and healthy of bacterial cells. On the other hand, the effective cellular growths of mutant R26 and wild type 2.4.1 in presence of DA permit to test photocurrents by adapted bacteria, with the aim of optoelectronic applications for energy production from bacteria. We demonstrate that DA is not detrimental for the bacterial growth, the cellular morphology and also produces an increasing photocurrent that is dopamine-dependent, as the monomer concentration rises. Adapted bacteria can represent the active layer of biodevices in bioelectronics, in which both the lifetime and electron transfer from the bacterial RC to the electrode is improved by DA.

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CONFINED SINGLE NICKEL ATOMS IN LOW CONDENSED CARBON NITRIDE AS EFFICIENT OXYGEN EVOLUTION CATALYST

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Carbon nitride (CN) has several properties appealing to an effective stabilization of Single Atom Catalysts (SACs). Indeed, an intrinsic feature of this structure is the presence of cavities, which are extremely suitable for the insertion of metal atoms, that strongly coordinate with the nitrogen atoms, stabilizing and confining them.¹ The substrate material CN is chemically synthesized starting from melamine and cyanuric chloride, through three steps of increasing temperature (0, 25, 140 °C).² The metalation is done through an impregnation method starting from nickel chloride, to obtain Ni-CN(x). The totality of synthesis of SACs based on CN reported in literature uses a high-temperature thermal condensation process, which necessitates the exfoliation of the material and the removal of metal nanoparticles.³ The TEM and XRD characterization reveal an exfoliated graphitic structure with the absence of Ni nanoparticles. The presence of Ni single atoms is confirmed by HAADF-STEM (Fig.1b) and XAS characterization (Fig.1c). The Ni-CN(x) structure reported in Fig.1a outcomes from both experimental and theoretical results, that include XRD and XPS DFT simulation. The catalytic activity for OER is studied through electrochemical techniques. In Fig.1d is reported the relation between current density and Ni content. Ni content determined by ICP-MS characterization, reported in the graph, demonstrates a direct relationship with the catalytic activity for 0<x<0.2 and constant current density for x>0.2. Therefore, this is the maximum Ni content that CN can stabilize as single atom. The stability of the materials was studied by HR-TEM and EXAFS post-accelerated ageing treatment.

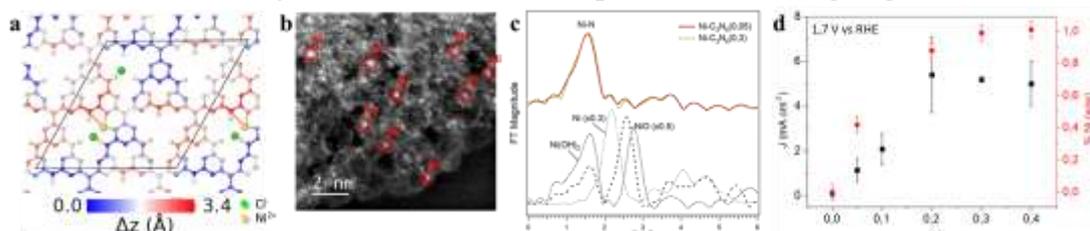


Fig.1: (a) Molecular structure of Ni-CN(x), x is the synthesis molar ratio Ni/CN; (b) HAADF-STEM image of Ni-CN(0.2); (c) FT-EXAFS spectrum; (d) current density (J) generated at 1.7 V vs RHE for x=0-0.4, red axis and red values are referred to the ICP-MS characterization.

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LUMINESCENT SOLAR CONCENTRATORS BASED ON POLY(METHYL METHACRYLATE) FROM RECYCLED SOURCES

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Luminescent Solar Concentrators (LSCs) are a smart solution to enhance solar harvesting by exploiting diffuse light and keeping costs low [1]. LSCs are usually made of poly(methyl methacrylate) (PMMA), a commodity plastic with a suitable refractive index and optimal internal transmittance. From the perspective of industrial production of LSCs, the amount of PMMA brought to market could increase considerably. The possibility of chemical recycling of PMMA [2] can give circularity to the economy of these devices. Here, we report the use of LSCs based on PMMA obtained from chemically recycled methyl methacrylate (r-PMMA). The performance of r-PMMA-based LSCs containing Lumogen Red 305 (LR305) as a state-of-the-art fluorophore [3] was compared with LSCs obtained from synthetic methyl methacrylate in terms of internal photonic efficiency (η_{int}), external photonic efficiency (η_{ext}), fluorescence quantum yield (QY) and electrical efficiency of the device (η_{dev}) when coupled to a silicon photovoltaic cell [4]. Devices made from chemically recycled monomers appear viable routes to more sustainable LSCs.

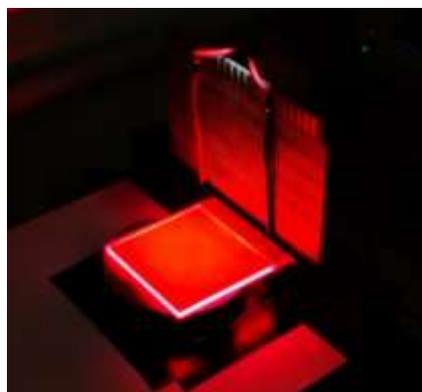


Figure 1. An LR305-containing LSC coupled to a PV cell under the radiation of a solar simulator.

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NI-LAMNO₃ NANOCOMPOSITES AS NOVEL PGM-FREE CATALYSTS FOR CH₄ COMBUSTION: EFFECT OF SYNTHETIC METHOD IN CATALYTIC PERFORMANCES

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Methane can represent a renewable and low carbon fuel when derived from biomass anaerobic digestion to biogas [1], which can be fed in the already existing natural gas pipelines and vehicles. CH₄ oxidation is a key reaction taking place in post-combustion three-way catalytic converters (TWC) applied to methane-fueled vehicles. However, conventional catalytic formulations rely on noble metal particles, especially Pd [2], hence its replacement with cheaper and more earth-abundant materials would be desirable. Metallic Ni is widely recognized as an active catalyst for CH₄ activation reactions, such as Steam Reforming and Dry Reforming. Perovskites were found suitable materials to stabilize the dispersion of Platinum Group Metals (PGMs) catalysts, thanks to a self-regenerative process in which PGMs can reversibly exit from and re-enter the perovskite lattice in oscillating reducing-oxidizing conditions typical of TWC operating around the stoichiometric air/fuel ratio [3]. There is some evidence that a similar mechanism can also occur for non-noble transition metals like Ni [4]. Based on the above considerations, we hereby propose perovskite-supported Ni catalysts for the complete CH₄ combustion to CO₂. The chosen support was a LaMn-perovskite, for its good oxidation activity and oxygen storage capacity, with A-site deficient composition (La_{0.8}MnO₃), which should favor the generation of oxygen vacancies and thus the absorption of gas-phase reactants. The synthesis was carried by means of the citrate sol-gel route with final calcination in air at 750°C; different citric acid amounts (molar ratio CA/metals = 1.1 or 1.5) were evaluated. Ni was added to the catalytic formulation according to two different methods: i) perovskite B-site doping to obtain La_{0.8}Mn_{1-x}Ni_xO₃ (x = 0.1 or 0.2) compositions, followed by Ni⁰ exsolution out of the oxide matrix through a reductive treatment in 5% H₂/Ar; ii) ammonia-driven deposition precipitation (ADP), i.e., Ni²⁺ precipitation onto pre-calcined La_{0.8}MnO₃ support by NH₃ addition, followed by calcination in air and subsequent reduction to Ni⁰ in 5% H₂/Ar. The obtained catalysts were characterized by XRD, BET, SEM-EDX, H₂-TPR and H₂-pulsed chemisorption. Catalytic CH₄ oxidation tests with stoichiometric O₂ were carried out on both calcined and reduced catalysts, in the temperature range 300-800°C. Correlations between synthesis parameters (amount of citric acid, Ni incorporation method), physicochemical properties and catalytic activity will be discussed.

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TiO₂-BASED HETEROJUNCTION WITH 2D BLACK PHOSPHORUS FOR EFFICIENT H₂ PRODUCTION

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The design of a suitable photocatalyst for effective transformation of sunlight into chemical energy is a promising, though challenging way to produce hydrogen from water by means of solar energy.^[1,2] After the pioneering study of photoelectrochemical splitting of water on an n-type TiO₂ electrode^[3], the production of H₂ by artificial photocatalysis has received enormous attention aiming to help overcoming the shortage of traditional fossil fuels. Several studies have shown that exfoliated black phosphorus (BP) is a promising candidate in the field of photocatalysis being a semiconductor with a high hole mobility, adjustable bandgap and wide optical absorption in the visible spectrum. Bearing this in mind, BP was added to TiO₂, which suffers from a narrow absorption spectrum (only UV) and a rapid recombination of charge carriers.^[4] Here, we report a new ternary TiO₂/BP/CoP nanocomposite which exhibits a UV-visible light photocatalytic H₂ evolution activity of 7400 μmol h⁻¹ g⁻¹, revealing ~28-fold enhancement compared to pristine TiO₂.

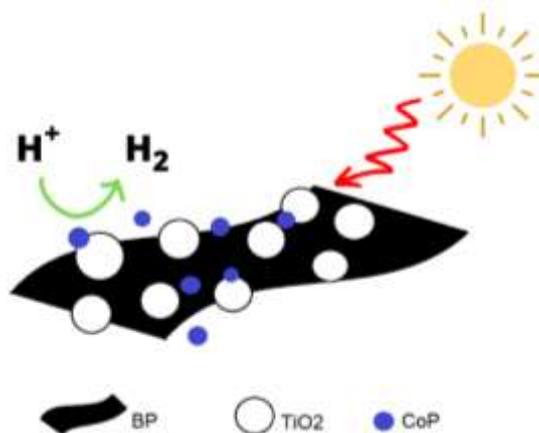


Figure 1: Photocatalytic hydrogen generation from water using TiO₂/BP/CoP composite under simulated sunlight irradiation.

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CORROSION OF AL ALLOYS TANKS IN BIO ETHANOL BLENDED GASOLINE FUEL

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

EXPERIMENTAL AND THEORETICAL STUDIES OF THE LiBH_4 - LiI PSEUDO-BINARY SYSTEM AND LiBH_4 - LiI - LiBr PSEUDO-TERNARY SYSTEM FOR SOLID-STATE ELECTROLYTES APPLICATIONS

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Solid state electrolytes have enabled the development of all solid-state batteries (SSB)¹, that have several advantages with respect to commercial batteries, including a reduction in weight and volume, an increase of energy density, a higher energy efficiency, and limited energy loss and flammability. Complex hydrides are a promising class of materials for solid-state electrolytes, for both Lithium-based and non-Lithium-based SSB, owing to their versatile structure.

In the present study, we focused our attention on LiBH_4 . It presents a low conductive orthorhombic structure at room temperature, but at 110 °C it shows a polymorphic transition to a hexagonal high conducting phase. The hexagonal structure of the LiBH_4 at room temperature can be stabilised by substituting the BH_4^- anion with I^{2-4} enabling high Li-ion conductive materials at room temperature.^{2,4} The pseudo-binary LiBH_4 - LiI system has been explored, investigating several compositions, synthesized by ball milling and subsequently annealed. X-ray diffraction and Differential Scanning Calorimetry have been exploited to determine structural and thermodynamic features of various samples. The monophasic zone of the hexagonal $\text{Li}(\text{BH}_4)_{1-x}(\text{I})_x$ solid solution has been defined equal to $0.20 \leq x \leq 0.55$ at 25 °C. For the formation of the h- $\text{Li}(\text{BH}_4)_{0.5}(\text{I})_{0.5}$ solid solution, a value of the enthalpy of mixing (ΔH_{mix}) has been determined experimentally equal to -19.33 ± 0.2 kJ/mol of compound. In addition, the enthalpy of melting has been measured for different compositions. Lattice stabilities of LiBH_4 and LiI have been determined by ab-initio calculations. Combining results of experiments, literature data and theoretical calculations, the pseudo-binary LiBH_4 - LiI phase diagram has been determined and assessed in all composition and temperature ranges by the CALPHAD method. Preliminary results on the pseudo-ternary LiBH_4 - LiI - LiBr system will be also presented, evidencing the existence of the hexagonal solid solution over an expanded compositional range.

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ENHANCED LIGHT HARVESTING EFFICIENCY BY FÖRSTER RESONANCE ENERGY TRANSFER (FRET) IN DYE-SENSITIZED SOLAR CELLS (DSSC)

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Dye-Sensitized solar cells (DSSCs) have received great attention in recent years, aiming to optimize their components in order to improve efficiencies. The synthesis of new organic photosensitizer for improving Light Harvesting Efficiency (LHE) in DSSC was the aim of this work. We focused on a metal-free antenna-sensitizer covalent adduct (**DYAD**),^[1] aiming to obtain a molecular system characterized by high molar attenuation coefficient and broad absorption spectrum in the visible region. We explored Förster Resonance Energy Transfer (FRET)^[2] as a mean to transfer energy between the **ANTENNA** and the dye **RI114** (Figure 1). Two molecular fragments with complementary light absorption properties were designed and prepared to be joined together using a CuAAC “click” reaction,^[3] as late-stage functionalization. The molecular fragments and the final dyad were spectroscopically characterized using absorption and emission spectroscopy techniques, and it was possible to prove that energy transfer occurred between the two units.

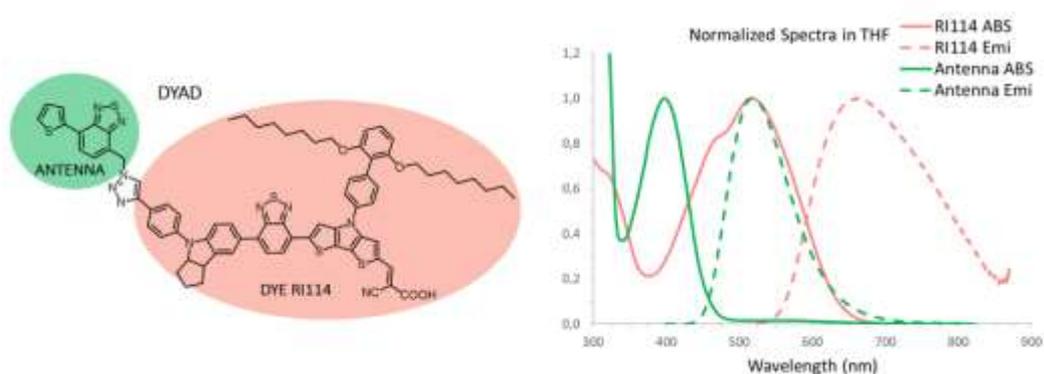


Figure 1. Left: design of the antenna- dye (**DYAD**). Right: overlap of normalized absorption and emission spectra of **RI114** and **ANTENNA** fragments.

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THE CHIRAL INDUCED SPIN-SELECTIVITY EFFECT AND ITS APPLICATIONS TO RENEWABLE ENERGY TECHNOLOGIES

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The Chiral Induced Spin Selectivity (CISS) effect is the ability of chiral materials to selectively conduct electrons with a preferential spin, depending on the handedness of the material itself¹. The CISS effect has major implications in various fields, from biology² to molecular electronics³, and can have a huge impact on several technological applications⁴.

In this lecture we will briefly go through an introduction of how the CISS effect works, how it was discovered and how it branches in several multidisciplinary topics. We will then focus on how it is possible to exploit it in renewable energy technologies.

Several recent works have shown how using spin-polarized currents in the electrolysis of water can lower the overpotential required for the Oxygen Evolution Reaction (OER), thus leading to improved efficiencies and a remarkable increase in the cell hydrogen production^{5,6}. While spin-polarized current can be obtained by using ferromagnetic electrodes and an external magnetic field, the same result can be obtained by using chiral catalysts. We will see several experimental systems that show how chiral OER catalysts of different nature systematically outperform their achiral homologous thanks to their spin-filtering properties.

The CISS effect has also been demonstrated to improve the Oxygen Reduction Reaction (ORR)⁷, and we will see some experimental results that highlight the potentiality of chiral electrocatalysts for this application.

To conclude, we will see some possible applications of spin-polarized electrochemistry to other important reactions for renewable energy technologies such as the Carbon Dioxide Reduction Reaction (CO₂RR) and the Nitrogen Reduction Reaction (NRR)⁸.

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DYE-SENSITIZED SOLAR CELLS: EXPLORING NEW DESIGNS OF ORGANIC DYES TO ENHANCE OPTICAL PROPERTIES

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Dye-Sensitized Solar Cells (DSSC) is an emerging photovoltaic (PV) technology that recently found its niches in the PV market with architectural value: indoor application and facades.^[1] The devices functioning and the use they are designed for are strictly correlated to the dyes design. Organic dyes for DSSC generally feature the established D-A- π -A design requiring non-symmetric structures: it allowed reaching outstanding performances at the cost of low-transparency and complex, unsustainable synthesis. Here we present new designs for organic dyes focusing on small symmetric molecules obtained with short synthetic strategies exploiting direct arylation.^[2] The dyes feature divergent optical properties ranging from pitch dark coloration to high transparency: also, uncommon colorations like green tones can be achieved (*Figure 1*).^[3,4] Assembling devices with different electrolytes and substrates enhance the optical properties of the dyes to meet architectural requirements. The resulting DSSC full devices show composition of the transmitted light fits the human eye sensitivity spectrum, satisfying the requirements for perceived transparency for Building-Integrated PV.^[5]

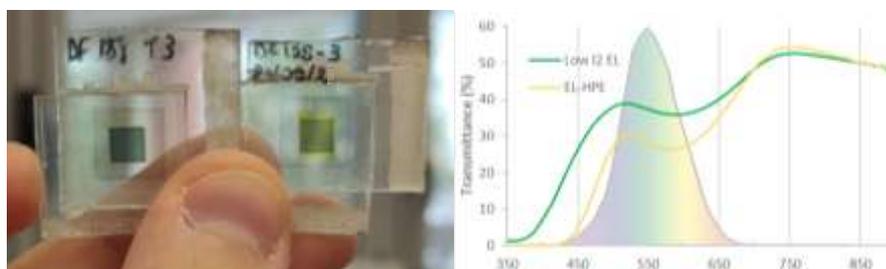


Figure 1. Left: full DSSC devices with a thienopyrazine green dye and different electrolytes. Right: devices transmittance, human eye sensitivity shown in the background as a comparison.

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ECO-FRIENDLY DEEP EUTECTIC SOLVENT ELECTROLYTE SOLUTIONS FOR DYE-SENSITIZED SOLAR CELLS

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Among photovoltaic technologies, dye-sensitized solar cells (DSSCs) offer high conversion efficiencies and low-cost manufacturing, but the presence of toxic volatile organic solvents (VOC) in their electrolyte solutions limits their sustainability and represents a serious issue.

In the last two decades, a new class of eco-friendly reaction media known as Deep Eutectic Solvents (DESs) has emerged in the literature. DESs are made of two or three safe and cheap components which, through hydrogen-bond interactions, form a eutectic mixture with a melting point much lower than both the individual components. These mixtures show very interesting properties, such as low volatility, low cost and thermal stability, that make them attractive in several fields of materials science (organic synthesis, CO₂ capture, electrochemistry, catalysis, ...).¹

DSSCs have grown up with the promise of sustainable electricity production, being devices inspired by natural photosynthesis. To reduce their environmental footprint, over the years much work has been devoted to developing water-based electrolyte solutions. Alternatively, several groups replaced the standard VOC with DESs to exploit their peculiar attributes, such as their eco-friendly nature and the tailorable characteristics of the solvent environment depending on the choice of DES components.²

In this lecture, different DESs successfully tested in DSSCs will be shown, describing the main steps made in the literature to understand the behaviour of these novel solvents in the device and to improve their performance.

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TOWARDS ANODELESS LITHIUM METAL NEGATIVE ELECTRODES FOR SECONDARY APROTIC BATTERIES

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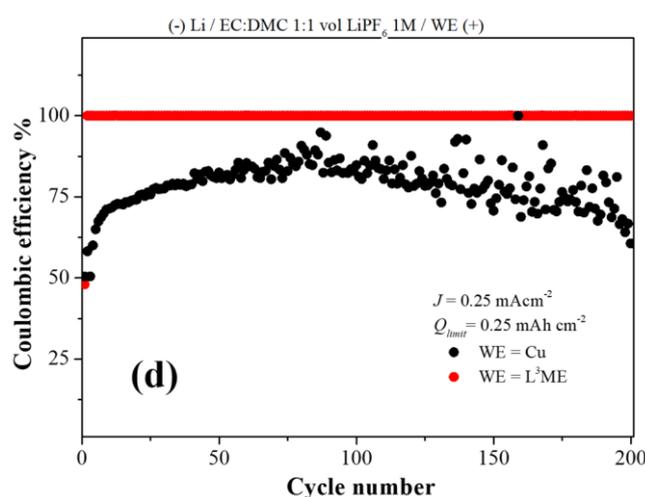
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In the last three decades massive research and development investments from companies, academia and national laboratories fed the development of batteries able to power the transition from mobiles to portable electronics, power tools and hybrid electric vehicles. This amazing technological shift roots in the lithium-ion intercalation chemistry and its unique versatility. Unfortunately, the lithium-ion intercalation paradigm is reaching its theoretical limits, thus opening the quest for a novel flexible process to store energy in batteries for the next technological challenge (e.g. massive stationary energy storage, full electron mobility).

Among all, the electrochemical plating/stripping of lithium metal at the negative electrode can in principle disclose a jump in performance, thanks to the outstanding theoretical figures of Li electrodes ($Q_{th} = 3860 \text{ mAhg}^{-1}$ and $E^\circ = -3.04 \text{ V}$ vs SHE, standard hydrogen electrode, to be compared to the commercial negative graphite electrodes for LIBs 372 mAhg^{-1} and $\approx -2.9 \text{ V}$ vs SHE).

Here we demonstrate the synergistic use of (a) laser induced periodic surface structure (LIPSS) patterning under ambient conditions and (b) coating with an artificial solid-state electrolyte (aSEI) to manufacture a stainless-steel (SS) lithium-less Li metal electrode (L^3ME) able to reversibly plate/strip lithium for hundreds of cycles in an aprotic galvanostatic cell. The optimized L^3ME material is a SS thin foils with a mesostructured surface patterned by a regular distribution of ripples constituted by Fe and Fe_2O_3 . This regular surface pattern is buried underneath a uniform and smooth polyethylene oxide- $LiNO_3$ composite film.



The L^3ME electrodes show superior performance in aprotic lithium cells being able to accommodate a fully reversible metallic Li stripping/deposition with coulombic efficiencies of 100% for hundreds of cycles.

Figure 1: Comparison of the measured coulombic efficiencies for Cu and L^3ME electrodes in lithium cells.

NOVEL ORGANIC SENSITIZERS FOR PHOTOANODE WATER SPLITTING IN DYE-SENSITIZED PHOTOELECTROCHEMICAL CELLS

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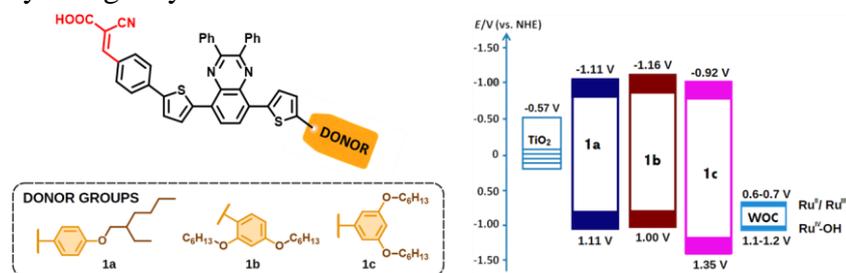
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Dye-sensitized photoelectrochemical cells (DS-PECs) for water-splitting are receiving increasing attention as a novel technology for visible light-induced solar fuels production¹. The water oxidation reaction, occurring at the photoanode (PA), represents the key rate-determining step in water splitting, therefore the assembly of efficient and stable photoanodes is an essential part of DS-PECs. Beside the semiconductor (SC) oxide and the water oxidation catalyst (WOC), the role of the dye is crucial for optimizing the harvesting of visible light and triggering the oxidation reaction at the catalytic active site. Most of the dyes tested to date in PA-DS-PEC for water splitting show a narrow absorption spectrum ($\lambda_{\text{max}} < 450$ nm) and poor stability. Therefore, the design of dye molecules with a broad optical response, appropriate energy levels, and good stability is urgently needed².



In this study, three novel metal-free organic dyes (**1a–c**), based on a quinoxaline central core, have been investigated as possible anode sensitizers. Compounds **1a–c** contains three slightly different donor moieties in order to modulate their HOMO energy level and use them in combination with the chosen WOC: Ru(bda)(pyP)₂ (pyP = pyridin-4-methyl phosphonic acid)³. All the compounds have been successfully obtained through a simple and general synthetic method leading to good overall yields. Preliminary studies, such as absorption and emission spectra and cyclic voltammetry, have been also carried out in order to evaluate their photoelectrochemical properties. All three compounds show promising energy levels, especially dye **1c**, for possible application in PA-DS-PEC.

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DYE SENSITIZED SOLAR CELLS FOR AMBIENT LIGHT IN DEEP EUTECTIC SOLVENTS

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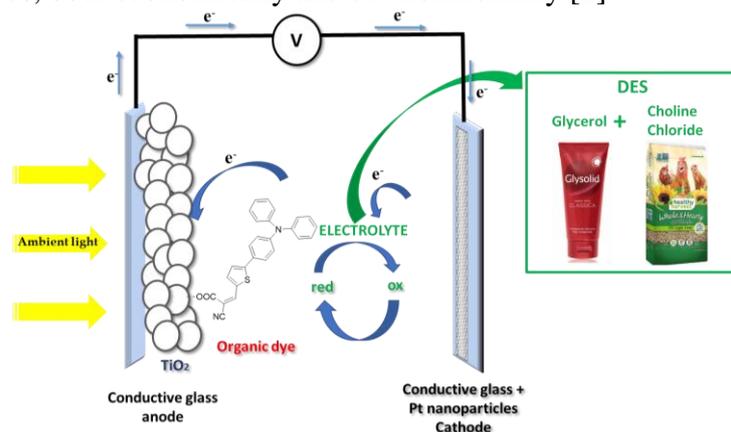
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The continuous increase in energy demand requires the search for renewable energy solutions. One of the most interesting approaches is the use of photovoltaics. To date, a new strand of solar cells is being developed that, in parallel with natural sunlight, uses ambient light, both natural and artificial, to power the numerous devices related to the Internet of Things (IoT). For this purpose, dye-sensitized solar cells (DSSCs) can be used. Compared to other solar cell technologies, they show outstanding performances under indoor conditions with an artificial diffused light source. By using an appropriate dye, thereby taking advantage of scattered light from artificial sources such as light bulbs, DSSCs can produce energy. To increase the sustainability of this type of solar cell, it is mandatory (in particular in home applications) to replace the often toxic and volatile organic solvents (VOCs), traditionally used for the electrolyte solutions, with environmentally friendly solvents, such as Deep Eutectic Solvents (DES). The latter are solutions of Lewis or Brønsted acids and bases that form a liquid eutectic mixture with a melting point far below that of either of the individual components. In this communication it can be stated that the coupling of organic dyes, specifically designed to work under artificial light, with a harmless electrolyte solution can lead to highly sustainable devices, both economically and environmentally.[1]



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SYNTHESIS AND CHARACTERIZATION OF NEW ORGANIC PRECURSORS OF HOLE-TRANSPORTING SELF-ASSEMBLED MONOLAYERS FOR PEROVSKITE SOLAR CELLS

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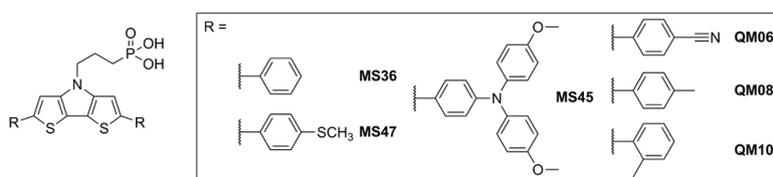
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Perovskite solar cells (PSCs) are one of the emerging technologies in the photovoltaic industry. Within them, the hole-transporting material (HTM), capable of transporting the holes formed after photo-excitation of the perovskite to the counter-electrode, plays an essential role in improving the performance of the device. This work aimed to design, synthesize and characterize spectroscopically and electrochemically a new class of compounds capable of forming self-assembling monolayers (SAMs) to be used as organic HTMs for inverted-configuration perovskite solar cells (*p-i-n* PSCs)¹. Six new SAMs with a common structure containing a dithieno[3,2-*b*:2',3'-*d*]pyrrolic (DTP) core acting as a heteroaromatic functional group, a propyl chain as a spacer and a phosphonic acid as an anchor group were synthesized and characterized.



A common synthetic procedure based on Pd-catalyzed cross-coupling reactions was developed for all the molecules, enabling them to be obtained in a few steps and with good yields. All the DTP-based derivatives possess the appropriate spectroscopic and electrochemical properties to act properly as HTMs within a PSC. All the new molecules have been successfully tested for the realization of *p-i-n* PSC devices and the most promising results in terms of the efficiency of conversion of sunlight into electric current (18.42%) have been obtained with **QM06**, slightly lower than the efficiency obtained with the literature reference SAM, **MeO-2PACz** (20.4 %).²

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HYDROGEN PRODUCTION FROM WASTEWATER: STUDY OF ELECTRODE MATERIALS FOR AMMONIA OXIDATION

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During the last three decades, there has been an exponential growth in the research of new technologies able to generate green energy by reducing the consumption of fossil fuels. In particular, the imposition of Carbon Neutrality by 2050 by the European Union requires an ecological transition to renewable sources, electric mobility, a circular economy, and energy storage.

Hydrogen has been identified as a potential alternative energy carrier. The chemical energy stored in hydrogen can be converted into useful energy in a number of ways, electric energy by a fuel cell, mechanical energy by a hydrogen combustion engine, and heat energy by a hydrogen water heater. To date, hydrogen-based technologies show critical issues that require further investigation. Among them, the main difficulties are associated with the costs of production, storage and safe transportation of hydrogen [1].

The degradation of pollutants in wastewater coupled with the production of energy by ammonia splitting is an attractive and interesting method that allows to reduce environmental pollution and simultaneously provide alternative energy sources. Within this context, the present project aims to study the electrolysis of nitrogen-rich polluting molecules in water. The preliminary results summarized in the present work regard the use of ammonia as a model molecule. In general, electrolysis, which separates water molecules into oxygen and hydrogen, is a clean but energy-intensive process.

Here, we combine the cathodic reaction that produce H_2 from water with an anodic oxidation that allows for the detoxification of an industrial or civil effluent by screening suitable electrodes. The reaction was carried out in the absence and in the presence of ultrasounds to enhance energetically the oxidation process and at the same time maintain clean the electrode's surface. Different electrodes have been tested, such as graphite and different metals (platinum, nickel, titanium, lead oxide, copper, palladium) and 304 stainless steel [2]. The materials that gave positive feedback were Platinum and Copper. Copper is an interesting material from an industrial perspective since it is cheaper than Platinum (it is not a precious metal) and much more widespread.

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QM/MM INVESTIGATION OF LONG-RANGE ELECTRON TRANSFER PATHWAYS IN BACTERIORHODOPSIN/TiO₂ HYBRID SYSTEMS

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Bacteriorhodopsin (bR) from *Halobacterium salinarum* is a light-harvesting membrane protein that has been used for technological applications such as photocatalysis, photoelectrochemistry, and bioelectronics in general. It has been employed as a sensitizer for TiO₂^{1,2} in photovoltaic and photoelectrochemical cells to convert solar energy into electricity or chemical fuels, such as H₂. bR shows several ideal properties for these purposes, such as stability in highly concentrated salt solutions (up to 5M NaCl), thermal stability to high temperatures (up to 80°C), and high quantum yield (~0.64)³.

In this work, we applied quantum mechanics/molecular mechanics (QM/MM) methods to investigate the possible long-range Electron Transfer (ET) pathways in bR/TiO₂ hybrid systems. Our aim is to gain knowledge about the pathways that transfer the electron from the retinal chromophore of the protein to the TiO₂ semiconductor. Such understanding would indeed drive the design of bR variants leading to more efficient electron injection from bR to the TiO₂ surface.

The bR/TiO₂ hybrid model systems were previously built in our laboratory using Steered Molecular Dynamics (SMD) and QM/MM simulations.⁴ Here, Mulliken population analysis (MPA) and Spin Density (SD) values were computed for six different QM regions. These regions included the retinal chromophore and amino acid residues selected among the ones that are known to be involved in the long-range ET in proteins (Tyr, Trp, Phe).^{5,6}

The results of this study allowed us to identify the most probable long-range ET pathways and the key redox amino acids (Tyr147, Tyr150, Phe153, and Phe154) involved. Moreover, the results will be the basis for further combined experimental and computational studies to develop novel bR-variants/TiO₂ systems with enhanced ET properties.

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PT-DOPED $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ FOR HIGHLY PERFORMING SYMMETRIC SOLID OXIDE CELLS (SSOCS)

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One of the most important problems for the efficient use of renewable energies is the development of innovative storage systems, to overcome the problems related to their intermittent nature. Among all, Solid Oxide Cells (SOCs) are a promising technology able to operate in the intermediate temperature range (600-850°C) in two operative modes: an electrolyser mode (SOEC), to convert stored energy to fuels, and a fuel cell mode (SOFC) to convert back that stored fuels into electrical energy [1]. The choice of efficient and cost-effective electrode materials able to stably work in both reducing/oxidizing conditions is one of the main issues in the development of Symmetric SOC (SSOCs) technology [2]. Among all, lanthanum strontium ferrites (LSF) perovskites are the most used, and the 20 mol% Co-doped is the best-performing material for Oxygen Reduction Reaction (ORR) and is mainly used for air electrodes [3]. A valuable solution in terms of cost and electrocatalytic performance is the substitution of 20 mol% of Co with a small amount of platinum, which can be easily recovered from automotive waste [4] and can improve the electrocatalytic activity. Here, a 5 mol% Pt-doped LSF (LSFPt) is proposed, with the aim of find a new performing material that can be efficiently used for both air and fuel electrodes thanks to the good catalytic activity of Pt. The material was investigated in an oxidizing atmosphere by XRD and EIS analysis to investigate the ORR performance, showing promising results in comparison with LSF_{Co} reference material. The material was also tested in H₂-reducing environment, showing metal nanoparticle exsolution and structural stability over red/ox cycles. A symmetric LSFPt/LSGM/LSFPt cells were tested in both SOFC and SOEC modes, with more than 300h reverse stability in red/ox conditions.

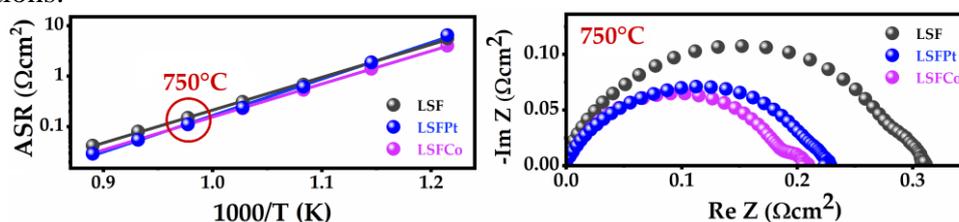


Fig1: ASR vs T measurement and EIS analysis at 750°C for LSF, LSFCo, and LSFPt.

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5 MOL% RU-DOPED PEROVSKITE OXIDE FOR SYMMETRICAL R-SOC

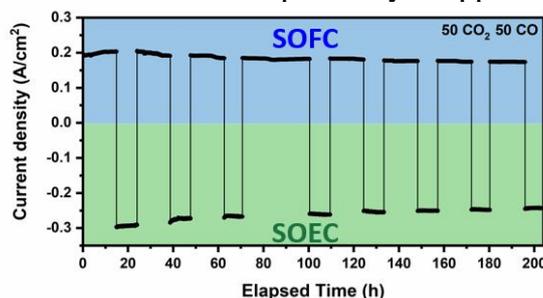
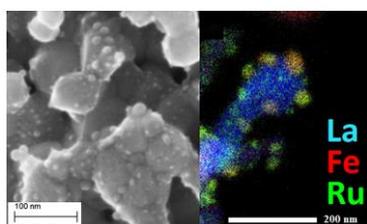
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Reversible solid oxide cells (r-SOCs) represent a promising alternative for energy storage and conversion, as they can efficiently cycle between energy storage (fuel cell, FC, mode) and conversion (electrolysis cell, EC, mode) [1]. In the last years, mixed ionic-electronic conductors (MIEC) perovskite oxides have been recently developed as one of the best alternative as state-of-the-art Ni-based cermets and Co-based oxides [2]. Moreover, a new symmetrical cell configuration, in which the same material is used as both anode and cathode, has been proposed to minimize the costs and the structural mismatch between different cell components [3]. In recent years, redox exsolution of metal nanoparticles has been proposed as an effective way to manipulate and improve their electro-catalytic activity: metal ions can migrate from the bulk to the surface of the perovskite after a single reduction treatment, forming metallic nanoparticles socketed in the original perovskite structure. These metallic nanoparticles, which can be earth-abundant or noble-metal based, are the primary responsible for the improved catalytic activity for most of the electrochemical reactions in all the electrochemical devices [3,4]. Therefore, new electrode materials need to be designed and developed for high-performance symmetrical RSOC.

In this work, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.95}\text{Ru}_{0.05}\text{O}_{3-d}$ (LSFR05) was synthesized and investigated as an electrode material for symmetrical RSOC working at medium-high temperatures. The crystal structure, the oxygen vacancies concentration, and the surface coordination of the active sites are evaluated, as well as the effect of reducing atmosphere on the structure and the formation of exsolved nanoparticles upon heating treatment. All these features are discussed and related to the performances of this material as electrode material for symmetrical reversible solid oxide cells (r-SSOCs) at high temperatures; exsolved Fe-Ru metallic nanoparticles showed noticeable activity toward H_2 and CO oxidation, as well as CO_2 reduction. The introduction of Ru sensibly enhances the electrochemical activity of LSF towards different electrochemical reactions, allowing further study on the possibility to use this material for multiple catalytic applications.



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BISMUTH-BASED PEROVSKITE NANOCRYSTALS FOR PHOTOELECTROCHEMICAL APPLICATIONS

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Metal halide perovskites have been widely studied in the fields of optoelectronics, due to their tunable optical and electronic properties. The typical structure, ABX_3 , involves a large monovalent cation (A) like Cesium or Rubidium, a divalent metal cation (B) (where Pb stands out for the optical properties)^[1], and a halogen (X).

A relatively novel application involves the use of dimensionally reduced perovskite nanocrystals (PNCs) in photocatalysis and photoelectrochemistry, where H_2 evolution^[2] and CO_2 reduction^[3] have been already demonstrated.

Due to the Pb toxicity and limited stability to standard environmental conditions, research is now focusing on developing lead-free halide perovskites, like the Bi-based vacancy-ordered perovskites ($A_3B_2X_9$) or the double perovskites ($A_2B(I)B(III)X_6$), where Pb^{2+} is replaced by a combination of +1 and +3 cations (such as Ag^+ and Bi^{3+}).

Our work is focusing on the synthesis and characterization of bismuth-based PNCs, where multiple candidates are being studied, such as the $Cs_3Bi_2X_9$ (X=Br,I) and $Cs_2AgBiBr_6$. A PNCs compact thin film is prepared to work as a photocarrier generator. However, due to perovskite instability in aqueous media, a conductive hydrophobic layer is used to ensure protection of the light absorber and mobility of charge carriers. Finally, other low-dimensional materials, such as 2D transition metal dichalcogenides (1T-MoS₂) and copper-based nanoparticles are integrated in the device architecture, in order to improve its activity in photoelectrocatalysis.

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DEVELOPMENT OF CHIRAL HALIDE PEROVSKITES FOR CHIROPTICAL AND FERROELECTRIC APPLICATIONS

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Hybrid metal halide perovskites have received significant attention as suitable materials for various electronic applications in photovoltaic cells, photodetectors, light emitting diodes, and sensors, owing to their outstanding and unique properties such as high-power conversion efficiency, tunable bandgap, and high absorption coefficient². Recently, the development of hybrid organic-inorganic chiral perovskites led to excellent piezoelectric and ferroelectric properties, thanks to the introduction of chiral molecule, such as Methylbenzylamine, which can lead to the breaking of the spatial inversion symmetry; thus, perovskites promise revolutionary design possibilities, by combining polarity and chirality^{1,3}. To extend the actual knowledge of these novel chiral systems, here we report the synthesis and the characterization of both lead and lead-free chiral perovskites, namely (R/S/rac-CIMBA)₂PbI₄, (R/S/rac-CIMBA)₂SnI₄ and (R/S/rac-CIMBA)₂GeI₄ with different kind of organic spacer incorporated and we provide an overview of future studies about chirality transfer, between the organic cation and the inorganic framework, spin-selectivity, ferroelectricity, and piezoelectricity.

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**PHOTOCATALYTIC DECOMPOSITION OF GASEOUS
ACETALDEHYDE
WITH $\text{Fe}_3\text{O}_4/\text{TiO}_2$ UNDER UV-LIGHT**

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Most of the Volatile Organic Compounds (VOCs) exist in a gaseous state at room temperature and are harmful to the human body. In particular, acetaldehyde, as a representing VOC, causes vomiting, dizziness and, in severe cases, unconsciousness. The aim of this study is to decompose acetaldehyde using magnetic TiO_2 with Fe_3O_4 nanoparticles. The $\text{Fe}_3\text{O}_4/\text{TiO}_2$ composites exhibit quasi-ferromagnetism and significant photocatalytic activity for mineralization of acetaldehyde. The photocatalytic activity varies depending on the ratio of Fe_3O_4 and TiO_2 . As a fraction of Fe_3O_4 increases, the photocatalytic activity decreases, because of blocking the active site. A further study is being underway.

CYANINES AS LOW-COST NIR DYES TOWARD COLORLESS DYE SENSITIZED SOLAR CELLS

Ana Yancy Segura Zarate,^a Simone Galliano,^b Matteo Bonomo,^a Nadia Barbero,^a Marco Giordano,^a Guido Viscardi,^a Raffaele Borrelli,^b Waad Naim,^c Fionnuala Grifoni,^c Fabio Matteocci,^d Vijay Challuri,^e Pauline Chotard,^e Sylvain Ceurstemont,^e Franck Barath,^e Aldo Di Carlo,^d Frederic Sauvage,^c Claudia Barolo,^a

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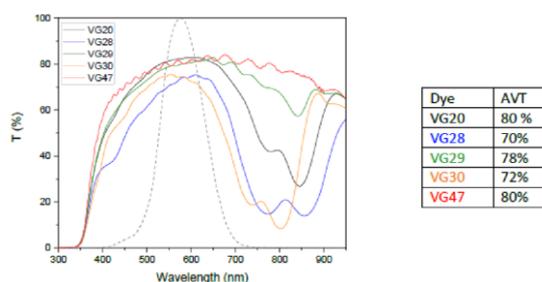
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The development of integrated PV in windows/facades on buildings take us deeper in different aspects like aesthetics, stability and performance, because even if the color is one of the principal characteristics of the DSSC, with this technology is possible to offer a sustainable option for transparent and colorless windows, due to their versatility in the selection of dyes [1,2]. Our group synthesized some polymethine dyes (cyanines and squaraines) focusing on the photosensitizer in a wavelength-selective NIR-DSSC [3], and the synthesis of these dyes were done in a one-step reaction under microwave heating, saving time and money in the process, and even increasing yields and purity. A simple crystallization of the crude products yielded a very low cost and industrially scalable product. Until now, some different chromophores (NIR dyes) have been investigated for DSSC devices with promising results in terms of transparency and performance. Recently, due to the joint efforts of different research groups within the IMPRESSIVE project, we proposed a fully transparent and colorless DSSC with 80 % transmittance in complete devices [2].

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ULTRAFAST HIGH-TEMPERATURE SINTERING OF FUNCTIONAL CERAMICS

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Ceramic based Barium Zirconate and Barium Cerate were suitable and innovative materials as solid oxides proton-conducting electrolytes. Among these materials, $\text{BaCe}_{1-x-y}\text{Zr}_x\text{Y}_y\text{O}_3$ (BCZY) showed interesting thermochemical stability and proton conductivity.

The conventional sintering process of ceramic-based solid-state electrolytes is typically a time and energy spending process, with poor compositional control due to the possible evaporation of volatile elements. In case of BCZY materials, the Barium evaporation during sintering can alter their functional properties. Therefore, innovative sintering techniques capable of drastically reduce operating time are needed. Recently, a rapid pressure-less sintering technique has been proposed [1], Ultrafast High-temperature Sintering (UHS), able to produce dense samples of a large set of ceramics, metals and intermetallics within tens of seconds.

Among the advantages of this technique, there are the unprecedented versatility and control on the grain growth and the possibility to scale down by orders of magnitude both the time (and energy consumption) for sintering and the experimental setup cost. Sintering velocity results effective in preventing volatile elements evaporation and phase segregation phenomena. In this work a dedicated setup for UHS is presented, together with results obtained for the proton conductor $\text{BaCe}_{0.65}\text{Zr}_{0.2}\text{Y}_{0.15}\text{O}_{3-\delta}$ and the n-type thermoelectric material Mg_2Si . Full dense Mg_2Si and BCZY samples with good mechanical properties were obtained with tens of seconds processing time. Morphology and composition analyses (SEM – EDS) and thermal conductivity (Laser Flash Analysis) of Mg_2Si and BCZY dense pellets were studied and compared with traditional sintering techniques and with the cold sintering process (CSP) technique

Perspectives and limits of this new sintering technique in general and for thermoelectric applications are discussed.

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OXYGEN REDUCTION REACTION CATALYZED BY PALLADIUM COMPLEXES ON MULTI-WALLED CARBON NANOTUBES FOR APPLICATION IN ALKALINE FUEL CELLS

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Energy problems are at the focus of international discussions; the progressive depletion of fossil reserves and the increase in energy demand have led to the rise in fuel and electricity prices. In this context, fuel cells are promising candidates for a sustainable future. Oxygen Reduction Reaction (ORR) is the bottle-neck strategic reaction ruling the fuel cell efficiency process. This reaction allows the release of chemical energy stored in the vector molecule O₂ in the form of electricity without producing any waste but only water. ORR can take place from a direct reduction to water, with the exchange of 4 electrons per oxygen molecule or from an intermediate reduction to hydrogen peroxide with the exchange of two electrons. Hydrogen peroxide is an undesirable and corrosive product. In order to properly boost the reaction, the use of an electrocatalyst is mandatory. It is well known that the best available catalysts belong to the so-called platinum group metals (PGM). PGM are very expensive, hence lowering the PGM content of ORR catalysts is among the most prevalent research focuses. In this field, Single-Ion catalysts formed by carbon nanotubes functionalized with palladium(II) complexes showed surprising catalytic activity [1]. New catalysts consisting of carbon nanotubes functionalized with a ligand of different structure [2] were treated by preparing dispersions and tested with electroanalytical techniques. ORR performances are evaluated recording linear sweep voltammetry and using a rotating ring-disk electrode (RRDE) it was possible to obtain the number of electrons exchanged per oxygen molecule and calculate the amount of hydrogen peroxide produced.

Results confirm that the materials tested catalyze the four-electron reaction pathway. Although carbon nanotubes (like many carbon materials) have strong catalytic activity due to their high surface area but show increased production of hydrogen peroxide, functionalisation with Pd(II) complexes makes it possible to change the catalytic mechanism of the ORR and reduce the amount of hydrogen peroxide formed. These results provide the basis for further developments to improve the efficiency of future low-cost catalysts for use in renewable energy technologies.

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CO-DEPOSITED NICKEL PHASES WITH TARTARIC ACID ON DIFFERENT SUPPORTS AS ANODIC ELECTRODES IN HALF AND COMPLETE CELLS FOR WATER ELECTROLYSIS

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To satisfy the entire world energy requirement is necessary to design efficient, available, and cheap electrocatalysts for Water Splitting that would help the sluggish kinetics of the limiting reaction, which is the Oxygen Evolution Reaction for Electrolysis (OER).

This study is focused on the Oxygen Evolution Reaction on nickel surfaces and nickel co-deposited with tartaric acid to verify the influence of Chiral Induced Spin Selectivity (CISS) on the oxygen evolution.

Indeed, the presence of chiral molecules on a conductive surface induces a local magnetic field which stabilizes the aligned spin of transmitted electrons. The result is a polarization of spin electrons that are transferred from intermediates to electrode surfaces and vice versa.

This effect has two main implications in the water electrolysis:

- The production of ³P Oxygen (which is the lower energy form)^{1,2}
- The inhibition of Hydrogen Peroxide as side product.^{1,2,3}

The magnitude of CISS effect has been studied in half and complete cells, in terms of onset potential and hydrogen peroxide produced during the processes and compared to nickel pure activity.

The half-cell tests have been realized on a nickel layer and nickel/L-tartaric co-deposited layer on glassy carbon by electrodeposition in Watts bath.

The found exchange electron number n is respectively 3.5 and 3.7 for nickel and nickel; while the onset potential is round 1.6V vs RHE in basic conditions.

To scale up the electrode surfaces destined to a real system as complete cells, different nickel crystalline phases have been synthesized on C cloth and nickel foam where the chiral specie increases the faradic efficiency of the reaction.

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DESIGN AND SYNTHESIS OF NEW PHOTOACTIVE MOLECULES FOR DYE-SENSITIZED-SOLAR-CELLS (DSSCs) OPERATING IN LOW-LIGHT CONDITIONS

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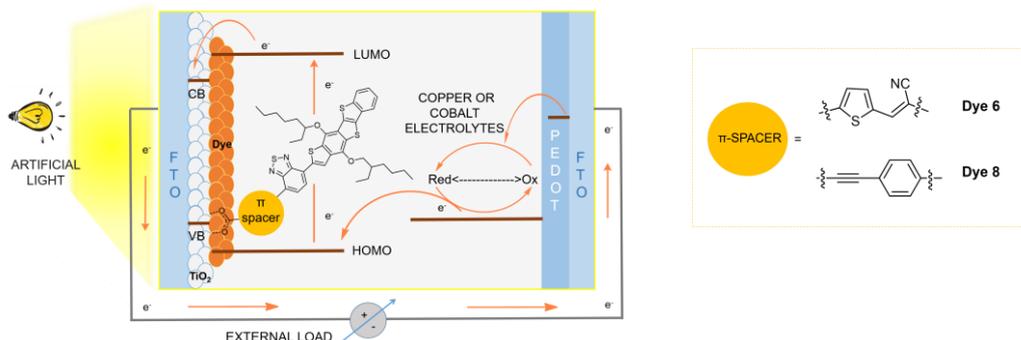
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Among all the photovoltaic technologies, **Dye-Sensitized Solar Cells (DSSCs)**¹ attracted the attention of researchers for their low manufacturing costs, easy availability of raw materials, and short payback times. The latest trend for DSSC applications is moving to **indoor or dim-light environments** because DSSCs have much higher efficiencies than Si-based solar cells (~ 30 %).² Thus, indoor photovoltaics are emerging as an important technology suited for IoT (Internet of Things) applications, household, and various electronic applications.³



Herein, the design and synthesis of two new photosensitizers for DSSCs indoor are presented. Both molecules have shown the properties suitable for this type of application, with a large light absorption in the visible region and redox potentials compatible with the most common organometallic redox couples. First preliminary DSSCs tests were run on **dye 6**, which showed promising efficiencies (up to 3.1%) when home-made electrolytes were used.

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NI-BASED OXIDES FOR DRY REFORMING OF METHANE: EFFECT OF SYNTHESIS METHOD ON SUPPORT PROPERTIES AND CATALYTIC ACTIVITY.

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CO₂ and CH₄ are the main greenhouse effective gases contributing to global warming and climate change [1]. Furthermore, the growing energy needs of society as well as the necessity of rational use of natural resources are causing an increased interest for alternative fuel sources. Dry reforming of methane (DRM) can be proposed as promising method of CO₂ and CH₄ conversion into valuable products (e.g., methanol, acetic acid and hydrocarbons) and environmentally sustainable fuels (in particular, hydrogen). However, the DRM is an endothermic reaction that requires the use of catalysts to lower the activation energy. In addition, the process is accompanied by several side reactions, such as methane decomposition, Boudouard reaction and CO reduction, contributing to carbon deposit and leading to severe deactivation of the catalyst [2]. In this scenario, the design of catalysts and their supports become crucial [3]. Ni-based catalysts found the largest application due to their relatively low cost and high availability. However, supported Nickel suffers from sintering under high temperatures and coke deposition, both phenomena can be reduced improving the characteristics of the support (e.g., ensuring dispersion of metal particles, increasing basic properties and the availability of the surface oxygen species) [4]. In this work 12 wt%Ni-La₂O₃ catalysts were synthesized by one pot hydrothermal method (HT) and precipitation assisted by microwave irradiation (MW). The so prepared samples were compared to 12 wt%Ni/La₂O₃ where Ni was deposited by wetness impregnation over La₂O₃ oxides obtained by HT and MW methods. The aim of the study was to evaluate how the support preparation conditions affect the nature, phase composition, and distribution of Ni phases and consequently the catalysts performance in DRM reaction.

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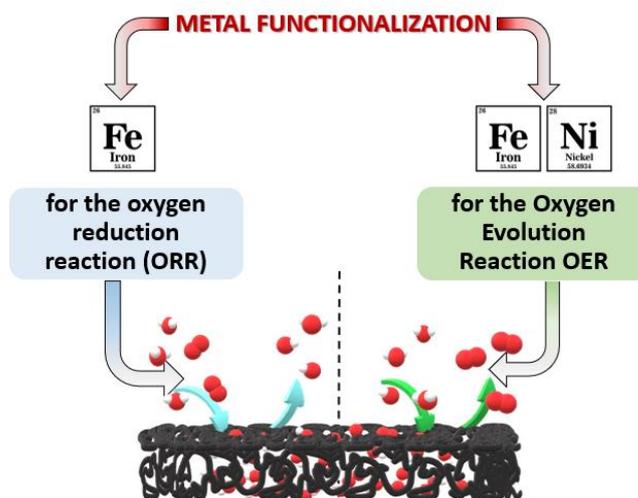
DEVELOPMENT AND CHARACTERIZATION OF BIFUNCTIONAL ELECTROCATALYSTS FOR THE OXYGEN REDUCTION AND EVOLUTION REACTION

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The development of inexpensive and efficient catalysts for oxygen reduction (ORR) and evolution reactions (OER) is important, not only for approaching electrochemical energy systems, such as water electrolyzers, metal-air batteries, and fuel cells such as anion/proton exchange membrane fuel cells, but also to replace expensive noble metal catalysts (Pt/C, IrO₂ or RuO₂ and Pt-Ru/C).^[1] A new class of nonnoble metal functionalized carbon systems are based on carbon materials decorated with nitrogen atoms that coordinate metals, such as iron or nickel (Fe/Ni@N-C), with high catalytic performance.^[2] The wide choice of precursors for obtaining a carbonaceous N-C matrix allows their shape to be modulated according to the required function. In this work, by combining electrochemical and spectroscopic techniques (Cyclic Voltammetry, Linear Voltammetry with rotating disk electrode, X-ray Diffraction (XRD)), porous organic polymer (POP) based catalysts were developed and optimized as high-performance electrocatalysts free of critical metals due to their high and modulable surface area, high density of nitrogen functional groups, and customized Fe/Ni content.



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SYNTHESIS OF IONIC LIQUIDS, BY GREENER METHODS, FOR HIGH-VOLTAGE LITHIUM-ION BATTERY APPLICATIONS

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Because of their high density and reliability, lithium-ion batteries (LIBs) are a vital energy storage system for portable electronic devices. To increase their energy density even more, it is essential to replace commonly used cathode materials (such as LiCoO₂) with new materials capable of working at higher potentials, like LiNi_{0.5}Mn_{1.5}O₄ (LNMO). As a result of the oxidation on the cathode surface, the typically employed electrolytes, containing carbonate-based solvents, are unstable at such high potentials. In order to increase the thermal and electrochemical stabilities of the electrolytes, ionic liquids (ILs) have recently been used as additives to them. In this study, two ILs containing borate anions, known to form the so-called cathode-electrolyte interphase (CEI) [1], a protective layer on the cathode surface, are synthesized using mostly water as solvent to minimize the impact of the syntheses on the environment [2].

The two synthesized ILs, *N*-ethoxyethyl-*N*-methylpiperidinium bis(oxalato)borate (PIP_{1,202}BOB) and *N*-ethoxyethyl-*N*-methylpiperidinium difluoro(oxalato)borate (PIP_{1,202}DFOB), did not show any crystallization behavior in differential scanning calorimetry, but instead exhibited a glass transition at -30 °C and -70 °C. The lack of crystallization is related to the presence of an oxygen in the cation structure. The two ILs resulted to be thermally stable up to at least 280 °C, according to thermal gravimetric analysis. During the first cycle of cycle voltammetry for both ILs an oxidation peak was observed, but subsequent cycles highlighted a decline in the oxidation current, indicating the formation of CEI.

The ILs have been used as the additive for battery components, specifically electrolyte and LNMO-electrode. In the former case, different concentrations of ILs were added to the commercially available 1M LiPF₆ in EC/DMC (LP30) electrolyte. In the latter case, slurries of LNMO containing the different percentages of ILs were deposited on an Al foil to form the electrodes. Lithium-metal cells have been assembled using the as prepared materials. The addition of the ILs to the electrode has led to a significant improvement of discharge capacity retention and coulombic efficiency of the cells, with only a minimal decrease of their specific discharge capacity.

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NEW SUSTAINABLE WHITE LEDS BASED ON A SINGLE MULTICHROMOPHORIC POLYMER CONTAINING LUMINESCENT LANTHANIDES COMPLEXES

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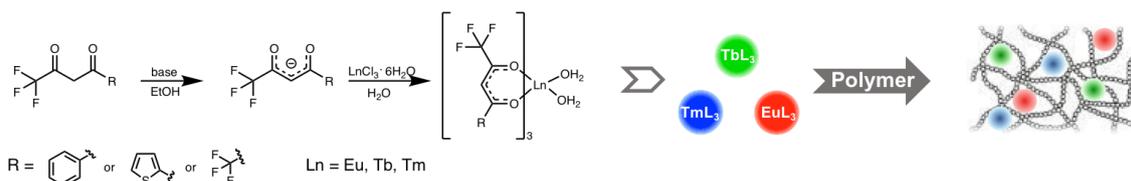
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The production of white or panchromatic light is based on the generation and the intensity control of the three fundamental (red, green and blue) or two complementary (e.g., turquoise and orange) colors in order to cover the whole visible range from 400 to 700 nm. The goal is usually achieved using different red, green and blue independently emitting small molecules. The major drawback of this strategy is the different stabilities of the emitters that reduces or changes the performances of the light emitting device over its lifetime. The use of a single molecule bearing two or more color centers will straightforwardly overcome the stability issue of the independent emitters, as they are now part of the same moiety. Light emitting lanthanide complexes are attractive for this kind of application as their emission generates from metal centered excited states which are only slightly affected by the coordination environment. Here, we propose an original strategy to realize new polychromic light emitting materials for the preparation of organic optoelectronic devices, based on a single organic polymer coordinating a suitable amount of red, green and blue phosphorescent lanthanide complexes, displaying a continuous gamut of color coordinates.



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HIGH ENTROPY PEROVSKITES OXIDES FOR THERMOCHEMICAL SYNTHESIS OF GREEN HYDROGEN

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High Entropy Perovskites Oxides (HEPOs) have gained significant attention in recent years as potential catalysts for the thermochemical synthesis of green hydrogen. This is because they exhibit several unique properties that make them well-suited for this application such as high stability, good activity, and the ability to operate under a wide range of conditions.^[1] In addition, high entropy perovskites have shown good activity and selectivity for these types of reactions thus suggesting their possible use to produce green hydrogen.^[2] Overall, HEPOs have the potential to play a significant role in the thermochemical synthesis of green hydrogen, and their unique properties make them an exciting area of research and development. The simplest configuration of a thermochemical cycle uses a metal oxide that reduces and re-oxidizes itself in two consecutive steps:^[3]



The first reaction (1) is endothermic and can use concentrated solar energy to provide the energy required to reduce the material (to $\text{ABO}_{3-\delta}$) and generate oxygen. The reoxidation reaction is conducted by adding water (2), producing hydrogen, and regenerating the original material (ABO_3). The endothermic reaction occurs at significantly lower temperature than water thermolysis (e.g., from 2573 K down to ≤ 1773 K), mitigating the challenges associated with extremely high temperatures, in addition to avoiding the recombination reaction of H_2 and O_2 .^[4] To date, few materials have shown to be suitable for the thermochemical synthesis of hydrogen, with ceria (and doped composition) being the most exploited materials. The twofold aim of the present work is therefore to develop novel materials with the aim of: i) increasing the presence of oxygen vacancies and thus the 'active sites' of the catalyst, and ii) to decrease the temperature at which they are formed (e.g., $T < 800\text{K}$). To achieve these objectives, we started to investigate perovskites oxides of general formula ABO_3 by adopting a chemometric approach to map the compositional space of the perovskite oxide. In particular, we focused on the following compositions on the site A we chose to keep Lanthanum due to its stability, while, on the B site, we defined different cation mixtures based on Cr, Mn, Fe, Co, Ni and Zn, to determine an experimental domain by including various experimental data, i.e. crystal structure, oxygen vacancies extent and temperature-dependance, and composition.^[5] The overall experimental results will allow to define the best compositions to be used for the thermochemical synthesis of hydrogen.

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ENVIRONMENTAL IMPACTS OF PEROVSKITE/SILICON TANDEM SOLAR CELLS.

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The main technological advantage of tandem solar cells is that the combination of multiple devices allows for the increase of the overall power conversion efficiency (PCE) beyond the single-junction limit[1]. However, like all photovoltaic systems, tandem photovoltaic cells are responsible for potential environmental impacts during their life cycle[2]. Hence, evaluating the resources depletion and the emissions released to the environment through the life cycle assessment (LCA) is fundamental to assessing the actual environmental sustainability of this technology.

Various studies[3]–[6] have largely explored the environmental impacts of perovskite-silicon tandem solar cells. These previous works brought scientists to different conclusions about the amount of greenhouse gas emissions and the impacts caused by the perovskite-silicon tandem solar cells compared to conventional silicon solar cells. However, in most of these studies, the end-of-life phase has been generally excluded due to lack of data; other studies have only considered landfill or incineration as the end-of-life scenario, thus completely excluding recycling.

In this study, we developed a harmonized comparative scenario-based LCA model focused on recycling as the end-of-life strategy for different Perovskite/silicon configurations. The aim is to provide insights into promising perovskite/silicon configurations and to quantify the environmental effects of different recycling strategies for sensible decision-making in Perovskite/silicon tandem research, development, and manufacturing.

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ALKYL LEVULINATES: GREEN SOLVENTS FOR PVDF MEMBRANE PREPARATION

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Membrane technology is widely recognized as an environmentally friendly technology and its use results in energy savings on the cost of production compared with other traditional separation processes. However, membrane preparation does not always meet sustainability requirements, especially when considering commonly used solvents, i.e., N-methyl-2-pyrrolidone, N, N-dimethylformamide [1,2]. Consequently, the goal of the last is to exploit a new solvent platform that has great potential to replace solvents hazardous to membrane preparation. Alkyl levulinates are derived from products derived from biomass such as levulinic acid with alcohols or directly from cellulose. They have suggested uses as solvents and additives for biofuels, lubricants, fragrances, or in the field of chemical synthesis [3]. In this work, for the first time, the alkyl levulinates (methyl- and ethyl- levulinates) were used for producing PVDF copolymer (Solef®PVDF6012) and homopolymer (Solef®PVDF-HFP 21510) membranes by coupling vapor induced phase separation with non-solvent induced phase separation (VIPS-NIPS) techniques. PVDF is a thermoplastic polymer and is one of the most suitable materials to prepare membranes for its properties such as good chemical resistance, high thermal and mechanical stability. It is used in various membrane sectors including water treatment, membrane distillation (MD) and membrane bioreactor (MBR) [1]. The effect of the length of the alkyl chain on the thermodynamics of the dope solution and on the phase inversion of the membranes was studied. Membranes were also prepared using polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) as pore-forming agents. The structure of the membranes was tailored by acting on the exposure time to humidity during VIPS process (from 0 to 5 min) and by using the water as a coagulation bath. The thermodynamic aspects (i.e. solubility parameters, polarity and polymer-solvent distance) and the kinetic parameter in terms of viscosity were well studied. It was possible to produce membranes with a control of the membrane morphology characterized by finger-like and/or sponge-like structures. The membranes exhibited a pore size in the ultrafiltration (UF) and microfiltration (MF) range.

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TERMOCHEMICAL CATALYSIS FOR CARBON DIOXIDE SPLITTING

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Global warming is leading to planet thermal increase with disastrous consequences. To prevent climate change from becoming irreversible big efforts are carried out to decrease the concentration and the emissions of CO₂. The approach afforded in this work is inspired to solar-based thermocatalytic activation¹: the catalyst is reduced at high temperature in an inert atmosphere releasing O₂. After this reaction, the catalyst is oxidized at a lower temperature. Carbon dioxide and/or water can be used to restore the reduced oxide so producing carbon monoxide and/or hydrogen. Several critical raw materials' free catalyst has been studied for this process, from La_{1-x}Sr_xGa_{1-y}Mg_yO₃ (LSGM) perovskites to strontium oxide, but iron spinel (Fe₃O₄) and ceria (CeO₂) seem the best performing. Both materials, however, present the same problem: they sinter at high temperatures. To solve this problem, the focus is on supporting catalysts on an inert material capable of stabilizing action². The state of the art indicates as the best catalyst for the splitting of carbon dioxide a nickel spinel doped magnesium (Ni_{0.9}Mg_{0.1}Fe₂O₄³), while as regards the support, both inert and less inert materials are used⁴. A possibility is to investigate the use of support that can act as "co-catalysts" to allow the reduction at lower temperature with respect to Fe₃O₄. The best materials turn out to be nickel oxide and cupric oxide⁴. In the present contributions we decided to use the industrial supports and mix them mechanically (by wet ball milling) with the catalysts, synthesized by sol-gel method using citric acid as a complexant⁵. Subsequently, a characterization of the materials was carried out by XRD, SEM, EDX and XPS. To study the oxygen exchange capability, TPR and TPO are carried out. Reactants and reaction conditions have been tuned to test the best cycling approach.

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VISIBLE LIGHT SENSITIZATION OF TiO₂ PHOTOANODES BY COUPLING WITH MO-DOPED BiVO₄

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Inspired by natural photosynthesis, the engineering of artificial photosynthesis to convert and store solar energy into clean hydrogen via photoelectrochemical (PEC) water splitting has emerged as one of the most promising technologies to replace fossil fuels.² Importantly, the performance bottleneck of a PEC cell is ascribable to the photoanode counterpart driving the oxygen evolution reaction (OER). For this reason, massive efforts are still being devoted to the rational improvement of the performance of semiconductor-based photoanodes able to drive water oxidation reaction using sunlight. TiO₂ is by far the most studied semiconductor oxide for this kind of applications. However, its high energy band gap of *ca.* 3.2 eV strongly limits the exploitation of a large part of the solar light spectrum.³ Coupling TiO₂ with a narrow band gap metal oxide, such as BiVO₄, would address this issue allowing for TiO₂ sensitization to visible light. Despite the unfavorable type I band alignment predicted at the interface of the two semiconductors in the TiO₂/BiVO₄ heterojunction, a hot electrons injection mechanism from BiVO₄ to TiO₂, active only at $\lambda \leq 490$ nm, i.e., for incident photons with an excess energy with respect to the BiVO₄ band gap, has already been demonstrated.⁴ Indeed, we verified that the coupled [system](#) outperformed only with respect to the TiO₂, not to the pure BiVO₄ (**Figure 1**). However, we succeeded in coupling TiO₂ with optimized molybdenum doped BiVO₄ with the consequence of a dramatic photoactivity increase of the resultant TiO₂/Mo:BiVO₄ heterojunction system with respect to both the undoped TiO₂/BiVO₄ composite material and each of the two single components (**Figure 1**). This result can

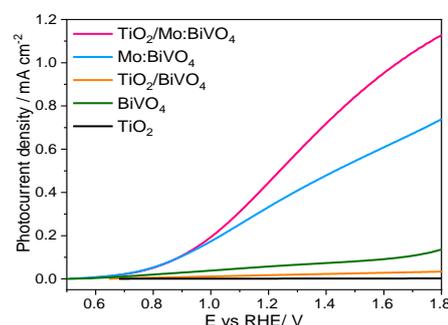


Fig. 1. LSV plots in 0.5 M Na₂SO₄ electrolyte under irradiation with $\lambda \geq 400$ nm.

be rationalized in light of structural distortions of the BiVO₄ crystal structure upon Mo⁶⁺ incorporation in the material bulk. According to recent theoretical studies, the relative band alignment of the two semiconductors in the heterojunction may strongly depend on the crystal facets at the interface of the two oxides.⁵ Therefore, we postulate that the structural modification caused by the introduction of Mo⁶⁺ atoms, may alter the relative band alignment from a type-I scheme to type-II, that favors the photopromoted charge carriers separation and, therefore, the overall system's photoactivity.

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LUMINESCENT SOLAR CONCENTRATORS: EFFECT OF DYE STRUCTURE ON FLUORESCENCE PROPERTIES AND DEVICE PERFORMANCES

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Luminescent Solar Concentrators (LSC) are a class of optical devices able to harvest, downshift and concentrate sunlight thanks to the presence of emitting materials embedded in a polymer matrix. Due to the low-priced materials and their innovative aesthetic properties, LSCs find an easy integration in architectural systems, such as roofs, windows, canopies, and greenhouse, matching the current push toward more sustainable and energy efficient structures.^[1] The choice of the proper organic fluorophore is fundamental to achieving good performance. It needs to meet several criteria: broad absorption range, large Stokes shift, high fluorescence quantum yield, precise matching between dye emission wavelength and PV absorption band, good optical efficiency, and good dispersion in the host materials.^[2]

In this work, we present the design, synthesis, characterization and application in LSC of a series of orange/red organic emitters featuring a benzo[1,2-*b*:4,5-*b'*]dithiophene 1,1,5,5-tetraoxide central core as an acceptor (A) unit. The latter was connected to different donor (D) and acceptor (A') moieties by means of Pd-catalyzed direct arylation reactions, yielding compounds with either symmetric (D-A-D) or non-symmetric (D-A-A') structures. The LSCs built with such compounds presented interesting optical and photovoltaic properties, which are greatly influenced by the nature of the substituents. A precise design of the fluorescent emitter brought performances close to the state-of-the-art, coupled with sufficient stability in accelerated aging tests.

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MODELLING OF ADVANCED Li STORAGE SYSTEMS

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Nowadays, rechargeable batteries are the best developed renewable energy technology, and, at present, the most successful rechargeable battery is the Li-ion battery (LIB), hence much of the research in the field of batteries in recent years has focused on the improvement of this technology, which relies on the properties of its components, namely the cathode, the electrolyte and the anode. MODALIS² (Modelling of advanced Li storage systems) project fits into this scenario, arising from the cooperation between different European academy and industrial partners, with the aim of providing a significant speed-up to novel cell design and a reduction of development costs.

The aim of this part of MODALIS² project is that of performing a quantum-mechanical study at the atomic scale of the processes underlying the functioning of a material for cathode, namely LiNiO₂, mainly focusing on the determination of the diffusion coefficient (D), one of the most important intrinsic physical properties of Li insertion materials for LIBs. A proper evaluation of D is crucial in assessing the performance of this technology and in designing new and improved materials for electrodes and solid electrolytes. At the same time, though, it is exceptionally difficult to estimate it computationally (and actually to measure it with good precision). In fact, published results span several orders of magnitude, from 10⁻¹⁵ to 10⁻⁸ cm² s⁻¹.

For this reason, the aim of this research is mainly that of finding out a reliable computational protocol for the estimation of D. Three different methodologies are considered: i) sampling the path of the particle to reconstruct the energy curve along it; ii) applying an external electrostatic field to simulate the effect of the actual electric field felt by the material in the device; iii) addition of an external history-dependent bias to reconstruct the free energy surface of the system *via* metadynamics (MeD) calculations (*Figure 1*). Moreover, two different programs are exploited: CRYSTAL¹ for performing path-sampling and CP2K² for running molecular dynamics and MeD simulations.

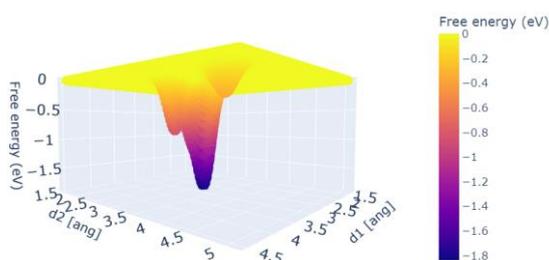


Figure 1: Free energy surface of LiNiO₂ reconstructed with MeD

From the results of this work, MeD appears to be the most suitable method for evaluating the Li ion path, because it does not constrain the motion of the particle, allowing to explore the path of even less well-known systems. However, as it tends to overestimate the value of the energy barrier, it has to be followed by path-sampling to find more reliable results. Path-sampling consists in dividing the so-identified path into different points and calculating the energy of each of them, in order to reconstruct the energy curve and accurately estimate the energy barrier (ΔE_a), a crucial quantity for calculating D according to the dilute diffusion theory³ for which $D = a^2 v^* \exp[-\Delta E_a/(k_B T)]$ (a^2 is the squared hop distance, v^* the effective frequency (10¹²-10¹³ s⁻¹), k_B the Boltzmann constant and T the temperature).

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RENEWABLE AMMONIA FOR SUSTAINABLE HYDROGEN GENERATION

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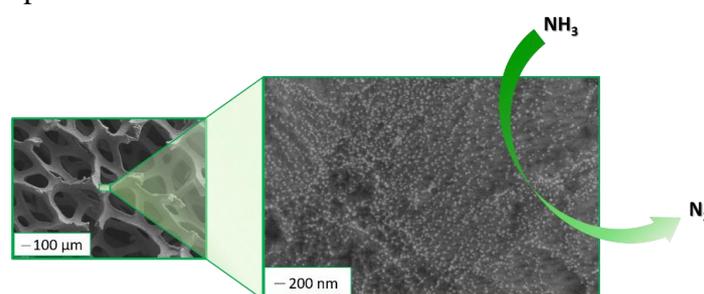
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One of the challenges of our time is integrating the paradigms of Circular Economy in our linear systems and production route: this implies a change of perspectives and valorisation of what is only recognized as waste. Ammonia and its derivatives are among the main pollutants present in sewage sludge^[1] but, at the same time, they represent key compounds for the chemical industry.^[2] In addition to it, ammonia has been evaluated as one of the promising fuels of the future.^[3] As a matter of fact, it shows several advantages: it easily surpasses hydrogen for facility of transportation (it can be liquefied or be stored as salts (e.g. ammonium sulphate)), has higher mass and volumetric energy density, and ammonia splitting is much more convenient than water splitting (in principle it requires 95% less energy).^[4] In this work, inorganic nanostructured materials were prepared and studied as anodes in an electrochemical cell for ammonia splitting. Nickel foam (NF) was chosen as porous support for Pt nanostructures, which were prepared via galvanic displacement (GD) and pulsed electrodeposition (PD), two synthetic methods that allow high dispersion also on 3D supports.^[5] Different parameters were investigated in order to find the best procedure and conditions that led to higher electrochemical active surface area (ECSA) and lower deposited mass of Pt. The so prepared materials were preliminary tested in an electrochemical cell towards the ammonia oxidation reaction showing significant selectivity for N₂ product.



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HYDROGEN STORAGE THROUGH WASTES: AN ECO-FRIENDLY SOLUTION FOR ENERGY TRANSPORTATION

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My research project is an eco-friendly solution for hydrogen (H₂) storage. Numerous high surface area porous materials have been proposed to this aim, but their controlled production is not easy, and up-scale is difficult. We decided to use carbon wastes (industrial residues from water purification filters manufacture and biomasses) as starting materials to reduce cost and C-footprint: this project contributes to CO₂ breakdown because this technology allows the diffusion of H₂ as a fuel and valorizes carbon wastes that generally are not recycled but disposed in a non-ecological way. To convert C-waste into H₂-storing Active Carbon (HAC) purification and activation are necessary. Activation can be obtained by chemical or physical way and aims to increase the surface area and to engineer the carbon surface. We pursue both strategies to individuate the economically and environmentally less impacting. Carbon doping is expected to improve H₂ storage through strengthened the gas-solid interaction by introducing metal nanoparticles or heteroatoms in the carbon matrix; this makes the adsorption/desorption easier. A multidisciplinary approach will be necessary: computational and surface modelling outcomes will be merged with experimental results obtained on C-waste derived materials exploiting the machine learning approach to foresee the optimal strategy for activation. The better protocols for purification and activation will drive the industrial production of HAC (from filter residuals and biomasses) to be inserted in a small vessel for easy and economic storage, transportation, and distribution of H₂. A demonstrator will be designed and realized upgrading the HAC vessel in a light duty vehicle (the ideal for urban distribution of goods) powered by a Fuel Cell.

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