



INTERDIVISIONAL GROUP OF CHEMISTRY FOR RENEWABLE ENERGY
(ENERCHEM)

ITALIAN CHEMICAL SOCIETY - 1st ENERCHM SCHOOL

CHEMISTRY FOR THE ENERGY TRANSITION

FIRENZE 20-24 FEBRUARY 2018

Book of Abstracts

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SCIENTIFIC PROGRAMME

TUESDAY, 20 FEBRUARY 2018

10:00-11:30 REGISTRATION

11:00-11:30 OPENING

Chairperson: Maria Assunta Navarra

11:30-13:00 L1 - **Stefano Passarini** "Safer and Environmentally Friendly Materials and Processes for Batteries"

13:00-14:30 LUNCH

14:30-16:00 L2 - **Antonino Salvatore Aricò** "Fuel cell systems and electrolytic hydrogen production"

16:00-16:45 J1 - **Filippo Monti** "Molecular engineering for solar-energy conversion, lighting and photocatalysis "

16:45-17:15 COFFEE BREAK

17:15-18:00 J2 - **Matteo Gigli** "Redox Flow Batteries: Challenges and Perspectives"

18:00-19:00 POSTER

19:30 DINNER

WEDNESDAY, 21 FEBRUARY 2018

Chairperson: Alessandro Abbotto

09:00-10:30 L3 - **Licheng Sun** "From Water Splitting Catalyst to Photoelectrochemical Cells"

10:30-11:00 COFFEE BREAK

11:00-12:30 L4 - **Sandra Rondinini** "Photoelectrochemical Energy Conversion: From basic concepts to Applications – Basic concepts"

L4 - **Alessandro Minguzzi** "Photoelectrochemical Energy Conversion: From basic concepts to Applications – Applications"

12:30-14:00 LUNCH

Chairperson: Paolo Foggi

14:00-14:45 T1 - **Riccardo Basosi** " EU Policies for ENERGY Research"

14:45-15:30 T2 - **Chiara Pocaterra** " Write a European project"

15:30-16:15 J3 - **Giulia Tuci** "Advanced Functional Materials: Synthesis and Application in Sustainable Energy Production "

15:55-16:45 COFFEE BREAK

16:45-18:15 L5 - **Luca Beverina** "Organic materials for solid state rechargeable batteries and electrochromic devices"

20:00 SOCIAL DINNER

THURSDAY, 22 FEBRUARY 2018

Chairperson: Fabio Bellina

09:00-10:30 L6 - **A. Di Carlo** "Dye Sensitized and Perovskite solar cells and modules"

10:30-11:00 COFFEE BREAK

11:00-12:30 L7 - **Jordi Llorca** "Hydrogen and fuel reformers for the energy transition"

12:30-14:00 LUNCH

Chairperson: Gianna Reginato

14:00-15:30 L8 - **Filippo De Angelis** "Modeling hybrid/organic PV: From dye-sensitized to perovskite solar cells"

15:30-16:15 J4 - **Federico Bella** "Polymeric Materials For Energy Conversion And Storage Devices"

16:15-16:45 COFFEE BREAK

- 16:45-17:15** T3 - **Lucia Curri** "ERC Calls: Opportunities for the Excellent Science"
- 17:15-18:15** O1 – **Norberto Manfredi** "Effect of the organic molecular design on the solar h₂ production efficiency""
O2 – **Simone Maranghi** "Methodologies for the sustainability evaluation of innovative renewable energy technologies"
O3 – **Giavanni Valenti** "Nano-graphitic templates and hierarchical nanostructures in multi-functional electrocatalysts for the artificial leaf"
O4 – **Mirko Magni** "Electrochemistry for renewable energy studies: the case of WO₃ photoanodes and of organic semiconducting films"
- 19:30** DINNER

FRIDAY, 23 FEBRUARY 2018

Chairperson: Massimo Innocenti

- 09:00-10:30** L8 - **Ugo Bardi** "Complex Systems and us: The Seneca Effect"
- 10:30-11:00** COFFEE BREAK
- 11:00-12:30** L9 - **Massimo Trotta** "Photosynthesis for a sustainable planet "
- 12:30-14:00** LUNCH

Chairperson: Massimo Innocenti

- 14:00-15:30** L10 - **Paolo Fornasiero** "Opportunities And Challenges Of Well-Defined Nanocatalysts"
- 15:30-16:15** J5 - **Gabriella Garbarino** "CO₂ adsorption and conversion on heterogeneous catalysts: bridging mechanisms and industrial processes"
- 16:15-16:45** COFFEE BREAK
- 16:45-17:45** O5-O8
- 17:45-18:45** POSTER
- 19:30** DINNER

SATURDAY, 24 FEBRUARY 2018

Chairperson: Adalgisa Sinicropi

09:00-10:30 L11 - **Alessandra Sanson** "Ceramics for energy: challenges and opportunity"

10:30-11:00 COFFEE BREAK

11:00-11:15 JUNIOR ENERCHEM AWARD ANNOUNCEMENT

11:15-12:45 L12 - **Fabrizio Passarini** "Energy considerations in the application of Life Cycle Assessment"

12:45 CLOSING

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

ABSTRACTS

Oral Presentations (O1-O4)

Effect of the organic molecular design on the solar h₂ production efficiency

Norberto Manfredi,^a Bianca Cecconi,^a Valentina Calabrese,^b Alberto Minotti,^b Francesco Peri,^b Riccardo Ruffo,^a Matteo Monai,^c Ismael Romero-Ocana,^c Tiziano Montini,^c Paolo Fornasiero,^c Alessandro Abbotto*^a

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The sustainable production of fuels from Sun and water is an emerging field of research, where the organic design is strategic to get improved technological performances. In our investigation on dye-sensitized solar cells we have pioneered a multi-branched multi-anchoring D(- π -A)₂ geometry, now widely used in the field.¹⁻²

Here, we present specifically engineered di-branched dyes to the dye-sensitized photochemical hydrogen production. Namely, we tested a series of D(- π -A)₂ dyes where D is a substituted phenothiazine donor core, A is the acceptor-anchoring cyano-acrylic group, and π are different thiophene spacers (Fig. 1).³ Improved optical properties and stability after longer irradiation times and enhanced performances in the production of hydrogen have been achieved. The unprecedented use of a glucose derivative for enhanced wettability revealed increased activity over conventional hydrophilic dyes,⁴ and the ability of the sugar dye to promote self-assembling on the catalyst center surface, for enhanced performances. Similar molecular structures, bearing different electron-donor moieties and structural geometries, have been investigated showing promising properties.⁵

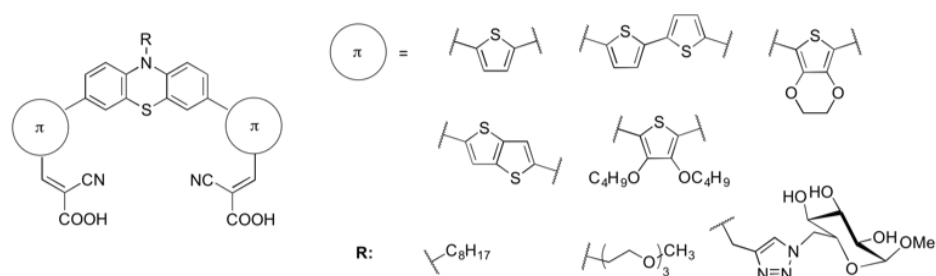


Fig. 1: General structure of heteroaromatic sensitizers for solar production of hydrogen.

References

- Cecconi, B.; Manfredi, N.; Montini, T.; Fornasiero, P.; Abbotto, A., *Eur. J. Org. Chem.* **2016**, 5194.
- Manfredi, N.; Cecconi, B.; Abbotto, A., *Eur. J. Org. Chem.* **2014**, 7069.
- Cecconi, B.; Manfredi, N.; Ruffo, R.; Montini, T.; Romero-Ocana, I.; Fornasiero, P.; Abbotto, A., *ChemSusChem* **2015**, 8, 4216.
- Manfredi, N.; Cecconi, B.; Calabrese, V.; Minotti, A.; Peri, F.; Ruffo, R.; Monai, M.; Romero-Ocana, I.; Montini, T.; Fornasiero, P.; Abbotto, A., *Chem. Commun.* **2016**, 52, 6977.
- Manfredi, N.; Monai, M.; Montini, T.; Salamone, M.; Ruffo, R.; Fornasiero, P.; Abbotto, A., *Sustainable Energy Fuels* **2017**, 1, 694.

Methodologies for the sustainability evaluation of innovative renewable energy technologies

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This lecture is focused on the sustainability assessment of energy technologies by investigating the main issues that need to be faced up when the Life Cycle Thinking approach is applied. After a general overview of the most common life cycle methodologies (LCA, LCC, SLCA, LCSA), the lecture will deal with the application of prospective LCA of a DSM (Dye-Sensitized Solar Modules), starting from the industrial production process to the use and decommissioning phases. The analysis aims to assess the environmental footprint of outdoor and BIPV applications as a viable and environmentally sustainable technology. An inspection of the methodological issues concerning the setting up of the case study model, the design of the use and End of Life phases will be discussed along with technical hints for drawing future market scenarios to understand the critical issues and opportunities of the novel photovoltaic technology and for assessing the market potential of DSM on a long-term perspective.

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Nano-graphitic templates and hierarchical nanostructures in multi-functional electrocatalysts for the artificial leaf

Giovanni Valenti,^a Michele Melchionna,^b Meng Liu,^a Massimo Marcaccio,^a Marcella Bonchio,^c Maurizio Prato,^b Paolo Fornasiero,^b and Francesco Paolucci^a

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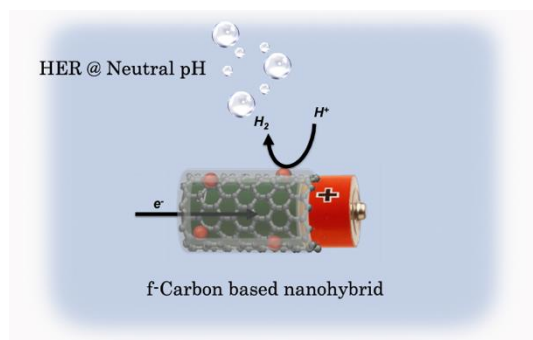
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Nanomaterials are nowadays at the forefront of materials science research. The design and realization of hierarchical nanoarchitectures, in which selected components are arranged to leverage their expected mechanistic functions are obtaining a wide range of applications, from the aerospace industry to bio-medicine, and as benchmarks for many catalytic reactions.

Carbon-based nanomaterials have been the main actors of nanotechnology since their very first discovery, and their unique morphological/electronic properties are particularly suited to be used in electrocatalytic applications. CNTs and graphene are indeed ideal supports in catalysis as they have an optimal electronic conductivity and provide percolation routes for charge transfer reactions to occur. The integration of nanocarbons into hierarchical materials is an effective strategy to further boost the potentiality of nanostructured catalysts. The generation of multiple interfaces in such hierarchical assemblies is responsible for their exceptional activity, whose origin is however only rarely understood.

We will show that, once embedded within nanoarchitectures made of multi-wall nanotubes or graphene and metal oxide the catalytic properties of nanoclusters metal nanoparticles ^[4,5] can be dramatically enhanced according to mechanisms which likely involve the concerted and synergic participation of all component building blocks in the electrocatalytic steps.



carbon shells, [1,2,3] and

References

- [1] Toma, F.M. et al., *Nature Chem.* **2010**, 2, 826.
- [2] Quintana, M. et al. *ACS Nano* **2013**, 7, 811.
- [3] Hof, F.; Boni, A.; Valenti, G.; Huang, K.; Paolucci, F.; Penicaud, A. *Chem. Eur. J.* **2017**, 23, 15283.
- [4] Mazzaro, R.; Boni, A.; Valenti, G.; Marcaccio, M.; Paolucci, F.; Ortolani, L.; Morandi, V.; Ceroni, P.; Bergamini, G. *ChemistryOpen* **2015**, 4, 268.
- [5] Valenti, G.; Boni, A.; Melchionna, M.; Cargnello, M.; Nasi, L.; Bertoni, G.; Gorte, R. J.; Marcaccio, M.; Rapino, S.; Bonchio, M.; Fornasiero, P.; Prato, M.; Paolucci, F. *Nature Commun.* **2016**, 7, 13549

Electrochemistry for renewable energy studies: the case of WO₃ photoanodes and of organic semiconducting films

Mirko Magni,^{*,a} Gian Luca Chiarello,^{*,a} Serena Arnaboldi,^a Massimo Bernareggi,^a Alessio Orbelli Biroli,^{b,c} Tiziana Benincori,^d Francesco Sannicolò,^a Elena Selli,^{a,c} Patrizia Mussini^{a,c}

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Electrochemistry is a powerful tool in the modern research. Its polyhedral nature makes this ensemble of techniques unique, not only in term of operating conditions (switching from synthetic to characterization methods), but also for the great ductility in the applications (including molecules in solution, solid films/coatings, and even working devices). Other important aspects are that characterizations can be performed *i) in situ/in operando*, a great advantage to understand how a material actually behaves in the devices, and *ii) in combination* with other techniques, enriching the portfolio of information coming from a multi-stimuli approach.

In this presentation examples of very recent studies in the field of renewable energies will be discussed, focusing on WO₃-based photoanodes and “smart” organic semiconductors.

A peculiar bilayer architecture of WO₃ coatings, obtained by radio frequency plasma sputtering, revealed remarkable photoelectrocatalytic performance neatly overcoming the main key parameters of control materials properly prepared. Electrochemical studies played a crucial role in the clarification of such behavior [1].

The second example concerns a study in progress as part of a broader project focused on a very promising class of inherently chiral organic semiconductors, acting as efficient and robust enantioselective layers for electrochemical sensors [2,3]. Such innovative materials seem to be exploitable also for other applications, including energetics. A deep and multivariate characterization is mandatory to reveal as much properties as possible that could be finally combined to depict a complete portrait of these conducting organic films. In particular an imaginary journey from the outside (*i.e.* surface area) to the inside (*i.e.* optical and electronic features) will be made.

The support of Fondazione Cariplo/Regione Lombardia (Project 2016-0923) and SmartMatLab are gratefully acknowledged.

References

- [1] Chiarello, G. L.; Bernareggi, M.; Pedroni, M.; Magni, M.; Pietralunga, S. M.; Tagliaferri, A.; Vassallo, E.; Selli, E. *J. Mater. Chem. A* **2017**, *5*, 12977.
- [2] Sannicolò, F.; Mussini, P.R.; Benincori, T.; Martinazzo, R.; Arnaboldi, S.; Appoloni, G.; Panigati, M.; Quartapelle Procopio, E.; Marino, V.; Cirilli, R.; Casolo, S.; Kutner, W.; Noworyta, K.; Pietrzyk-Le, A.; Iskierko, Z.; Bartold, K. *Chem. Eur. J.* **2016**, *22*, 10839.
- [3] Arnaboldi, S.; Benincori, T.; Cirilli, R.; Kutner, W.; Magni, M.; Mussini, P.; Noworyta, K.; Sannicolò, F. *Chem. Sci.* **2015**, *6*, 1706.

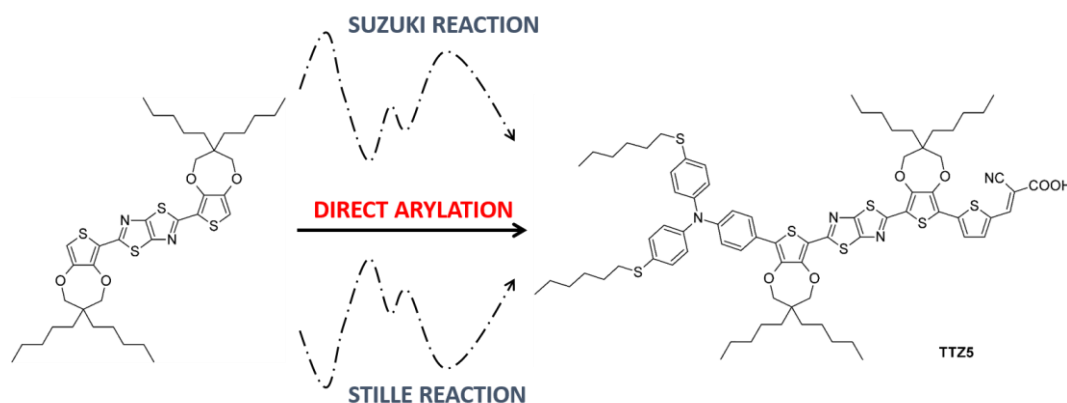
Posters (P1-P28)

Shorter is better: the role of direct arylation in the synthesis of thiazolo [5,4-*d*]thiazole-based dyes.

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In the last years, totally organic dyes have been heavily used as photo-sensitizers for the solar-driven production of energy and hydrogen.^[1,2] The employment of this class of dyes is often preferred not only from an environmental point of view, thanks to the absence of heavy or toxic metals (ruthenium, lead), but also because their photo-electrochemical properties can be finely tuned by a careful design of the molecular structures.^[1] Unfortunately, in many cases, the synthesis of such dyes are laborious and require a high number of synthetic steps, which often prevents a large-scale application of the corresponding devices. This issue was present also in the case of our thiazolo[5,4-*d*]thiazole-based dyes, which indeed performed well both in Dye-Sensitized Solar Cells (DSSCs)^[3] and in the H₂ photocatalytic production,^[4] but were characterized by a long and complex synthesis. Aiming to prepare our best performing dye (TTZ5) in large scale, we completely revised the synthetic strategy and, taking advantage of the direct arylation reactions, were able to achieve grams of the desired dye through a shorter and more sustainable process.



References

- [1] Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595.
- [2] Cecconi, B.; Manfredi, N.; Montini, T.; Fornasiero, P.; Abboto, A. *Eur. J. Org. Chem.* **2016**, 5194.
- [3] Dessì, A.; Calamante, M.; Mordini, A.; Peruzzini, M.; Sinicropi, A.; Basosi, R.; Fabrizi de Biani, F.; Taddei, M.; Colonna, D.; Di Carlo, A.; Reginato, G.; Zani, L. *Chem. Commun.* **2014**, *50*, 13952.
- [4] Dessì, A.; Monai, M.; Bessi, M.; Montini, T.; Calamante, M.; Mordini, A.; Reginato, G.; Trono, C.; Fornasiero, P.; Zani, L. *ChemSusChem* **2018**, *10*.1002/cssc.201701707.

Kuquinone as photocatalyst in water oxidation

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Water splitting is one of the most studied processes in chemistry, because exploits solar energy to produce molecular oxygen but most of all hydrogen, which is considered the ideal fuel from the future. Water oxidation to molecular oxygen has been considered the bottleneck of the reaction. However, O₂ may not be the only product, indeed if the reaction goes via a two electrons process hydrogen peroxide is formed. This molecule is a strong green oxidant, nowadays it is synthesized by the anthraquinone process that requires high energy for its production and high cost for transportation. So it is highly interesting to find new processes for its production and possibly *in situ*. Few years ago, in our laboratory a new pentacyclic quinoid compound, called KuQuinone, has been synthesized. Such molecule shows a large absorption spectrum and favourable reduction potential.[1] It has been, then, tested as a photosensitizer on ITO surface obtaining satisfactory results in terms of IPCE.[2] A recent study showed that its electrochemical behaviour is appropriate to perform the oxidation of water both to dioxygen or to hydrogen peroxide.[3] In this contribution, the preliminary results of KuQuinone as photoactive species in catalytic water oxidation to hydrogen peroxide will be presented.

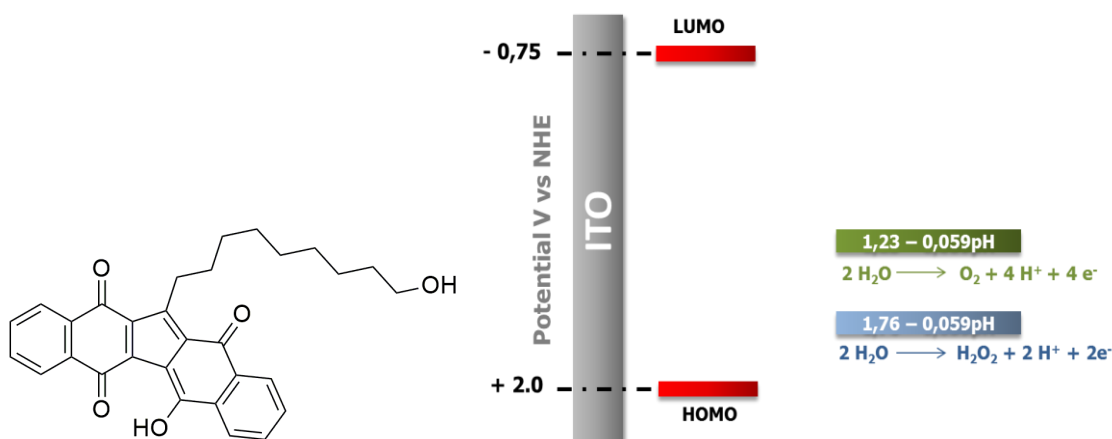


Fig. 1 (left) Structure of KuQ derivate (right) Energy diagram for photocatalytic water oxidation perform by KuQ in ITO surface.

References

- [1] Coletti, A.; Lentini, S.; Conte, V.; Floris, B.; Bortolini, B.; Sforza, F.; Grepioni, F.; Galloni, P. *J. Org. Chem.* **2012**, *77*, 6873-6879.
- [2] Sabuzi, F.; Armuzza, V.; Conte, V.; Floris, B.; Venanzi, M.; Galloni, P.; Gatto, E. *J. Mater. Chem. C*, **2016**, *4*, 622.
- [3] Bonomo, M.; Sabuzi, F.; Di Carlo, A.; Conte, V.; Dini, D.; Galloni, P. *New J. Chem.* **2017**, *41*, 2769-2779.

New Photocatalytic reactor for the production of H₂ and regenerated fuels from CO₂

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This work represents two different photocatalytic process, with the aim of biofuels formation in the presence of bare and metal loaded TiO₂ (P25) with an innovative cylindrical photoreactor (Fig.1), which can operate in variable pressure (up to 20 bar) [1, 2].

- i) Photoreforming of glucose at ambient pressure was investigated with P25 for 5h at different temperatures. The significant amount of H₂ produced ($3.1 \text{ mol kg}_{cat}^{-1} h_{irr}^{-1}$) at 80 °C with 0.25 gL⁻¹ of catalyst concentration. This primary results are so far very remarkable with respect to similar research on conventional photoreactors, which is a prerequisite for the elaboration of future investigations and studying the effect of different variables.
- ii) The high pressure photoreduction of CO₂, results in formation of both liquid (HCOOH, HCHO and CH₃OH) and gas phase products (CO, H₂, CH₄), depending on catalyst formulation and reaction conditions [3]. The mechanism of product formation, implies the role of a sacrificial inorganic hole scavenger (Na₂SO₃) in the formation of liquid products during the first hours of reactions. Later, with total consumption of Na₂SO₃, the organic products formed act as hole scavengers and are consumed with formation of syngas. The results demonstrate a flexible pathway for the formation of desirable of HCOOH and HCHO in considerable amount.

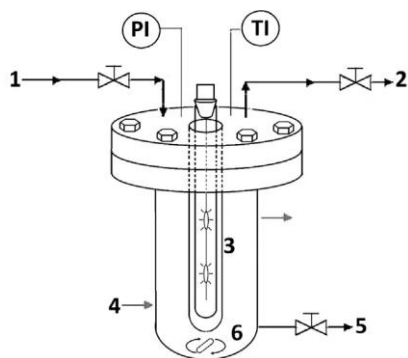


Fig. 1. Sketch of the high pressure photoreactor:

- 1: Pressure reducer, 2: Sample valve for gas phase, 3: Lamp, 4: Double-walled thermostatic system, 5: Sample valve for liquid phase, 6: Magnetic Stirrer.
PI: pressure indicator; TI: temperature indicator.

References

- [1] Rossetti, I.; Villa, A.; Compagnoni, M.; Prati, L.; Ramis, G.; Pirola, C.; Bianchi, C.L.; Wang, W.; Wang, D. Catal. Sci. Technol. 2015, 5, 4481.
- [2] Rossetti, I.; Villa, A.; Pirola, C.; Prati, L.; Ramis, G.; RSC Adv. 2014, 4, 28883.
- [3] Galli, F.; Compagnoni, M.; Vitali, D.; Pirola, C.; Bianchi, C.L.; Villa, A.; Prati, L.; Rossetti, I. Appl. Catal., B. 2017, 200, 386.

Graphite Intercalation Compounds as Effective Platforms for the Preparation of Highly-Active Electrocatalysts toward oxygen reduction reaction

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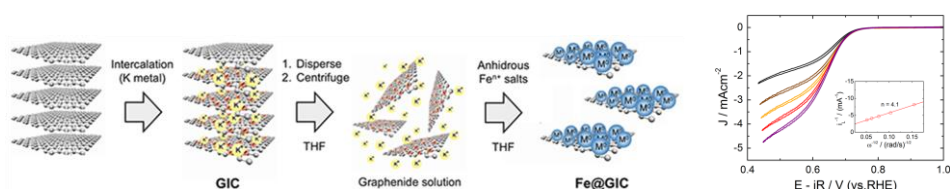
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The integration of carbon materials in appropriate nanostructures has been recognized as a very powerful approach to improve the performance of state-of-the-art catalytic materials.¹ In the context of energy conversion, the peculiar properties of carbon nanotubes, graphene and other derivatives are widespread used to boost the rate of electrocatalytic reactions.²

Graphite intercalation compounds (GICs) can be readily exfoliated to monolayer graphene in organic solvents, and the resulting GICs solutions are composed of charged graphene layers. Due to their size and surface area, graphitic nanocarbons are an interesting and promising carbon starting material for GICs.

By using the redox potential of different types of GICs, different metal nanoparticles (NPs) like Fe, Cu and Mo are attached to the carbon frameworks. Up to date, the vast majority of examples published on the generation of NPs/graphene composites rely on surfactant/water based dispersions of graphene or graphene oxide and on the addition of metal salts as well as reducing agent to that dispersions. The direct reaction of GICs with metal salts has advantages over the above mentioned process, as the reduction of the metal takes place in close proximity of the carbon lattice. This results in NPs with a unique distribution in size, and a preferential growth near the edges of the GICs.³

The Fe/nanocarbon composites have been thoroughly measured as cheap, earth-abundant electrode materials for the oxygen reduction reaction in basic solutions. The composites show high mass activities, comparable to that of precious metals, and good stabilities over time. A detailed electrokinetic analysis by the RDE technique shed light into the reaction mechanism, providing insights for the role of Fe in the catalytic area.



References

- [1] Hong, W.; Risch, M.; Stoerzinger, K.; Grimaud, A.; Suntivich, J.; Shao, Y. *Energy Environ. Sci.* **2015**, *8*, 1404.
- [2] Su, D.; Perathoner, S.; Centi, G. *Chem. Rev.* **2013**, *113*, 5782.
- [3] Hof, F.; Boni, A.; Valenti, G.; Huang, K.; Paolucci, F.; Penicaud, A. *Chem. Eur. J.* **2017**, *23*, 15283.

N-Doped carbon encapsulated cobalt nanoparticles as pH selective electrocatalyst for oxygen reduction

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Electrochemical oxygen reduction (ORR) is a widely investigated reaction because of its central role in fuel cell performance. Nevertheless, it has recently attracted attention as a viable strategy for environmentally sustainable hydrogen peroxide production, that is a very relevant industrial molecule [1]. Non-precious metal catalysts with high activity and stability have become a major focus of this field of research, and carbon-encapsulated transition metal nanoparticles can be considered suitable for this approach as they show unique stability in a wide pH range because the carbon nanoshells prevent direct contact of the active transition metal species with reactants and electrolyte solutions, as well as avoiding agglomeration of the nanoparticles [2]. We synthesized and investigated a material presenting unique pH-dependent selectivity features towards ORR. The material consists of Co nanoparticles encapsulated in nitrogen-doped graphitic carbon. The material has been proven to be active for the oxygen reduction reaction both in acidic and alkaline environment, with a complete switch in product selectivity at different pH. In fact the H₂O₂ Faradaic efficiency is almost quantitative at pH 1, while operating at alkaline pH the selectivity is reversed, with water being the major product (almost 100% Faradaic efficiency). The onset potential of the reaction are very positive, (0,5V vs RHE in acidic environment and 0,7V vs RHE in alkaline environment), making this material a very appealing purpose-driven electrocatalyst for ORR.

References

- [1] D. Iglesias; A. Giuliani; M. Melchionna; S. Marchesan; A. Criado; L. Nasi; M. Bevilacqua; C. Tavagnacco; F. Vizza; M. Prato; P. Fornasiero, *Chem*, **2018** DOI: 10.1016/j.chempr.2017.10.013
- [2] Wang, J.; Gao, D.; Wang, G.; Miao, S.; Wu, H.; Liab, J.; Bao, X.; *J. Mater. Chem. A*, **2014**, 2, 20067

Mo Doped BiVO₄ Photoanodes for Oxygen Evolution

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Among the most promising photocatalysts for water oxidation, BiVO₄ has emerged thanks to its visible light harvesting properties with a relatively narrow bandgap of 2.4 eV, its stability over a wide pH range and a valence band edge position suitable for water oxidation [1,2]. In order to improve its typically poor electron transport properties [3], donor-type doping of BiVO₄ photoanodes with Mo has been investigated [4]. Optically transparent thin films of this material with different doping levels have been prepared by spin coating of the precursor solutions onto FTO and characterized through photoelectrochemical (PEC) and spectroscopic techniques. As shown by Linear Sweep Voltammetry (LSV) and Internal Quantum Efficiency (IQE) analyses (Fig. 1), doping with Mo significantly increases the PEC performance of pure BiVO₄. The IQE results recorded with both back and front side irradiation (Fig. 1b) demonstrate the beneficial impact of doping on the charge carriers mobility of this material. The best performing doping concentration was determined from the comparison of the PEC results with the optical properties of the investigated photoanodes. Photocatalytic reduction experiments of molecular probes such as methyl viologen allowed us to assess the conduction band reduction potential of doped BiVO₄ with respect to pure BiVO₄. Further information on the role that Mo doping has on the recombination of photogenerated charge carriers are expected from transient absorption spectroscopy studies in the picosecond time scale.

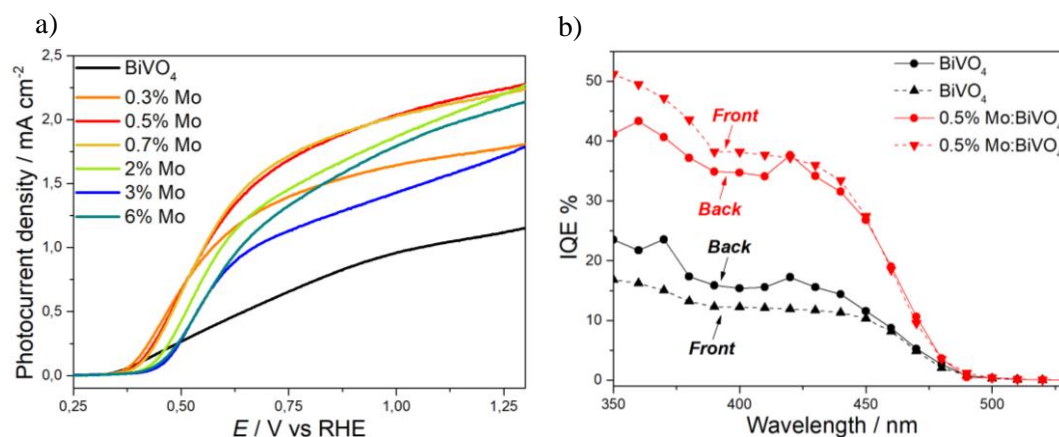


Fig. 1. a) LSV and b) IQE analyses of BiVO₄ photoelectrodes with different Mo doped levels, at 1 V vs RHE in 0.5 M Na₂SO₃ with 0.5 M potassium phosphate buffer (pH = 7).

References

- [1] Grigioni, I.; Stamplecoskie, K. G.; Selli, E.; Kamat, P. V. *J. Phys. Chem. C* **2015**, *119*, 20792.
- [2] Rettie, A. J. E.; Lee, H. C.; Marshall, L. G.; Lin, J.-F.; Capan, C.; Lindemuth, J.; McCloy, J. S.; Zhou, J.; Bard, A. J.; Mullins, C. B. *J. Am. Chem. Soc.* **2013**, *135*, 11389.
- [3] Park, Y.; McDonald, K. J.; Choi, K. S. *Chem. Soc. Rev.* **2013**, *42*, 2321.
- [4] Eisenberg, D.; Ahn, H. S.; Bard, A. J. *J. Am. Chem. Soc.* **2014**, *136*, 14011.

Graphene based electrocatalyst for oxygen reduction reaction

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The Oxygen Reduction Reaction (ORR) is a fundamental process for sustaining life and is an important process utilized in biosensing analysis[4]. Additionally, this process is applicable to artificial energy devices such as fuel cells and metal-air based batteries. The reaction proceeds at a very slow kinetic rate requiring a catalyst to reduce the activation barrier. Platinum is an ideal catalyst but it is neither cheap nor environmentally friendly. The prospect of a cheap and green alternative is intriguing and has yielded considerable research in the past decade. Amongst the most promising materials as catalysts carbon-based systems, such as carbon nanotubes (CNT) and graphene derivatives are particularly intriguing[1,2,3].

New synthetic strategies allow to produce tunable graphene-based materials, starting from graphene oxide (GO). These are based on the reduction of the oxidized groups of GO in the presence of compounds capable of adding functional groups or heteroatoms to the carbon lattice.

We were particularly interested in the material obtained by doping GO with nitrogen and boron through its reduction in presence of hydrazine and borazine. Such reduced graphene oxides (rGO) show almost the same electronic properties as graphene, with some X-C (X= N or B) regions within the graphene lattice that have a useful dipole moment which helps the interaction between the oxygen molecule and the catalytic substrate; thus, such sites represent those active for the ORR catalysis.

We have investigated the electrochemical behavior of a selection of such material and their electrocatalytic activity for the ORR.

References

- [1] Maldonado, Stephen; Morin, Stephen; Stevenson, Keith J. *Carbon*, **2006**, 44 (8), 1429.
- [2] Dai Liming et al., *CHEM REV*, **2015**, 115, 4823
- [3] *J. Phys. Chem. C*, **2009**, 113 (17), pp 7069–7078
- [4] A. Xu, S. Jiang, Z. Hu, S.Q. Liu. *ACS Nano*, **2010**, 4 (7), pp 4292–4298

Bis(1,10-phenanthroline) copper complexes with tailored molecular architecture: from electrochemical features to application as redox mediators in dye-sensitized solar cells.

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In the last few years, copper complexes turned out to be excellent competitors of cobalt complexes as redox mediators in the formulation of iodine-free electrolytes for dye-sensitized solar cells (DSSCs). The lack of a clear correlation between electrochemical signatures of copper complexes (*i.e.* half-wave potential and heterogeneous electron transfer rate) and photoelectrochemical performance of solar devices makes difficult the optimization of their coordination sphere. Therefore, to partially fill this gap and to elucidate the intrinsic correlation between the molecular architecture of these complexes and their electrochemical features, we prepared four Cu⁺²⁺ redox couples in which the copper center is coordinated by two 1,10-phenanthrolines with different substituents in position 2. These complexes were characterized, from both electrochemical and spectroscopic point of view, and tested as electron shuttles in photoelectrochemical cells sensitized with two efficient π -extended benzothiadiazole dyes. It appeared that 2-aryl-1,10-phenanthrolines effectively combine suitable optical and electrochemical properties. While a fast electron transfer kinetics seems to positively affect the dye regeneration process, a more balanced value leads to an increase of the overall DSSC performance.

Semitransparent perovskite solar cells with ultra-thin metal top electrodes for bipvs and tandem applications

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Organometal trihalide perovskite solar cells (PSCs) have recently achieved impressive advancements in power conversion efficiencies (PCEs) to the current world record of 22.1% thanks to their superior optoelectronic properties.¹ The low cost and ease of processing, together with their exceptional performances, make PSCs suitable and promising candidates for a wide range of technological applications.

Among others, one advantage of PSCs is their possibility to be made semitransparent. Semitransparent perovskite solar cells could find application in building integrated photovoltaics (BIPVs) as electricity-generating windows, facades and roofs, or in tandem devices, combined with other solar cells (e.g. silicon or CIGS) to form multi-junction architectures with enhanced light-harvesting and higher efficiency.²

Semitransparent devices can be fabricated by reducing the thickness of the active layer and substituting the conventional nontransparent and highly reflective metal top electrodes (typically 100 nm thick Al, Ag or Au) with suitable transparent alternatives. One of the key challenges to realize such devices consists in developing materials with an optimal trade-off between light transmittance and conductivity to be used as top electrodes. Composite transparent electrodes based on dielectric/metal/dielectric (DMD) structures, where an ultra-thin metal film is embedded between two dielectric materials, represent valid candidates for this purpose, exhibiting promising features such as mechanical and thermal stability, low roughness, processing conditions that are compatible with PSCs, and tunable opto-electrical properties.³ Their conductivity is mainly dependent on the thickness of the metal layer, while their optical transmittance can be tuned by varying the nature and thickness of the dielectric materials.

In this work, a series of semitransparent mixed-halide perovskite solar cells with a regular planar architecture (FTO/compact-TiO₂/CH₃NH₃PbI_{3-x}Cl_x/Spiro-OMeTAD/top electrode) and with different thicknesses of the perovskite layer was fabricated, in which a DMD top electrode composed of a MoO₃ (6 nm) / Au (11 nm) / MoO₃ (20 nm) stack was thermally evaporated. Opaque reference cells were prepared by depositing 6 nm of MoO₃ as buffer layer and 100 nm of Au as rear contact, and exhibited efficiencies as high as 14.24%. Semitransparent devices also showed considerable performances, with the highest PCE equal to 10.71% given by the solar cell with the thickest perovskite layer, and different average transmittances (AVTs) depending on the considered wavelength range (400-800 nm for BIPV, 600-1000 nm for tandem) and on the thickness of the active layer (the maximum AVTs in the two ranges were exhibited by the solar cell with the thinnest perovskite layer, equal to 27% and 42% respectively).

References

- [1] M. L. Petrus et al. *Adv. Energy Mater.* **2017**, 7 (16), 1700264.
- [2] Q. D. Tai and F. Yan. *Adv. Mater.* **2017**, 29 (34), 1700192.
- [3] J. Yun. *Adv. Funct. Mater.* **2017**, 27 (18), 1606641.

Multivariate investigation on hydrogel electrolytes for hybrid solar cells

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Nowadays, dye-sensitized solar cells (DSSCs) with water-based electrolytes are considered as one of the possible breakthrough towards DSSCs large-scale diffusion. If opportunely developed and optimized, aqueous solar cells can be considered a truly low impact photovoltaic device with non-toxic components [1,2]. Moreover, the possibility of gelling the electrolyte into a polymeric matrix can reduce the leakage outside the device, thus increasing the long-term stability. Above all, bio-derived polymers appear promising being renewable and easy available with low cost [3].

In this contribution, the investigation on bio-derived hydrogel electrolytes for dye-sensitized solar cells is proposed. Moreover, the use of design of experiments (DoE) is demonstrated to be a useful chemometric technique for the concurrent investigation of a series of experimental factors that directly influence the photovoltaic performances of solar cells. Results obtained enlighten that a solid mathematical-statistical approach is fundamental to support the researchers and effectively drive the experiments towards the achievements of optimal operating conditions for aqueous solar cells.

References

- [1] Galliano, S.; Bella, F.; Gerbaldi, C.; Falco, M.; Viscardi, G.; Grätzel, M.; Barolo, C. *Energy Technol.* **2016**, *5*, 300.
- [2] Bella, F.; Galliano, S.; Falco, M.; Viscardi, G.; Barolo, C.; Grätzel, M.; Gerbaldi, C. *Chem. Sci.* **2016**, *7*, 4880.
- [3] Bella, F.; Galliano, S.; Falco, M.; Viscardi, G.; Barolo, C.; Grätzel, M.; Gerbaldi, C. *Green Chem.* **2017**, *19*, 1043.

Synthesis of Pechmann derivatives for potential application in organic electronics or photovoltaics

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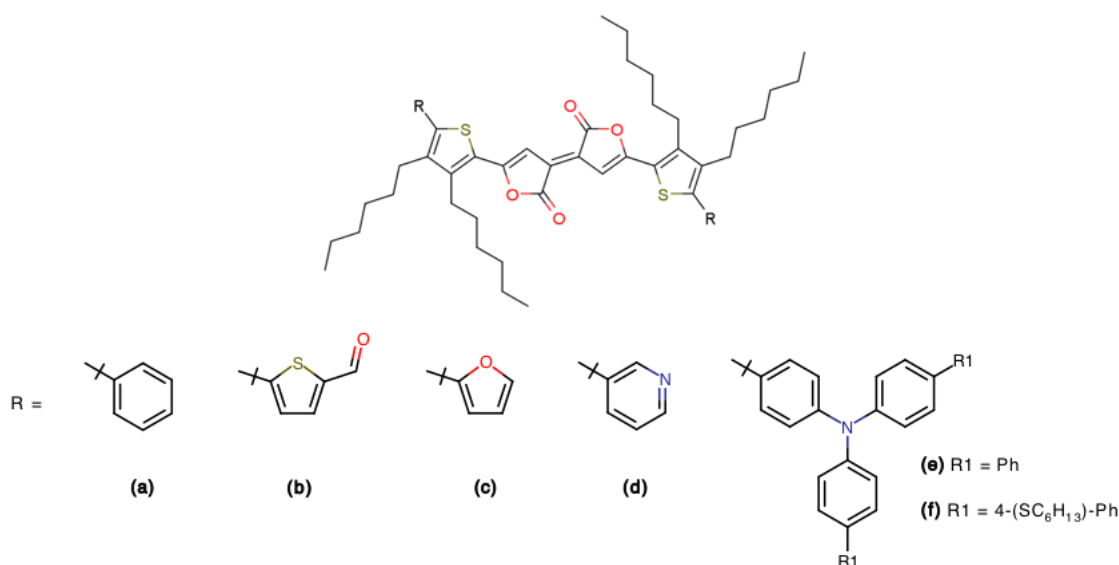
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The synthesis of the (E)-3,3'-bifuranylidene-2,2'-dione heterocyclic system has been first published in 1882 by Von Pechmann.¹ Recently promising optical and electronic properties² have been demonstrated in some Pechmann derivatives and this fact has stimulated further studies concerning the preparation of such scaffold and its incorporation into longer conjugated systems, which might have a potential interest for organic electronics.³

In this work, the preparation and spectroscopic characterization of some symmetrical small molecules containing the so-called Pechmann lactone and featuring an extended conjugation, are reported. The absorption and emission spectra of the new molecules obtained have been recorded in solution and clearly show how the photophysical properties can be modulated by a proper choice of the (hetero)aromatic terminal groups. All the compounds prepared in this study have interesting optical properties and could find application as semiconductors in organic electronics or photovoltaics.



References

- [1] H. Von Pechmann, *Ber. Dtsch. Chem. Ges.*, 1882, **15**, 881.
- [2] a) T. B. Norsten, E. A. B. Kantchev, M. B. Sullivan, *Org. Lett.*, 2010, **12**, 4816; b) E. A. B. Kantchev, T. B. Norsten, M. L. Y. Tan, J. J. Y. Ng, M. B. Sullivan, *Chem. Eur. J.*, 2012, **18**, 695; c) E. A. B. Kantchev, T. B. Norsten, M. B. Sullivan, *Org. Biomol. Chem.*, 2012, **10**, 6682.
- [3] M. Hayashi, F. Toshimitsu, R. Sakamoto, H. Nishihara, *J. Am. Chem. Soc.*, 2011, **133**, 14518.

Light-powered artificial molecular pumps

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LEAPS, "Light Effected autonomous molecular pumps: Towards active transporters and actuating materials" is a research project, funded by an European Research Council Advanced Grant, whose goal is to develop supramolecular systems capable of performing directed and autonomous translational movements activated by light energy and use for transporting molecular substrates in a variety of set-ups.

The system that we are developing is pseudorotaxane assembly in which a molecular ring passes unidirectionally through a molecular axle in response to photochemical and chemical stimulation. It is composed of a molecular ring (1) and a non-symmetric molecular axle that comprises: a cyclopentyl unit as passive pseudo-stopper (2) at one end, an ammonium cation as central recognition site for the ring and an azobenzene stopper as bistable photoswitchable unit (3) at the other end. The ring should enter exclusively from the *E*-azobenzene side of the axle for kinetic reasons, affording a pseudorotaxane in which the macrocycle encircles the recognition site on account of hydrogen-bonding interactions between the oxygen atoms and the ammonium centre and, possibly, π -stacking forces involving the naphthalene and azobenzene units. Subsequently, light irradiation converts the *E*-azobenzene unit into the bulkier *Z* form, a process that causes a destabilization of the supramolecular complex and dethreading of the components (Figure 1a). The next step will be to develop a "second generation pump" by replacing the cyclopentyl pseudostopper with an appropriately substituted phenyl unit, that is easier to functionalize (Figure 1b), in order to add further components to the system.

Another option is to append an alkyl chain of suitable length at the pseudostopper side, which can act as a reservoir for collecting molecular rings, pumped by light. A nanodevice of this kind is of high interest because it would convert the energy of the incident photons into chemical energy in the form of molecular rings stored under a non-equilibrium condition.

[1] Ragazzon, G. Baroncini, M. Silvi, S. Venturi, M. Credi, A. Nature Nanotechnology **10**, 70–75 (2015)

[2] Ragazzon, G. Baroncini, M. Silvi, S. Venturi, M. Credi, A. Beilstein J. Nanotechnol **6**, 2096–2104 (2015)

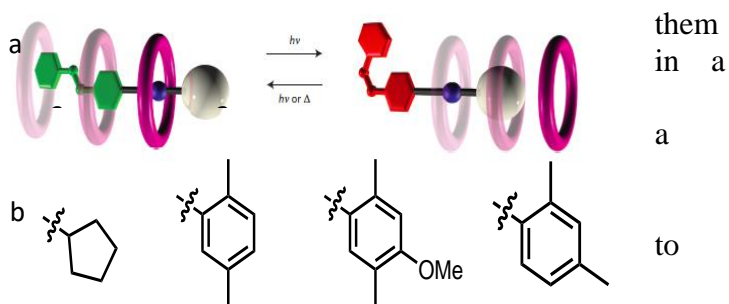


Figure 1. a) Schematic representation of the relative unidirectional translations of the ring and axle components triggered by light. b) candidate end,

Intermediate Temperature Electro-Reforming (ITER)

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The electro-oxidation of short chain aliphatic alcohols at intermediate temperatures (100-250°C) in devices like Direct Alcohol Fuel Cells (DAFCs) and Alcohol Electro-Reformers is an essentially unexplored field. At temperatures above 150°C in acidic conditions, the kinetics of ethanol oxidation on Pt catalysts are fast and proceed through the C-C bond breaking pathway, thus improving the efficiency of the electro-oxidative process due to the total conversion to CO₂ [1]. Electro-Reformers and DAFCs are more efficient devices using strong alkaline environments (pH ~ 14) due to faster alcohol oxidation kinetics and lower corrosion of the cell components. However, the partial oxidation of alcohols to carboxylates at high pH limits their energy efficiency [2]. In order to achieve total conversion of alcohols to CO₂, we have set up an electrochemical autoclave to study, for the first time, the electrooxidation of alcohols in 2M aqueous KOH at temperatures up to 180°C. Palladium is the most suitable catalytic material for the electro-oxidation of alcohols in alkaline environment [2]. We have synthesized nanostructured palladium-based catalysts supported on nickel foam with a “nanoflower” morphology. The three-dimensional structure of these catalysts guarantees fast mass transport of the alcohol fuel in the liquid phase. In addition, the 3D open structure exhibits enhanced gas permeability, avoiding the formation of bubbles on the electrode. These catalysts are electrochemically characterized both in half-cells and in a complete *Intermediate Temperature Electro Reformers*. The Pd catalysts are used as anodes and are coupled with a nanostructured NiCoP@Ni_{foam} cathode for the hydrogen evolution reaction [3]. Alcohol electroreforming at temperatures over 100°C in a pressurized vessel, couples the advantages of increased catalyst's activity and selectivity with the production of pure and safe pressurized hydrogen (up to 30 bar).

Charge transfer dynamics in β and meso patterned panchromatic porphyrins

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Transient optical studies, at the nanosecond and femtosecond timescales, have been carried out on three structurally different porphyrin dyes to probe their charge transfer dynamics relevant to spectral sensitization and DSSC operation.[1] Two of them, showing a β substitution pattern, were previously reported: ZnB bearing an ethynylphenyl cyanoacrylic acceptor group and ZnBT bearing an additional π -conjugated dithienylethylene (DTE) chromophore in the acceptor pendant.[2] The new porphyrin ZnMT, showing a donor-acceptor system in 5,15-meso position and the DTE unit as well, is characterized by a smaller HOMO-LUMO energy gap and by a more significant push-pull character which guarantees more intense and red-shifted absorption bands compared to β -substituted dyes. Besides, the introduction of the DTE unit promotes a remarkable gain in spectral sensitization both in β and meso positions.

We have demonstrated that the population of the absorption manifold resulting from the presence of the additional DTE chromophore leads to charge separation on a time scale of ca. 200 fs, irrespective of either the meso or β substitution position, resulting in the generation of a long-lived charge separated state surviving for several microseconds after injection. Thus, dyes equipped with the DTE bridge display the ability to convert photons in the 450-550 nm range, where more common push-pull design do not show optimal absorption.[3] Further, we have confirmed that β substitution may represent an effective strategy to combine extended spectral sensitization and optimal charge transfer rates with a synthetic and up-scalable feasibility.

References

[1] Di Carlo, G.; Caramori, S.; Casarin, L.; Orbelli Biroli, A.; Tessore, F.; Argazzi, R.; Oriana, A.; Cerullo, G.; Bignozzi, C. A.; Pizzotti, M. *J. Phys. Chem. C* **2017**, 121, 18385.

[2] Di Carlo, G.; Orbelli Biroli, A.; Tessore, F.; Pizzotti, M.; Mussini, P. R.; Amat, A.; De Angelis, F.; Abbotto, A.; Trifiletti, V.; Ruffo, R. *J. Phys. Chem. C* **2014**, 118 (14), 7307.

[3] Di Carlo, G.; Caramori, S.; Trifiletti, V.; Giannuzzi, R.; De Marco, L.; Pizzotti, M.; Orbelli Biroli, A.; Tessore, F.; Argazzi, R.; Bignozzi, C. A. *ACS Appl Mater Interfaces* **2014**, 6 (18), 15841.

Organic Sensitizers For Dye-Sensitized Water Splitting

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Among the new approaches to solar energy conversion, photoelectrochemical cells (PEC) represent an interesting solution to obtain hydrogen and oxygen from solar driven water splitting. Hydrogen is a clean fuel, with zero carbon footprint, and is very versatile since it can be used to produce electricity but also as an automotive fuel that ensures a far bigger range than batteries for electric cars.

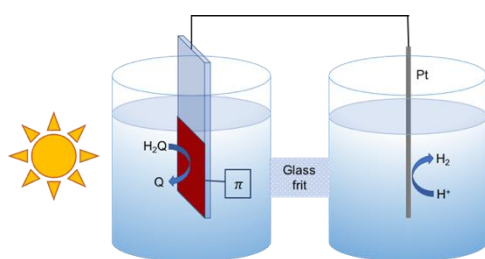
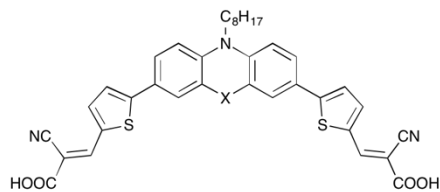


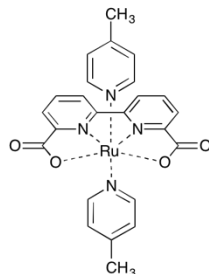
Figure 2. Scheme of a device for dye-

or carbazole donor core, A is the acceptor-anchoring cyano-acrylic group, and π is a thiophene spacer (Fig. 2), previously used in photocatalytic hydrogen production (2, 3). The dyes were studied both in presence of a sacrificial electron donor (hydroquinone, H₂Q) and of a common

Ru-based water oxidation catalyst (Ru(bda)(pic)₂). The reference dye (phenothiazine-based dye) (4) gave the best results thanks to its optical properties, IPCE and enhanced photocurrent in photoelectrochemical experiments.



CBZ-Th X = none
POZ-Th X = O
PTZ-Th X = S



[Ru(bda)(pic)₂]

References

- [1] Manfredi, N.; Cecconi, B.; Abbotto, A. *Eur. J. Org. Chem.* **2014**, 7069 (review).
- [2] Manfredi N.; Monai M.; Montini T.; Salamone M. M.; Ruffo R.; Fornasiero P.; Abbotto A. *Sustainable Energy Fuels*, **2017**, 1, 694-698.
- [3] (A). Manfredi N., Monai M., Montini T., Peri F., De Angelis F., Fornasiero P. and Abbotto A. *ACS Energy Letters*, **2017**, DOI: 10.1021/acscenergylett.7b00896, 85-91. (B). Manfredi, N.; Cecconi, B.; Calabrese, V.; Minotti, A.; Peri, F.; Ruffo, R.; Monai, M.; Romero-Ocana, I.; Montini, T.; Fornasiero, P.; Abbotto, A. *ChemComm* **2016**, 52, 6977.
- [4] Cecconi, B.; Manfredi, N.; Ruffo, R.; Montini, T.; Romero-Ocaña, I.; Fornasiero, P.; Abbotto, A. *ChemSusChem* **2015**, 8, 4216.

Environmental impact analysis applied to Solar Pasteurization Systems

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Water crisis are considered by several scientists, politics and economists as one of the most hazardous risks for human life in future scenarios. Indeed, the desertification of extensive areas of the planet is going to determine the death of millions of people living in extreme conditions of lack of water. Furthermore, in many under-developed regions of the world, most of the population lives in rural villages, where traditional potabilization systems are too expensive and technologically complex and the electrical grid is not available; for such reasons, millions of people in the world die each year because of diseases due to water contamination [1]. Therefore, water, energy, environment and sanitation are strictly connected. In this context Solar Pasteurization Systems represents a promising alternative to address such problem, as they can disinfect water by thermal way only exploiting solar energy, thus without any fossil fuels consumption or electrical grid connection [2,3].

In this work Life Cycle Assesment (LCA) and Exergo-environmental analysis have been performed in order to compare two disinfection systems based on solar pasteurization technology and to evaluate the most sustainable solution for the environment and for human life also based on specific social aspects related to the installation site and several possible scenarios.

References

- [1] Duff, W.S.; Hodgson, J.A. A simple high efficiency solar water purification system. *Sol. Energy* 2005, 79, 25–32. doi:10.1016/j.solener.2004.10.005.
- [2] Manfrida, G.; Petela, K.; Rossi, F. Natural circulation solar thermal system for water disinfection, *Energy* 141 (2017) 1204e1214
- [3] Dainelli, N.; Manfrida, G.; Petela, K.; Rossi, F. Exergo-Economic Evaluation of the Cost for Solar Thermal Depuration of Water, *Energies* 2017, 10, 1395

In silico design of near-IR D-A- π -A Sensitizers for DSSC

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In this work we focused on the computational design of novel organic sensitizers for dye-sensitized solar cells. The proposed dyes contain the Pechmann scaffold, which is a strong electron-withdrawing system with a brilliant red-purple colour [1]. The use of the Pechmann scaffold allows extending the light absorption spectrum of the dyes in the red/near-infrared (NIR) region and obtaining unusual blue-green coloured dyes that are currently of high interest [2,3]. The light absorption feature would enhance the light harvesting efficiency and, consequently, increase the overall efficiency of the solar device [4]. In order to raise the light-harvesting properties beyond the usual D- π -A dyes, an additional acceptor unit inside the π -bridge (D-A- π -A structure) is also used. Several types of modifications were considered (including replacement of the molecular anchor and modification of the spacer groups) and 13 derivatives were investigated by means of Density Functional Theory (DFT) and time dependent DFT calculations performed with the Gaussian09 program package. The same strategy was successfully applied in previous studies [5-6]. We found that the new dyes show: i) vertical absorption maxima ranging from 600 to 800 nm that confirms their red to infrared light absorption; ii) high oscillator strength values which in turns should give high extinction coefficients; iii) wave function plots of frontier molecular orbitals involved in the excitation process in favour of an intramolecular charge-transfer nature of the excitation. All these features, along with an appropriate alignment of the dye energy levels, suggest that the novel designed Pechmann-based organic sensitizers are compatible with a proper and potentially successful use in DSSCs.

References

- [1] Von Pechmann H. *Ber.*, **1882**, 15, 885
- [2] De Angelis F., Kamat, P. "A Conversation with Michael Grätzel" *ACS Energy Lett.*, **2017**, 2, 1674
- [3] Wu Y., Zhu W. H. *Chem. Soc. Rev.*, **2013**, 42, 2039
- [4] Jradi F. M., Kang X., O'Neil D., Pajares G., Getmanenko Y. A., Szymanski P., Parker T. C., El-Sayed M. A., Marder S. R. *Chem. Mater.*, **2015**, 27, 2480
- [5] Dessì A., Calamante M., Mordini A., Peruzzini M., Sinicropi A., Basosi R., Fabrizi de Biani F., Taddei M., Colonna D., Di Carlo A., Reginato G. and Zani L., *RSC Advances*, **2015**, 5, 32657 and *Chem comm*, **2014**, 50, 13952
- [6] Bernini C.; Zani L.; Calamante M.; Reginato G.; Mordini A.; Taddei M.; Basosi R.; Sinicropi, A., *J Chem Theory Comput*, **2014**, 10 (9), 3925

La_{0.6}Sr_{0.4}Fe_{0.95}Pd_{0.05}O_{3-δ} AS ELECTROCATALYST SOFCs

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Pd-doped lanthanum strontium ferrite powder La_{0.6}Sr_{0.4}Fe_{0.95}Pd_{0.05}O_{3-δ} (LSFPd) was synthesized by citrate-nitrate auto-combustion method and investigated as electrocatalyst for SOFCs. X-ray diffraction (XRD), surface area (BET) and temperature programmed reaction (TPR) analyses were performed on LSFPd powders. Electrical measurements were carried out on sintered pellets at 1250 °C. Electrolyte (La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-δ}) supported cells were prepared using LSFPd and a mixture of LSFPd (70 wt.%) and gadolinium doped ceria (GDC) (30 wt.%) as electrodes. The electrochemical performances were evaluated both in hydrogen and CH₄/CO₂ (biogas).

Fig. 1 shows the I-V and power density curves of LSFPd+GDC/LSGM/LSFPd cell at different temperatures in 100 cm³·min of H₂. The performances were remarkable in comparison to similar cells [1, 2]. The catalytic activity of LSFPd and LSFPd and GDC mixture for the dry reforming of methane (DMR) and partial oxidation of methane (POX) was measured to investigate the role of Pd as noble metal dopant. At 850°C LSFPd+GDC/LSGM/LSFPd cell showed an OCV of 0.8 mV and a power output of 156 mW·cm⁻² in a mixture containing the 60% of CH₄ and the 40% of CO₂. The microstructural analysis after cell tests confirmed good tolerance to carbon deposits.

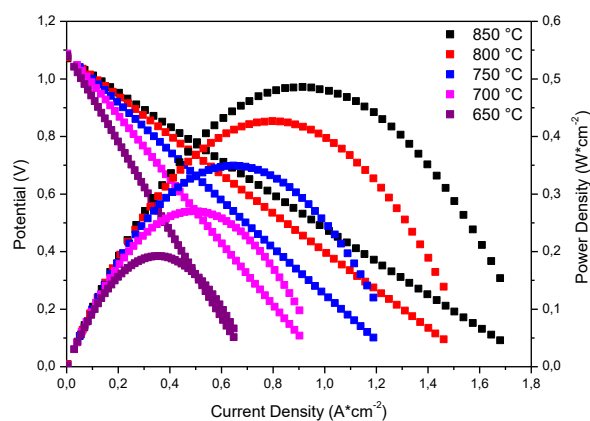


Fig.1 I-V and power density curves of LSFPd4005+GDC/LSGM/LSFPd4005 in the temperature range between 850-650 °C

References

[1] Zurlo, F.; Di Bartolomeo, E.; D'Epifanio, A.; Felice, V.; Natali Sora, I.; Tortora, L.; Licoccia, S.; *J. Power Sources*, **2014**, 271, 187.

[2] Zurlo, F.; Natali Sora, I.; Felice, V.; Luisetto, I.; D'Ottavi, C.; Licoccia, S.; Di Bartolomeo, E. *Acta Materialia*, **2016**, 112, 77.

Nitrogen doped mesoporous carbons, prepared from templating propylamine functionalized silica, as interesting material for supercapacitors

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Highly accessible surface area and heteroatom-doping are desirable properties for carbon electrode materials to be used in electrochemical supercapacitors [1]. In this paper, nitrogen doped carbon materials with wide pores (4-8 nm) were synthesized according to a hard template method by pyrolysis at 950 °C for 2 h of sucrose and employing propylamine functionalized silica as templating agent (NMC-1) [2]. The resulting materials were compared with mesoporous carbon obtained by pyrolysis of sucrose or 1,10-phenanthroline but employing a non-functionalized silica as templating agent while showing similar texture properties (pore size and surface area). X-ray photoemission spectroscopy, elemental analysis and EDX showed the presence of nitrogen groups in NMC-1, confirming the doping action of the functionalized silica. The interconnected pore structure was confirmed by scanning electron microscopy and transmission electron microscopy. The interest of this investigation is to understand how doping occurs when a functionalized silica is employed, and whether the nitrogen doping remains a surface property or it is extended also to the bulk of the material, influencing the morphological and the electrical properties of the resulting carbon. The comparison of electrochemical behaviors in term of capacitor performances were also evaluated considering the different synthetic approaches. The prepared materials were fully characterized by cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy in 0.5 M H₂SO₄ and 6 M KOH.

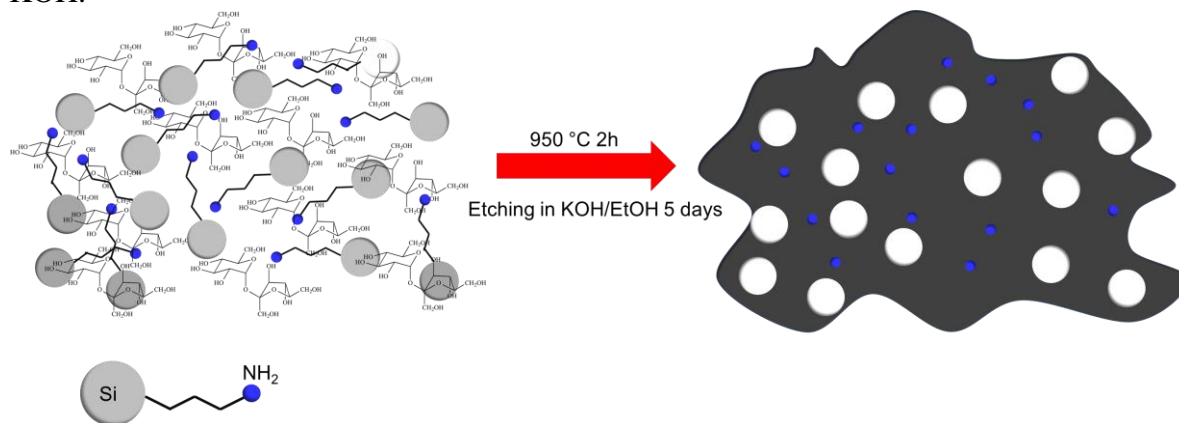


Figure 1. Hard template approach employing propylamine functionalized silica and sucrose.

References

- [1] C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang, J. Zhang, *Chem. Soc. Rev.*, 2014, **44**, 7484– 7539.
- [2] R. Brandiele, L. Picelli, R. Pilot, V. Causin, A. Martucci, G.A. Rizzi, A.A. Isse, C. Durante, A. Gennaro *Chemselect*, **2017**, 2, 24, 7082–7090.

Ligand-Free Suzuki-Miyaura Cross-Coupling Reactions With Aryl Boronic Acids And Potassium Aryl Trifluoroborates In Deep Eutectic Solvents

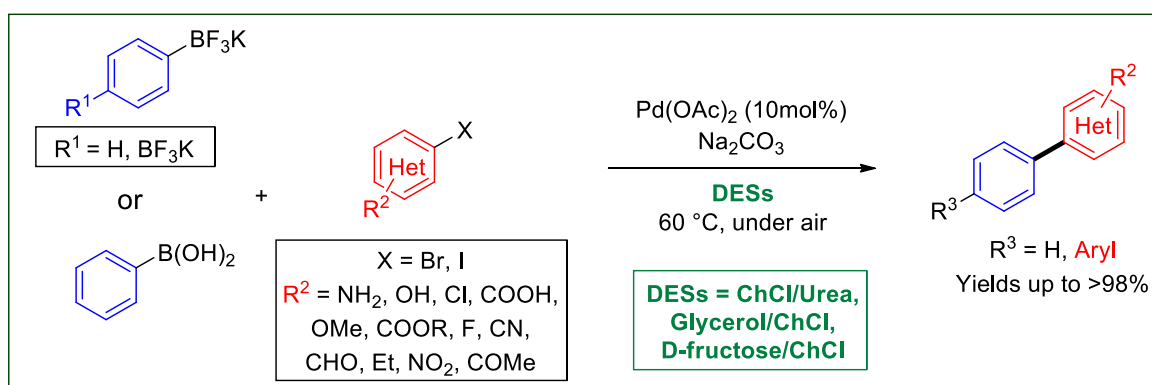
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The environmental impact associated with chemical synthesis has recently posed severe and compelling demands for sustainable chemistry. The development of cost-effective and environmentally benign reaction systems in place of volatile and harsh organic molecules represents an active field of research. In the last decade, Deep Eutectic Solvents (DESs) have emerged as new and promising alternative green reaction media. They are generally composed of two or three safe and inexpensive components which are able to engage in hydrogen-bond interactions with each other to form an eutectic mixture with a melting point much lower than that of either of the individual components [1].

Building on our recently investigations on the use of organometallics in unconventional reaction media (e.g., DESs, water) [2], in this communication the effectiveness of bio-based DESs in forging new bi- and tri(hetero)aryl adducts (yields up to > 98%) by exploiting a ligand-free Suzuki-Miyaura cross-coupling reaction with either arylboronic acids or aryl potassium trifluoroborates, under mild reaction conditions (T = 60 °C) and under air, will be discussed.



References:

- [1] 1. Francisco, M.; van den Bruinhorst, A.; Kroon, M. C. *Angew. Chem. Int. Ed.*, **2013**, *52*, 3074. 2. Smith, E. L.; Abbott, A.; P. Ryder, K. S. *Chem. Rev.*, **2014**, *114*, 11060. 3. García-Álvarez, J.; Hevia, E.; Capriati, V. *Eur. J. Org. Chem.* **2015**, *4*, 6779.
- [2] 1. Mallardo, V.; Rizzi, R.; Sassone, F. C.; Mansueto, R.; Perna, F. M.; Salomone, A.; Capriati, V. *Chem. Comm.*, **2014**, *50*, 8655. 2. Sassone, F. C.; Perna, F. M.; Salomone, A.; Florio, S.; Capriati, V. *Chem. Comm.*, **2015**, *51*, 9459. 3. Cicco, L.; Sblendorio, S.; Mansueto, R.; Perna, F. M.; Salomone, A.; Florio, S.; Capriati, V. *Chem. Sci.*, **2016**, *7*, 1192. 4. Dilauro, G.; Dell'Aera, M.; Vitale, P.; Capriati, V.; Perna, F. M. *Angew. Chem. Int. Ed.*, **2017**, *56*, 10200.

Investigation of the promoting effect of Mn on a Pt/C catalyst for the steam and aqueous phase reforming of glycerol

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Hydrogen is regarded as a clean energy vector suitable to replace the common fossil fuels. In order to achieve a production of fully green hydrogen, renewable feedstock, like biomass, should be used [1]. Due to the complex nature of biomass, however, model molecules are commonly employed in the reforming reactions for hydrogen production, and the addition of a promoter is often used to improve the performances of the catalysts [2]. In this work, a Pt-based catalyst was modified by the addition of a Mn promoter, and tested in the steam (SR) and aqueous reforming (APR) of glycerol, which was chosen as model molecule of polyols and as by-product of the bio-diesel industry [3]. The reactions were carried out at 225 °C with 10 wt.% glycerol aqueous solution. The presence of Mn had a major impact on the catalyst, mostly reflected in the SR reaction, with an increase in hydrogen productivity and total conversion of factors of 3 and 4, respectively. A weaker promoting effect was found in the APR reaction, with enhancements factors of 1.3 and 1.4. The addition of Mn introduced peculiar surface acidic sites in the form of few, strong Lewis acid sites, as detected by ammonia temperature programmed desorption experiments and attenuated total reflectance infrared analyses using pyridine as probe molecule. These sites, likely generated by exposed Mn^{δ+} sites in close proximity to Pt sites, contributed to the activation of the glycerol molecules. In fact, at comparable conversion levels, the hydrogen productivity of the bimetallic Pt-Mn/C catalyst outperformed the Pt/C catalyst. Under APR conditions, although the improvement in hydrogen productivity and conversion were lower than in SR, the selectivity toward hydrogen was increased. Moreover, most of the Mn leached out. These findings can be explained by the formation of an alloy between Mn and Pt, which prevented some of the Mn to be leached and promoted the CO spillover from the Pt sites [4]. The C-O bond cleavage activity of the catalyst was not significantly altered, whereas under SR conditions was favoured at the expenses of the C-C cleavage [5].

References

- [1] Marbán, D; Valdés-Solís, T. *Int. J. of Hydrogen Energ.* **2006**, 32, 1625.
- [2] Dal Santo, V.; Gallo, A.; Naldoni, A.; Guidotti, M.; Psaro, R. *Cat. Today* **2012**, 197, 190.
- [3] Quipse, C. A. G.; Coronado, C. J. R.; Carvalho Jr., J. A. *Renew. Sust. Energ. Rev.* **2013**, 27, 475.
- [4] Wei, Z.; Karim, A.; Li, Y.; Wang, Y. *ACS Catal.*, 2015, 5, 7312.
- [5] Bossola, F.; Pereira-Hernández, X.I.; Evangelisti, C.; Wang, Y.; Dal Santo, V. *J. Catal.* **2017**, 349, 75–83.

Highly redox stable composite anode for SOFCs

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An innovative composite material: $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Mn}_{0.2}\text{O}_{3-\delta}$ (LSFMn) (60wt.%) and $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{2-\delta}$ (SDC) (40wt.%) was investigated for anodic applications in IT-SOFCs.

Literature results report that $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSF) undergoes phase transition: from cubic perovskite (ABX_3) to Ruddlesen-Popper (RP) phase ($\text{A}_{n+1}\text{B}_n\text{X}_{3n+1}$) switching from oxidizing to reducing atmosphere and Fe nanoparticles exsolve providing more oxidation active sites [1]. Nevertheless, the main limitation of LSF is the phase instability at low P_{O_2} . To improve the redox stability the addition of Mn was evaluated being $\text{La}_{0.6}\text{Sr}_{1.4}\text{MnO}_4$ a highly stable RP structure with poor electrocatalytic properties [2]. SDC was added to provide a highly ionic conducting phase, enhancing the triple phase boundary (TPB) length and minimizing the TEC difference with the GDC based electrolyte.

Electrolyte supported cells were fabricated depositing the anodes by slurry spin coating technique and tested using three different fuels: hydrogen, ethanol and methane. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ (LSFC) (70wt.%) and GDC (30wt.%) was used as cathode. Fig. 1 shows: I-V curves along with power density curves (a) and Nyquist plots (b) of LSFMn-SDC/GDC/LSFCo-GDC cell at 800 °C using three different fuels. Morphological and chemical analyses of electrodes were performed by scanning electron microscope (SEM) and energy dispersive analysis (EDS).

To promote the direct oxidation of methane and enhance cell performance, a minimum amount (5 wt%) of Ni was homogeneously included into SDC. An improvement of performance and a long-lasting stability of the cell was revealed.

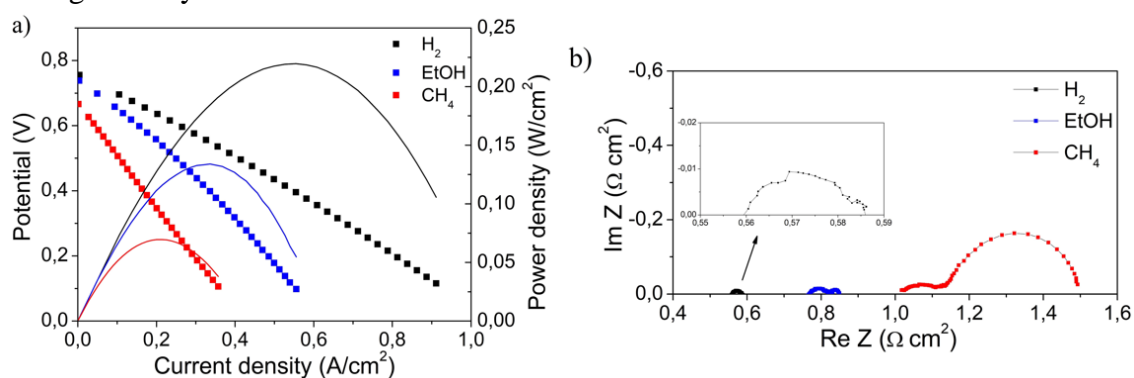


Figure 1 IV and power density curves (a) and Nyquist plot (b) of LSFMn-SDC/GDC/LSFCo-GDC cell in at 800°C fueled by different fuels.

References

- [1] R. Thalinger, M. Gocyla, M. Heggen, B. Klötzer, S. Penner, *J. Phys. Chem. C*, **2015**, 119, 22050–22056.
- [2] Y. S. Chung, T. Kim, T. H. Shin, H. Yoon, S. Park, N. M. Sammes, W. B. Kim and J. S. Chung, *J Mater Chem A*, **2017**, 5, 6437-6446

Theoretical Insights At The Dye-Electrode Interface In p-Type Dye-Sensitized Solar Cells

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Since the pioneering work by 'O Regan and Grätzel [1], dye-sensitized solar cells (DSSCs) have attracted great academic and industrial interest and still represent a promising technology in solar energy conversion, thanks to their low costs, eco-friendly materials and high efficiencies even under diffuse and indoor light conditions [2]. Despite their ability to reach higher power conversion efficiencies (PCE) than DSSCs, perovskite solar cells still suffer from important instability issue [3], so there is a revival of DSSCs as third generation photovoltaics [4]. In particular, the possibility to make tandem cells by facing n-type and p-type devices would push the PCE beyond the thermodynamic limit. However, p-type DSSCs have very low efficiencies and represent the limiting factor for the deployment of tandem DSSCs [5]. In order to improve their performances in solar, an in-depth understanding of structure-property relationships of p-type DSSC component materials and interfaces is essential for the rational design of new high-performing devices. In particular, since the DSSC operational principles are based on electronic processes that occur at the dye-electrode interface, ab initio simulations represent a key tool to address the undergoing photo-electrochemical processes, but so far, only few computational studies have been focused on the dye-electrode interface in p-type DSSCs [6].

In this work, we address the electronic properties of organic push-pull dyes together with those of the dye-electrode interface by considering the adsorption of the dye on the nickel oxide surface Ni (001). For the photo-active molecular components, we report DFT and TD-DFT results characterizing both ground- and excited-state properties. For the electrode bulk and surface slab we report spin-polarized DFT+U calculations within a periodic super-cell approach. From these results, we obtain a reliable description of dyes optical properties, especially concerning to the intramolecular charge transfer (ICT) upon excitation. Moreover, from the data regarding the dye-NiO (001) interface we provide evidence on how the ICT character of the dye can enhance the hole injection, from one side, and hinder the recombination process, on the other. This investigation on dye-NiO interface allows us to provide important insights and new information that can be implemented in design principles for innovative better performing p-type DSSCs.

References

- [1] 'O Regan, B.; Grätzel, M. *Nature*, **1991**, *353*, 737
- [2] Freitag, M.; Teuscher, J.; Saygili, Y.; Zhang, X.; Giordano, F.; Liska, P.; Hua, J.; Zakeeruddin, S. M.; Moser, J. E.; Grätzel, M.; Hagfeldt, A., *Nat. Photonics*, **2017**, *11*, 372
- [3] Asghar, M. I.; Zhang, J.; Wang, H.; Lund, P. D. *Renew. Sust. Energy Rev.*, **2017**, *77*, 131
- [4] Saygili, Y.; Söderberg, M.; Pellet, N.; Giordano, F.; Cao, Y.; Muñoz-García, A.B.; Zakeeruddin, S.M.; Vlachopoulos, N.; Pavone, M.; Boschloo, G.; Kavan, L.; Moser, J.E.; Grätzel, M.; Hagfeldt, A.; Freitag, M., *J. Am. Chem. Soc.*, **2016**, *138*, 15087
- [5] Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595
- [6] Muñoz-García, A. B.; Pavone, M. *Phys. Chem. Chem. Phys.* **2015**, *17*, 12238

UV-induced polymer electrolytes for all solid-state lithium batteries

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We all desire a long-lasting, non-explosive, flexible and small lithium-ion battery (LIB) for our portable electronic devices and (future) electric vehicles. The use of a solid polymer as electrolyte, instead of a flammable solvent, is currently the most promising solution for thinner and safer LIBs. Poly(ethylene oxide)-based polymers (PEO) are widely used, even commercially, thanks to their good ability to transport lithium ions at temperatures over 60 °C [1].

In our Lab, we focus on the structuring of classic –EO– based backbones by photo-polymerization, a fast, cost-effective and solvent-free technique. Solid polymer electrolytes (SPEs) based on different monomers/oligomers are prepared. By incorporating high amounts of plasticizers [2,3] and lithium salts, outstanding ionic conductivities are obtained ($\sigma > 10^{-4}$ S cm⁻¹ at 20 °C) along with wide electrochemical stability window (>5 V vs. Li⁺/Li) as well as good interfacial stability. Besides, SPEs have remarkable morphological characteristics in terms of homogeneity, flexibility and robustness (Fig. 1).

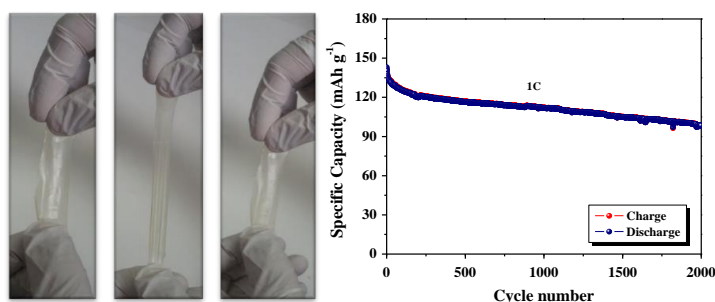


Fig. 1. Appearance of a cross-linked polymer electrolyte (left) and long-term cycling at ambient temperature in LiFePO₄/Li lab-scale polymer cell (right).

All-solid lithium-based polymer cells show very good cycling behavior in terms of rate capability and stability over a wide range of operating temperatures, which confirms the promising prospects of photocured polymer electrolytes for practical application at ambient/sub-ambient temperatures.

Acknowledgements

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References

- [1] M. Armand, and J.-M. Tarascon, *Nature* **2008**, *451*, 652–657.
- [2] L. Porcarelli, C. Gerbaldi, F. Bella, J. R. Nair, *Sci. Rep.* **2016**, *6*, 19892.
- [3] J. R. Nair, L. Porcarelli, F. Bella, C. Gerbaldi, *ACS Appl. Mater. Interfaces* **2015**, *7*, 12961-12971.

In situ gel formation of high quality kesterite thin films

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Conventional methods for fabricating chalcogenide-based solar cells involve vacuum processes, e.g. co-evaporation and sputtering, even if the most performing devices based on the kesterite compound $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ have been realized using a solution-based methodology. Moreover, non-vacuum processes present significant advantages as lower production costs, higher productivity and uniformity of the final stoichiometry composition. In this context, we present a new chemical procedure to obtain a superior quality $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{FeSnS}_4$ films composed by highly soluble and inexpensive precursors in a non-toxic and environmentally friendly solvent. Therefore, the films were prepared by a Sol-Gel method, starting from the metal salts in organic solvent (dimethylsulfoxide); thiourea was used as a source of sulphur. The influence of the composition of solutions containing metal ions was studied: solutions of metal salts containing non-coordinating anions and coordinates ones were compared to evaluate the role of anions and their coordination with metal ions in the formation of a pure and homogeneous phase. To obtain information about the complex mechanism of interaction between the metals and the various components of the solution Raman measurements and electronic paramagnetic resonance (EPR) were performed. The film deposition was carried out by in situ gel formation on fluorine doped tin oxide coated glass. The subsequent heat treatment guarantees the formation of the correct crystalline phase, without sulfurization but in Argon atmosphere [and at temperature suitable also for flexible and plastic substrates]. The films obtained were characterized by Raman spectroscopy, X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX), morphologically by electronic scanning electron microscopy (SEM). Raman and EPR measurements have shown that thiourea plays a primary role in coordinating metallic ions in solution, also highlighting the reductive power on copper; the coordinating effect of acetate ions, employed as precursors, plays a primary role in ensuring homogeneity in solution and consequently in the film. XRD confirms the absence of secondary phases. Therefore, the developed methodology has successfully identified an innovative way to achieve high quality kesterite thin films for photovoltaic applications; relate devices optimization is currently underway.

Study of CO₂ reduction over nanostructured catalysts: effect of ceria as co-catalyst

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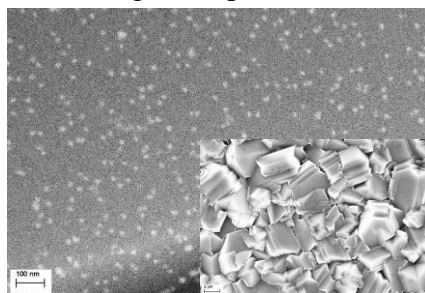
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Significant effort is being spent to limit the concentration of greenhouse gases in the atmosphere and to convert CO₂ to fuels, such as formic acid methane or ethane, by electrochemical reduction, using renewable power sources.

Ceria-based materials are well known as co-catalysts for low-temperature catalytic combustion of hydrocarbons, CO and CH₃OH [1]. We have studied the CO₂ reduction reaction (CO₂RR) on electrocatalysts consisting of ceria and different metal nanoparticles, mainly to assess the products selectivity. We have used different supporting materials: (i) boron doped diamond (BDD) [2], because of its chemical inertness, low background currents and wide potential region for water stability, which limits the HER, a process competitive with CO₂RR, and (ii) carbon nanotubes (CNTs), because of their great surface area and good conductivity.

We deposited Pt-NP using pulsed electrodeposition, obtaining even particles distribution on the supports surface and a narrow size distribution from 5 to 10 nm). Then we covered the Pt-NP films of ceria, produced by an electrochemically precipitation. By varying the cathode potential, obtained ceria deposits with

Preliminary results showed that CO₂RR on Ceria-at potential close to formate standard reduction gave formate yields close to those of the best reported in literature, even if at that low overpotential the current was low. A significant formate yield was obtained for Ceria-BDD system too. These results showed that ceria enhances the selectivity for formate in the CO₂RR.



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Pt-BDD, potential, catalysts

References

- [1] Li, D.; Yuan, Y.; Bi, H.; Yao, D.; Zhao, X.; Tian, W.; Wang, Y.; Zhang, H. *Inorg. Chem.* **2011**, *50*, 4825. [1] E. Verlato et Al., *Chem. Eng. J.*, **317** (2017) 551-560.
[2] T.A. Ivandini, Y. Einaga., *Chem. Comm.*, **53** (2017) 1338-1347.

Green organic dyes for DSSC application based on D-A- π -A design bearing Indigo structure

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Although dyes for DSSC capable of providing relatively high efficiencies have already been obtained and the path for improving the dye stability has already been undertaken, there are other issues which have been less investigated and need to be addressed. The new challenge in the field of building integrated photovoltaics is to complete the palette of colorations available for DSSCs. The development of libraries of dyes characterized not only by long-term stability and considerable high efficiency but also by a wide choice of colours, would make the exploitation of DSSCs much more appealing from an architectural point of view.

In this work, the preparation of near-IR absorbing green dyes is reported. The obtained compounds were spectroscopically and electrochemically characterized and the innovative dyes were employed to sensitize DSSC devices to evaluate their photo-electronic properties.

To design dyes possessing the desired coloration, we referred to D-A- π -A structures. With such design, a relatively small energy gap between the frontiers orbitals is predicted resulting in near-IR absorption. The dyes reported in this work (*Figure 1 right*) are characterized by Indigo internal acceptor. The peculiar blue coloration of Indigo structures is due to the cross-conjugated system of two electron-donating functions and two acceptors (the amines and the carbonyl functions respectively) known as H-Chromophore (*Figure 1 left*).

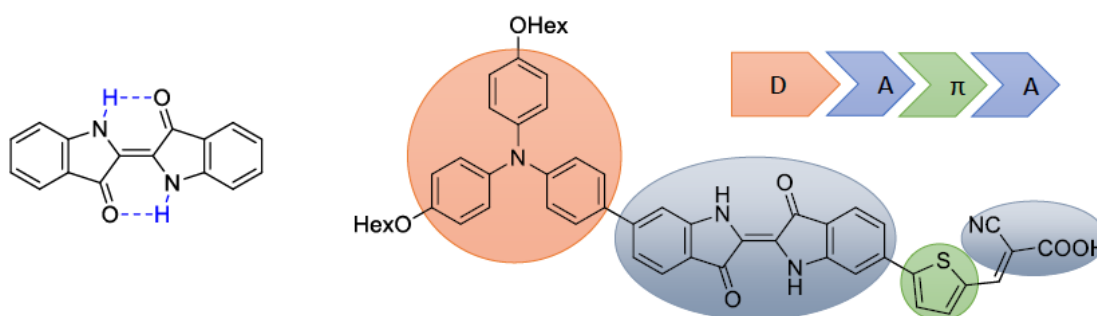


Figure 1: on the left-hand side the H-Chromophore is highlighted on the Indigo's structure. An example of a D-A- π -A dye bearing Indigo as the internal acceptor is reported on the right-hand side.

The solubility issue of Indigo was solved with Boc protection of the amine. The elongation to the designed dyes was performed by means of palladium catalyzed cross-coupling reactions. Once the Boc protection was released the dyes displayed a good solubility and an interesting intense green coloration. Such feature was found to be the result of the combination of two absorption band one attributed to the charge transfer between the D-A moieties and the other one relative to the released Indigo's H-Chromophore. The photo-electronic properties of the dyes, obtained from DSSC sensitized with the synthesized dyes, will be reported.

Green/Yellow-emitting Conjugated Heterocyclic Fluorophores for Luminescent Solar Concentrators

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The research project developed through the research group of A.Mordini has the purpose to design, synthesize and characterize new benzothiazole derivatives as organic dyes for LSC (Luminescent Solar Concentrator). LSC are polymeric materials doped with luminescent molecules, attached to solar cell. Their application consists to increase the photovoltaic efficiency of solar cells, to maximize it. The photovoltaic efficiency is the ratio between the energy of the solar radiation, absorbed and converted in electrical energy, and the incident total radiation on the surface of the panel. This efficiency would be maximized if the value would be near 100%. It depends on the range of wavelength in which the maximum absorption of the semiconductor material in the photovoltaic cell is observed. Actually the principal semiconductor material in solar cell is silicon. To increase this value of solar cell, new systems are designed which could emit energy in the spectral range of the maximum absorption of silicon.

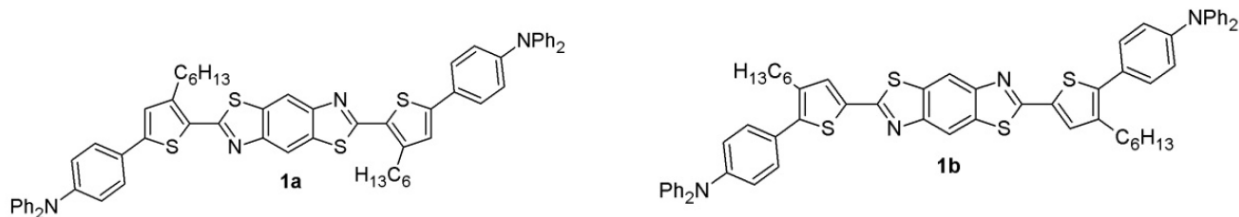
The research focalizes its attention to LSC, as luminescent material capable to meet to this purpose.

The features to be a photoconcentrator are:

- 1) A good, large Stokes shift, which is the difference of energy (expressed in eV or in nm) between their absorption peak and the emission one.
- 2) A high value of luminescent quantum yield (Φ), which corresponds to ratio between the number of emitted photons to absorbed ones.

The first one is correlated to the region of wavelength in which silicon absorbs; the second one quantifies the absorption of the semiconductor material in solar cell. To maximize the efficiency of the cell, the Stokes shift should be very large, to have a low overlap between the absorption and emission spectrum of the LSC, and the luminescent quantum yield, in which the maximum value is 1, should be very high, near 1, to quantify the energy that could be absorbed by the silicon.

In this project, we design and synthesis three compounds from benzothiazole derivatives: **CP03 (1b)** and **CP07 (1a)**, with a structure D- π -D, in which D is a donor molecule and π indicates a conjugated bridge.



For all molecules, spectrum of absorption and of emission are registered in different decreasing concentrations from 10^{-5} M, using Coumarine 6 as standard. While the Stokes shift of **CP03** was found to be higher than **CP07** one (142 nm vs 92 nm), the fluorescence quantum yield results the opposite (0.42 vs 0.68). For this reason, we choose **CP07** to test it in the production of a LSC device with PMMA. This compound reports a maximum of optical efficiency about 6.42% with a concentration of 1.4wt%. In conclusion, two benzo[1,2-d:4,5-d']bisthiazole derivatives are synthesized, designed and characterized with NMR, MS(ESI), HRMS. The measurements are registered with absorption spectroscopy and fluorimetry. **CP07** results a good and interesting fluorophore for application in LSC devices. In the next studies, we would design and characterize compounds, with a different structure as symmetrical system with acceptor groups. Instead, we would synthesize and test a benzo[1,2-d:4,5-d']bisthiazole derivatives with an asymmetrical structure D- π -A. In the end, the research group of A. Mordini would be concentrated to search of other different dyes to new applications for LSC.

Pyridine-Decorated Carbon Nanotubes As Heterogeneous Metal-Free Catalysts For Mild CO₂ Reduction To Methanol With Hydroboranes

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Exploiting carbon dioxide for the production of chemicals and fuels is one of the hottest topics of current sustainable catalysis. On this ground growing interest is devoted to the conversion of carbon dioxide to methanol regarded as a valuable alternative energy source. Unfortunately, CO₂ chemical inertness and thermodynamic stability make its reduction difficult. Many reducing agents in combination with transition metal-based heterogeneous catalysts have been employed successfully for the conversion of CO₂ into products of added value but, on a longer term vision, a sustainable, cheap and environmentally benign alternative is offered by metal-free catalysts. Recently, a variety of organocatalysts operating under *homogeneous* conditions has emerged for CO₂ reduction into valuable products.¹ In particular, N-heterocycles featured by N⁻² or C⁻³ basic sites have shown remarkable activity in CO₂ hydroboration to methanol. Following our experience on metal-free N-decorated carbon nanomaterials (N-CNMs) successfully employed in several key catalytic transformations,⁴ pyridine-decorated carbon nanomaterials have been tested for chemical reduction of CO₂ to methanol with different hydroboranes. Catalyst recycling tests have also been run showing complete recovery of its performance even after several runs. With turn-over numbers close to those claimed for other metal and metal-free homogeneous catalysts of the *state-of-the-art* and its effective re-use in catalysis, pyridine-decorated carbon nanomaterial candidates as a heterogeneous benchmark for this process.⁵ In addition, a hydroboration mechanism has been proposed on the joint basis of experimental data and *ab initio* simulations, suggesting the key role of the carbon nanotube carrier as an electronic reservoir for the dangling pyridine active arms.

References

- [1] M.-A. Courtemanche, M. Légaré, L. Maron, F.-G. Fontaine, *J. Am. Chem. Soc.* **2014**, *136*, 10708
- [2] C. D. N. Gomes, E. Blondiaux, P. Thuéry, T. Cantat, *Chem. Eur. J.* **2014**, *20*, 7098
- [3] S. C. Sau, S. K. Mandal, *et al.*, *Angew. Chem. Int. Ed.* **2016**, *55*, 15147
- [4] a) G. Tuci, G. Giambastiani, *et al.*, *ACS Catal.*, **2013**, *3*, 2108. b) G. Tuci, G. Giambastiani, *et al.*, *Chem. Mater.* **2014**, *26*, 3460. c) G. Tuci, G. Giambastiani, *et al.*, *Chem. Commun.* **2015**, *51*, 14393. d) G. Tuci, G. Giambastiani, *et al.*, *ACS Appl. Mater. Interfaces* **2016**, *8*, 30099. e) G. Tuci, G. Giambastiani, *et al.*, *Adv. Funct. Mater.*, **2017**, *27*, 1605672
- [5] G. Tuci, A. Rossin, L. Luconi, C. Pham-Huu, S. Cicchi, H. Ba, G. Giambastiani, *Catal. Sci. Technol.*, **2017**, *7*, 5833