



**2<sup>nd</sup> Congress of the Interdivisional Group  
on Chemistry for Renewable Energy of  
the Italian Chemical Society – SCI**

**ENERCHEM**

# ***BOOK OF ABSTRACTS***

PADOVA 12-14 FEBRUARY 2020



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DEGLI STUDI  
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# **Book of Abstracts**



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**Book editors:** Monica Fabrizio, Cristina Tubaro, Ketì Vezzù

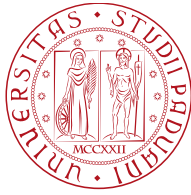
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# SCIENTIFIC PROGRAMME

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WEDNESDAY 12<sup>th</sup> FEBRUARY 2020

Polo Vallisneri

**12:00-13:45**      **REGISTRATION**

*AULA MAGNA*

**13:45-14:15**      **CONGRESS OPENING**

*Chairperson:*                      *A. Mordini*

**14:15-15:00**      PL01 - **A. Abate**: Novel materials for stable perovskite solar cells

**15:00-15:30**      KN01 - **P. Mustarelli**: Beyond lithium-ion batteries: the key role of the electrolyte

**15:30-16:00**      **COFFEE BREAK**

*Session “Electrochemistry and electrocatalysis I” (AULA MAGNA)*

*Chairperson:*                      *C. Durante*

**16:00-16:20**      OP01 - **V. Baglio**: Nickel-cobaltite Spinel Catalysts for Bifunctional Oxygen Electrodes

**16:20-16:40**      OP02 - **E. Musella**: Layered double hydroxides with a well-defined Me(II)/Me(III) ratio: new electrochemical Synthesis and Application for oxygen evolution reaction

**16:40-17:00**      OP03 - **E. Verlato**: CeO<sub>2</sub> nanostructured BDD electrodes for CO<sub>2</sub> reduction

**17:00-17:20**      OP04 - **R. Brandiele**: Synthesis and characterization of Pt<sub>3</sub>Y alloyed NPS by Laser Ablation in Liquid and activity towards Oxygen Reduction Reaction

- 17:20-17:40** OP05 - **A. Nale:** Electrocatalysts with a low Pt loading for the Oxygen reduction reaction comprising a hierarchical Graphene-based “core” and a Carbon Nitride “shell”
- 17:40-18:00** OP06 - **A. Khusnuriyalova:** Electrochemical generation of catalytically active Cobalt nanoparticles"
- 18:00-18:20** OP07 - **M. Magni:** Reuse of Zinc: from galvanized scrap to galvanized steel. The role of cathodic plasma electrolysis

*Session “Photoassisted Processes & Solar Fuels I” (AULA B)*

*Chairperson:* **N. Manini**

- 16:00-16:20** OP08 - **L. Zani:** Interplay Effects in Dye-Sensitized Photocatalytic Hydrogen Production
- 16:20-16:40** OP09 - **C. Barolo:** Low cost NIR dyes for transparent Dye-Sensitized Solar Cells
- 16:40-17:00** OP10 - **C. Boldrini:** Eco-friendly sugar-based natural deep eutectic solvent electrolyte solutions for dye-sensitized solar cells
- 17:00-17:20** OP11 - **A. Macchioni:** Half-sandwich Ir(III) complexes bearing pyridine-carboxamide ligands as efficient catalysts for formic acid dehydrogenation
- 17:20-17:40** OP12 - **C. Papucci:** High optical efficiency of quinoxaline based compounds in acrylate polymer matrix
- 17:40-18:00** OP13 - **N. Sangiorgi:** Improving the efficiencies of fiber-shaped dye-sensitized solar cells by using organic dyes
- 18:00-18:20** OP14 - **M. Cossi:** Designing Layered Hybrid Perovskites with tunable Band Gap and Enhanced Conductivity
- 19:45-21:15** **WELCOME PARTY** - Sala Rossini (Caffé Pedrocchi)

**THURSDAY 13<sup>TH</sup> FEBRUARY 2020**

**Polo Vallisneri**

*AULA MAGNA*

*Chairperson:*                    **A. Abbotto**

**8:30-9:15**                    PL02 - **V. Artero**: Artificial photosynthesis: from multi-electron multi proton catalysts to photoelectrochemical cells

**9:15-9:45**                    KN02 - **E. Giamello**: Photochemistry and photocatalysis of visible light active (VLA) systems

**9:45-10:15**                    **COFFEE BREAK**

*Session “ Electrochemistry and electrocatalysis II” (AULA MAGNA)*

*Chairperson:*                    **M. Musiani**

**10:15-10:35**                    OP15 - **M. Bevilacqua**: H<sub>2</sub>O<sub>2</sub> electrochemical production and sensing: a focus on updated research and applications

**10:35-10:55**                    OP16 - **G. Valenti**: Hierarchical nanostructures in multi-functional electrocatalysts for CO<sub>2</sub> conversion

**10:55-11:15**                    OP17 - **Y.M. Chu**: Impact of morphology on the Oxygen Evolution Reaction of 3D Hollow Cobalt-Molybdenum Nitride

**11:15-11:35**                    OP18 - **G. Daniel**: Effects of S-doped carbon support on Fe-N-C active site formation and activity versus oxygen reduction

**11:35-11:55**                    OP19 - **U. Petek**: N-Doped Carbon Electrocatalyst for Oxygen Reduction with Zn Ion-Imprinted Active Sites

**11:55-12:15**                    OP20 - **D. Sassone**: Metal-doped organic conductive polymers for CO<sub>2</sub> reduction

**12:15-12:35**                    OP21 - **I. Capone**: Electrochemomechanical Properties of Red Phosphorus with Lithium, Sodium and Potassium

**12:35-12:55** OP22 - **C. Simari**: Transport properties and electrochemical performance of nanocomposite PEMs based on non-fluorinated polymers

**12:55-13:15** OP23 - **Y. Birdja**: Towards a critical evaluation of electrocatalyst stability

*Session “Photoassisted Processes & Solar Fuels II” (AULA B)*

*Chairperson:* **M. Maggini**

**10:15-10:35** OP24 - **E. Selli**: Ultrafast Transient Absorption Spectroscopy vs. Photoelectrochemical Performance of WO<sub>3</sub>/BiVO<sub>4</sub> Photoanodes

**10:35-10:55** OP25 - **A. Sartorel**: Photocatalytic routes in the water oxidation reaction

**10:55-11:15** OP26 - **F. Zaccaria**: Strategies for the development of efficient Ir-based water oxidation catalysts

**11:15-11:35** OP27 - **M. Bellini**: Self-pressurized H<sub>2</sub> production from the electrochemical reforming of ethanol at 150 °C

**11:35-11:55** OP28 - **L. Calvillo**: Copper Phorphyrin – Carbon Nitride Hybrid for the Photoelectroreduction of CO<sub>2</sub> to CO and Formate

**11:55-12:15** OP29 - **M. Melchionna**: Use of reducible metal oxides in CO<sub>2</sub> conversion to formic acid

**12:15-12:35** OP30 - **C. Decavoli**: Design of organic based photosystems for photoelectrochemical production of solar fuels

**12:35-12:55** OP31 - **M. Paganini**: Cerium doped transition metal oxides as visible light photoactive interfaces

**12:55-13:15** OP32 - **L. Bergamini**: All-inorganic perovskite for photo-electrochemical CO<sub>2</sub> reduction

**13:15-14:15** **LUNCH**

*AULA MAGNA*

*Chairperson:* ***E. Selli***

**14:15-14:45** KN03 - **M. Fleischer:** The future energy system and its links via electrochemistry to the energy in molecules

**14:45-15:15** KN04 - **E. D. Glowacki:** Nanocrystalline organic semiconductor photocatalysts – a dominance of oxygen reduction reactions

**15:15-15:45** **COFFEE BREAK**

*Session “New Methods” (AULA MAGNA)*

*Chairperson:* ***M. Fabrizio***

**15:45-16:05** OP33 - **M. Ferrara:** Fast screening for N<sub>2</sub>RR catalytic activity with RRDE analysis

**16:05-16:25** OP34 - **S. Agnoli:** Exploring the Flatland of 2D materials by Electrochemical STM: visualization of active sites in *operando* conditions

**16:25-16:45** OP35 - **A. Marrani:** Unravelling the surface chemistry of electrodes for Li-O<sub>2</sub> cells by means of X-ray photoelectron spectroscopy

**16:45-17:05** OP36 - **A. Minguzzi:** Recent advances in (photo) electrochemical *operando* X-ray absorption spectroscopy. Analysis on time- and space-resolution

*Session “2D Materials” (AULA B)*

*Chairperson: E. Menna*

**15:45-16:05** OP37 - **F. Risplendi**: Co-doped reduced graphene oxide as novel electrocatalyst for the oxygen and carbon dioxide reduction reaction

**16:05-16:25** OP38 - **G. Tuci**: Surface Engineering of MoS<sub>2</sub> with Tailored Functional Groups: a Rational Design of Heterogeneous Catalysts for Renewable Energy Applications

**16:25-16:45** OP39 - **M. Serrapede**: Mixed 1T-2H MoS<sub>2</sub> nanoflakes electrodes for Li-ion supercapacitors and electrocatalyst for HER

**16:45-17:05** OP40 - **M. Re Fiorentin**: Tunable optical absorption and charge separation in black/blue phosphorene interfaces

**17:05-18:15** **POSTER SESSION**

*Spritz drink*

**19:15** *Bus Departure for Villa Sagredo*

**20:00-20:45** **CONCERT**

**20:45-23:00** **SOCIAL DINNER**

## FRIDAY 14<sup>th</sup> FEBRUARY 2020

Polo Vallisneri

AULA MAGNA

Chairperson: *A. Macchioni*

- 8:30-9:15** PL03 - **M. Koper**: Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide to fuels
- 9:15-9:45** KN05 - **S. Bennici**: Thermochemical heat storage: issues, solutions and applications
- 9:45-10:15** **COFFEE BREAK**

*Session "Energy Storage" (AULA MAGNA)*

Chairperson: *V. Di Noto*

- 10:15-10:35** OP41 - **A. Lamberti**: Laser-induced graphene as active materials for energy storage into flexible and stretchable micro-supercapacitors
- 10:35-10:55** OP42 - **S. Link**: Novel approaches for the application of electrodeposited silicon anodes for lithium ion batteries
- 10:55-11:15** OP43 - **F. Nobili**: Enhancing Performance and Stability of Nanocomposite Alloying Anodes for Li-ion Batteries
- 11:15-11:35** OP44 - **G. Pagot**: Iodoaluminate Ionic Liquid Electrolytes for Advanced Multivalent Twin Metals Secondary Batteries
- 11:35-11:55** OP45 - **S. Santangelo**: C-encapsulated T-Nb<sub>2</sub>O<sub>5</sub> nanocrystals for high performance Li- and Na-ion batteries
- 11:55-12:15** OP46 - **A. Tsurumaki**: Functionalization of ionic liquid-based electrolytes for advanced lithium ion batteries

**12:15-12:35** OP47 - **B. Wang**: Quantitative Lithiation of Graphite Anode in Li ion Batteries: an in situ Electron Paramagnetic Resonance Study

**12:35-12:55** OP48 - **B. Jin**: High Efficient Nanotubes Arrays Supercapacitors Electrodes Enabled by Engineered MoO<sub>x</sub>/MoP Heterostructure

*Session “Circular Economy and sustainability” (AULA B)*

*Chairperson:* **S. Agnoli**

**10:15-10:35** OP49 - **I. Rossetti**: Are renewable-based processes economically sustainable today? The case of H<sub>2</sub> production and distributed energy cogeneration from bioethanol

**10:35-10:55** OP50 - **A. Pezzella**: Eumelanin as Novel (Bio)Material for Energy Applications?

**10:55-11:15** OP51 - **D. Pérez**: Flowable semi-solid electrodes enable a concept for battery sustainability

**11:15-11:35** OP52 - **C. Mortalò**: H<sub>2</sub> purification through BaCe<sub>0.65</sub>Zr<sub>0.20</sub>Y<sub>0.15</sub>O<sub>3-δ</sub>-Ce<sub>0.85</sub>Gd<sub>0.15</sub>O<sub>2-δ</sub> ceramic dual-phase membrane

**11:35-11:55** OP53 - **S. Maranghi**: Life Cycle Assessment of Perovskite Solar Cells technology: environmental profile harmonization of the manufacturing process

**11:55-12:15** OP54 - **L. Limousy**: Conversion of grape marc residue into biochar for soil amendment in a circular economy approach

**12:15-12:35** OP55 - **M. Halimi**: Biomass derived carbon and water in salt electrolyte for green supercapacitor

**12:35-12:55** OP56 - **M. Buckingham**: Renewable electricity generated utilising benign redox-couples through thermoelectrochemistry

**13:00-14:15** **LUNCH**



*AULA MAGNA*

*Chairperson:* **M.A. Navarra**

**14:15-15:00** PL04 - **S. Passerini:** Li-ion batteries: from High Energy to Sustainability

**15:00-15:35** KN06 - **Enerchem Premium**

**M. Bonomo:** Design, synthesis and application of innovative organic and hybrid materials for emerging PV devices

**Poster Prizes**

**15:35-16:00** **COFFEE BREAK**

*Session “Photoassisted Processes & Solar Fuels III” (AULA MAGNA)*

*Chairperson:* **L. Armelao**

**16:00-16:20** OP57 - **M. Meneghetti:** Eco-friendly spray deposition of perovskite films on macro-scale textured surfaces

**16:20-16:40** OP58 - **J. Barichello:** The golden fig: a combined study of the plasmonic gold effect with a natural dye in DSSC

**16:40-17:00** OP59 - **L. Cinà:** Charge recombination dynamics in Perovskite based devices: a guide to correlate steady-state and dynamic measurements

**17:00-17:20** OP60 - **A. Polo:** Understanding the role of hydrogenation on the performance of ZnFe<sub>2</sub>O<sub>4</sub> photoanodes for water oxidation

**17:20-17:40** OP61 - **R. Mazzaro:** Hematite nanostructures: An old material for a new story. Simultaneous photoelectrochemical oxidation of benzylamine and hydrogen production through Ti doping

*Session "Catalysis" (AULA B)*

*Chairperson:* **I. Rossetti**

- 16:00-16:20** OP62 - **C. Evangelisti**: Indium promoted Cu/SiO<sub>2</sub> catalyst for improved hydrogen productivity in the steam reforming of methanol
- 16:20-16:40** OP63 - **F. Bossola**: All-in-one catalytic sites for the methanol steam reforming as electron-poor copper nanoparticles on amorphous zirconia-silica
- 16:40-17:00** OP64 - **F. Basile**: Water-gas shift membrane reactor and steam reforming membrane reactor for pure hydrogen production
- 17:00-17:20** OP65 - **D.G. Yakhavarov**: Electrochemical Methods as a Green Way for Synthesis of Organometallic and Organophosphorus Compounds
- 17:20-17:40** OP66 - **A. Fasolini**: H<sub>2</sub> production and levulinic acid hydrogenation to GVL using the co-produced formic acid as H<sub>2</sub> source

*AULA MAGNA*

**17:40** **CONGRESS CLOSING**

# POSTER SECTION

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- | <i>number</i> | <i>Title / Presenting Author</i>   |
|---------------|--|
| <b>P01</b>    | Fungal laccase with increased redox potential, redox mediator activity and stability: biochemical and electrochemical studies<br><b>O. Aleksejeva</b>  |
| <b>P02</b>    | Tuning the Electro- and Photochemical Properties of Gold Nanoclusters<br><b>S. Antonello</b>   |
| <b>P03</b>    | MD and QM/MM investigation of Bacteriorhodospin/TiO <sub>2</sub> system<br><b>M. Avelar</b>  |
| <b>P04</b>    | Nano-emulsions of Phase Change Materials for Heat Transfer/Storage and Solar Applications<br><b>S. Barison</b>   |
| <b>P05</b>    | Strelitzia-like titanium oxide nanopetals grown onto single wall carbon nanostructures for photocatalytic applications<br><b>S. Battiston</b>  |
| <b>P06</b>    | Charge-discharge performance of 1D- metal-organic frameworks based on nickel complexes<br><b>E. Beletskii</b>  |
| <b>P07</b>    | How to kill two birds with a stone:urban mining and CO <sub>2</sub> partners in the production of lanthanide molecular precursors for surface functionalization<br><b>L. Bellucci</b>                              |
| <b>P08</b>    | Binderless graphene / three-dimensional microfibrinous carbon paper composites electrode for electrochemical applications<br><b>T. Bordjiba</b>  |
| <b>P09</b>    | Optimization of silicon anode composition for all-solid-state lithium battery<br><b>M. Branchi</b>   |
| <b>P10</b>    | High-Energy Olivine Doped Cathode Materials for Secondary Lithium Batteries<br><b>F. Brombin</b>   |
| <b>P11</b>    | Innovative preparation and loading of Ni/CeO <sub>2</sub> nanocomposite for CO <sub>2</sub> methanation<br><b>E. Brusamarello</b>  |
| <b>P12</b>    | Engineered Ferroelectric PVDF Composites Containing BaTiO <sub>3</sub> @AO <sub>2</sub> (A = Ti, Si) Inclusions: Effective Dielectric Properties and 3D FEM Modelling of Field Distribution<br><b>V. Buscaglia</b> |
| <b>P13</b>    | Guidelines to design and understand Eu(III)-based luminescent thermometers and a model to predict their behavior<br><b>A. Carlotto</b>   |

<i>number</i>	<i>Title / Presenting Author</i>
<b>P14</b>	Visible light photoactive Rare Earth oxides - ZnO interfaces investigated by EPR spectroscopy (da controllare) <b>E. Cerrato</b>
<b>P15</b>	Photocatalytic production of regenerated fuels under unconventional conditions <b>F. Conte</b>
<b>P16</b>	Understanding interfacial charge transfer between the lead halide perovskite and novel phenothiazine-based organic hole transport materials <b>C. Coppola</b>
<b>P17</b>	Hybrid Inorganic-Organic Membranes based on [Nafion/(WO <sub>3</sub> ) <sub>x</sub> ] as Efficient Barrier Toward Vanadium Crossover in Redox Flow Batteries <b>G. Crivellaro</b>
<b>P18</b>	Thermal properties and cyclic stability of nickel metal-complex conductive polymer with Schiff base <b>S. Danilov</b>
<b>P19</b>	New organic sensitizers with improved spectral properties for application in greenhouse-integrated Dye-Sensitized Solar Cells <b>A. Dessi</b>
<b>P20</b>	Electrochemical recycling of platinum from spent catalytic structures <b>C. Diac</b>
<b>P21</b>	Polymer-based water-processable blend nanoparticles as a tool to improve OPV sustainability <b>M. Diterlizzi</b>
<b>P22</b>	Features of the crystal structure of LiFePO <sub>4</sub> cathodes of lithium-ion batteries under the influence of cyclic charge exchange on the surface layers <b>V. Ershov</b>
<b>P23</b>	The physicochemical properties of lithiated Nafion swollen with binary low-molecular-weight plasticizer <b>E. Evshchik</b>
<b>P24</b>	Aqueous solar cells: strategies for electrodes and electrolytes design <b>L. Fagiolari</b>
<b>P25</b>	High temperature phase change materials for reaction temperature control <b>A. Fasolini</b>
<b>P26</b>	Efficient electrochemical production of carbon monoxide and formic acid from CO <sub>2</sub> in a gas-liquid buffer layer flow cell employing carbon cloth electrodes functionalized with a fac-Mn(apbpy)(CO) <sub>3</sub> Br complex as gas diffusion cathodes <b>J. Filippi</b>
<b>P27</b>	PGM-free catalysts for anion exchange membrane fuel cells <b>W. Freitas</b>
<b>P28</b>	Diketopyrrolo-pyrrole based molecules for Organic Field Effect Transistors (OFETs) <b>S. Fusco</b>

<i>number</i>	<i>Title / Presenting Author</i>
<b>P29</b>	Dye-sensitized photoanodes for photoelectrochemical water oxidation with a novel class of quinoid photosensitizers <b>V. Gagliardi</b>
<b>P30</b>	Fructose dehydration to 5-hydroxymethylfurfural in the presence of Nb <sub>2</sub> O <sub>5</sub> based (photo)catalysts <b>E.I. Garcia-Lopez</b>
<b>P31</b>	Hydrothermal synthesis of copper vanadates NanoBelts on FTO and their photoelectrochemical properties <b>L. Girardi</b>
<b>P32</b>	Hybrid Silicon Nanocrystals for Color-Neutral and Transparent Luminescent Solar Concentrators <b>A. Gradone</b>
<b>P33</b>	Ionic liquids as suitable electrolytes for non-aqueous vanadium redox flow batteries: a first insight <b>L. Guglielmero</b>
<b>P34</b>	Optimization of Cu-based catalyst for the electrocatalytic reduction of CO <sub>2</sub> to fuels <b>H. Guzman</b>
<b>P35</b>	Development of Cu-based hybrid catalysts for the electrocatalytic CO <sub>2</sub> reduction to added value products <b>H. Guzman</b>
<b>P36</b>	Design, synthesis and application of new phenothiazine-based Hole Transporting Materials (HTMs) for Perovskite Solar Cells (PSCs) <b>R. Infantino</b>
<b>P37</b>	Optimization of the visible light driven HOPG/CdSe/PDAC composite architecture through photochemical studies and surface analysis <b>A. Kaur</b>
<b>P38</b>	Electrochemical dispersion route for preparation of Pt-, Pd-, Rh-based electrocatalytic materials <b>A. Kuriganova</b>
<b>P39</b>	Lattice Boltzmann Simulation of Water Transport in Compressed Gas Diffusion Layer of PEMFC <b>S.H. Lee</b>
<b>P40</b>	Electrochemical Impedance Spectroscopy of V <sup>2+</sup> /V <sup>3+</sup> and VO <sup>2+</sup> /VO <sub>2</sub> <sup>+</sup> Redox Couples on Carbon-based Electrodes for Vanadium Redox Flow Battery <b>P. Leuaa</b>
<b>P41</b>	Phosphorescent iridium(III) complexes with Nature-inspired β-diketone ligands as emitting layer for OLED devices <b>V. Lino</b>
<b>P42</b>	HER catalysts based on MX <sub>2</sub> /Graphene hybrid microspheres (M = Mo, W; X = S, Se) <b>M. Lunardon</b>

<i>number</i>	<i>Title / Presenting Author</i>
<b>P43</b>	A Sub-stoichiometric Calcium Titanate Perovskite $\text{CaTiO}_{3-\delta}$ as Electrode Additive in Direct Methanol Fuel Cells (DMFCs) <b>L. Mazzapioda</b>
<b>P44</b>	Micro- and Meso-porosity effect on the formation and activity of Fe-N-C active sites for Oxygen Reduction Reaction <b>M. Mazzuccato</b>
<b>P45</b>	Luminescent Solar Concentrators from waterborne polymer dispersions <b>C. Michieletti</b>
<b>P46</b>	Microwave-assisted sintering of $\text{Na-}\beta''\text{-Al}_2\text{O}_3$ electrolyte in 2450 and 5800 MHz single mode cavities <b>C. Mortalò</b>
<b>P47</b>	Mechanistic studies on the enhanced carbocatalytic oxidation of alcohols by Graphene Acid <b>D. Mosconi</b>
<b>P48</b>	Investigation of Hydrogen Interaction (Electrosorption and Evolution) with Si in Hydrogen Fluoride Electrolyte <b>M. Neergat</b>
<b>P49</b>	Development of an efficient CFD model for monolithic steam methane reactor using effectiveness factor correlations <b>Y.S. Oh</b>
<b>P50</b>	Functionalized graphene oxide for efficient capacitive deionization <b>A. Pedico</b>
<b>P51</b>	Water-soluble polythiophenes: a further step towards green energy production <b>D. Quadretti</b>
<b>P52</b>	$\text{BiO}^+$ -based nanocomposite for environmental remediation: modulation of the functional properties by composition tailoring <b>M. Rancan</b>
<b>P53</b>	Electrochemical Formation of Nitrogen-Doped Reduced Graphene Oxide/Hematite Heterojunction: Characterization and properties <b>G. Riveros</b>
<b>P54</b>	p- and e- type Silver functionalized Dense Titanium Dioxide Semiconductor Layer for Efficient Perovskite photovoltaics (SOLAR) <b>N. Ross</b>
<b>P55</b>	Chemical Modification of Carbon Nano Structures for Solar Energy Conversion <b>C. Santin</b>
<b>P56</b>	$\text{SnO}_2$ -based composite anodes for high energy density LIBs <b>L. Sbrascini</b>
<b>P57</b>	The Effect of RTILs-PVDF/HFP as Gel Electrolytes for High Voltage Supercapacitor <b>P. Shabeeba</b>

<i>number</i>	<i>Title / Presenting Author</i>
<b>P58</b>	Comparative Life Cycle Assessment of Solar Home Systems <b>A. Sinicropi</b>
<b>P59</b>	Zeta potential of activated carbon on the performance of electric double layer capacitors in salt aqueous electrolyte <b>P. Skowron</b>
<b>P60</b>	Energy harvesting and storage system for indoor application <b>R. Speranza</b>
<b>P61</b>	Monitoring of Solid Oxide Fuel Cell Performance Through Deconvolution of Electrochemical Impedance Spectra <b>A. Staffolani</b>
<b>P62</b>	Electrochemical performance of doped hematite/reduced graphene oxide nanocomposites as anode materials for Na-ion batteries <b>C. Triolo</b>
<b>P63</b>	Kesterite solar-cells by drop-casting of inorganic sol-gel inks <b>G. Tseberlidis</b>
<b>P64</b>	Graphene Aerogel as a support for highly dispersed metals for catalytic reactions <b>U. Unal</b>
<b>P65</b>	Dye-sensitized photoanodes for water oxidation based on a novel KuQuinone dye <b>G.A. Volpato</b>
<b>P66</b>	Flexible and high temperature laser induced graphene supercapacitor based on ionic liquid, a de-rated voltage analysis <b>P. Zaccagnini</b>
<b>P67</b>	Highly selective on site electrochemical H <sub>2</sub> O <sub>2</sub> production from functionalized graphene derivatives <b>Y. Zhang</b>
<b>P68</b>	Synthesis of NIR Rylene Dyes and Cobalt-based Redox Couple for Colourless Dye-sensitized Solar Cells <b>M. Giordano</b>

# **ABSTRACTS**

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**Plenary Lectures (PL01-PL04)**

**Keynote Lectures (KN01-KN06)**

**Oral Presentations (OP01-OP66)**

**Posters (P01-P67)**



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## Novel Materials for Stable Perovskite Solar Cells

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Halide perovskites are quickly overrunning research activities in new materials for cost-effective and high-efficiency photovoltaic technologies. Since the first demonstration from Kojima and co-workers in 2009, several perovskite-based solar cells have been reported and certified with rapidly improving power conversion efficiency. Recent reports demonstrate that perovskites can compete with the most efficient photovoltaic materials, while they still allow processing from solution as a potential advantage to deliver a cost-effective solar technology. Compare to the impressive progress in power conversion efficiency, stability studies are rather weak and often controversial. An intrinsic complication comes from the fact that the stability of perovskite solar cells is strongly affected by any small difference in the device architecture, preparation procedure, materials composition and testing procedure. In the present talk, we will present new materials and preparation procedures which improve the device lifetime without giving up on high power conversion efficiency.

## Artificial Photosynthesis From Multi-Electron Multi Proton Catalysts to Photoelectrochemical Cells

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Mimicking photosynthesis and producing solar fuels is an appealing way to store the huge amount of renewable energy from the sun in a durable and sustainable way. Hydrogen production through water splitting has been set as a primary target for artificial photosynthesis,<sup>1</sup> which requires the development of efficient and stable catalytic systems, only based on earth abundant elements, for the reduction of protons from water to molecular hydrogen or the reduction and valorization of carbon dioxide. We will report on our contribution to the development of various series of catalysts for H<sub>2</sub> evolution and CO<sub>2</sub> reduction,<sup>2-4</sup> including the establishment of methodologies towards the rational benchmarking of their catalytic activity. Besides, we will also describe our effort towards the combination of such catalysts with various photoactive motifs for the preparation of photoelectrode materials<sup>5-7</sup> that can be implemented into photoelectrochemical (PEC) cells for water splitting.<sup>8</sup>

### References

1. Queyriaux, N.; Kaeffer, N.; Morozan, A.; Chavarot-Kerlidou, M.; Artero, V. *J. Photochem. Photobiol. C* **2015**, *25*, 90-105.
2. Coutard, N.; Kaeffer, N.; Artero, V. *Chem. Commun.* **2016**, *52*, 13728-13748.
3. Queyriaux, N.; Sun, D.; Fize, J.; Pecaut, J.; Field, M. J.; Chavarot-Kerlidou, M.; Artero, V. *J. Am. Chem. Soc.* **2019**.
4. Roy, S.; Sharma, B.; Pecaut, J.; Simon, P.; Fontecave, M.; Tran, P. D.; Derat, E.; Artero, V. *J. Am. Chem. Soc.* **2017**, *139*, 3685-3696.
5. Kaeffer, N.; Massin, J.; Lebrun, C.; Renault, O.; Chavarot-Kerlidou, M.; Artero, V. *J. Am. Chem. Soc.* **2016**, *138*, 12308-12311.
6. Chandrasekaran, S.; Kaeffer, N.; cagnon, I.; Aldakov, D.; Fize, J.; Nonglaton, G.; Baleras, F.; Mailley, P.; Artero, V. *Chem. Sci.* **2019**.
7. Kaeffer, N.; Windle, C. D.; Brisse, R.; Gablin, C.; Léonard, D.; Jusselme, B.; Chavarot-Kerlidou, M.; Artero, V. *Chem. Sci.* **2018**, *9*, 6721-6738.
8. Windle, C.; Kumagai, H.; Higashi, M.; Brisse, R.; Bold, S.; Jusselme, B.; Chavarot-Kerlidou, M.; Maeda, K.; Abe, R.; Ishitani, O.; Artero, V. *J. Am. Chem. Soc.* **2019**, *141*, 9593-9602.

## Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide to fuels

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The electrocatalytic reduction of carbon dioxide is a promising approach for storing (excess) renewable electricity as chemical energy in fuels. Here, I will discuss recent advances and challenges in the understanding of electrochemical CO<sub>2</sub> reduction. I will summarize existing models for the initial activation of CO<sub>2</sub> on the electrocatalyst and their importance for understanding selectivity. Carbon–carbon bond formation is also a key mechanistic step in CO<sub>2</sub> electroreduction to high-density and high-value fuels. I will show that both the initial CO<sub>2</sub> activation and C–C bond formation are influenced by an intricate interplay between surface structure (both on the nano- and on the mesoscale), electrolyte effects (pH, buffer strength, ion effects) and mass transport conditions. This complex interplay is currently still far from being completely understood.

### Reference

1. Y.Y.Birdja, E.Perez-Gallent, M.C.Figueiredo, A.J.Göttle, F.Calle-Vallejo, M.T.M.Koper, *Nature Energy*, **2019**, 4, 732-745

## Li-ion batteries: from High Energy to Sustainability

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The announcement of major car manufacturers worldwide to electrify their product line within less than a decade has triggered the large increase of battery cell manufacturing. This will gain even greater momentum once other OEMs will be following this ambition. Lithium-ion batteries are the energy storage technology of choice to enable the deployment of electric vehicles avoiding the use of fossil fuels. However, a transition to a more sustainable production of these cells is required. Consequently, efforts are being invested to develop non-toxic and abundant active materials, for instance, by reducing (if not excluding) the use of cobalt and nickel. Implementing aqueous processing for lithium-ion positive electrodes is another key step towards the achievement of environmentally benign battery production.

Targeting these urgent necessities, we have developed along the years a simple approach leading to the aqueous processing of the high-voltage  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO). This active material is, in fact, considered the most promising for the realization of cobalt-free next generation lithium-ion batteries. First we demonstrated the feasible use of bio-derived polymers, e.g., sodium carboxymethylcellulose, guar gum and chitosan<sup>1-3</sup>, as electrode binders in combination with phosphoric acid, for active material particles and current collector protection, and citric acid, for polymers cross-linking. Then, to achieve positive electrode tapes readily available for large-scale, high-energy lithium-ion batteries, the use of carbon-coated current collector was introduced, which provides functional groups to crosslink the electrode coating layer to the underlying aluminum foil. The resulting electrodes demonstrate significant improvements concerning the electrode to current collector adhesion and their capacity retention. Through the further optimization of the initial formation cycles, these electrodes offer an electrochemical performance exceeding that of LNMO-based reference electrodes, comprising state-of-the-art poly(vinylidene difluoride) (PVdF) as binder.

### References

1. Bresser et al., *Energy Environ. Sci.* **2018**, *11*, 3096-3127.
2. Loeffler et al., *J. Power Sources* **2014**, *248*, 915.
3. Kuenzel et al., *ChemSusChem* **2018**, *11*, 562–573

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## Beyond lithium-ion batteries: the key role of the electrolyte

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More powerful, durable, safer, greener and cheaper batteries are needed to fulfil the compelling requirements of automotive and grid applications. Addressing most of these requirements passes through the development of new-generation electrolytes able to overcome the issues of the state-of-the-art liquid ones, which are based on highly volatile and flammable organic solvents.<sup>1</sup> At the same time, the quest for new electrolytes is strictly related to the attempt of replacing the graphite anode with lithium metal, so opening the way to full exploitation of new post-lithium chemistries, e.g. Li-air and Li-sulphur.

Here, I critically review some original concepts which were recently proposed as routes for the development of liquid and quasi-solid electrolytes with improved performances in terms of safety, chemical and electrochemical stability, and capability to sustain high current densities. Attention will be devoted to the problem of lithium dendrites formation, and to the electrolyte families able to eliminate/control their development. Finally, some examples of our present research are reported.<sup>2,3</sup>

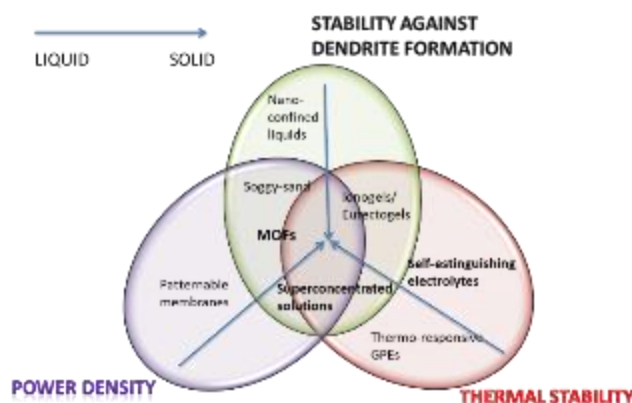


Figure 1. New liquid and quasi-solid electrolytes at a glance

### References

1. Quartarone, E., Mustarelli, P. *Journal of Electrochem Soc.*, in press.
2. Dall'Asta, V et al. *Electrochim. Acta*, **2017**, 247, 63-70.
3. Pianta, N. et al. *Electrochim. Acta*, **2019**, 320, 134539.

## Photochemistry and photocatalysis of visible light active (VLA) systems

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Photocatalytic processes aim to exploit the energy of light to promote chemical transformations. This scope can be pursued in various applications including pollution remediation (total oxidation of pollutants), solar fuels production (e.g. water photosplitting and CO<sub>2</sub> reduction) and, more generally, in all types of chemical processes in which the required thermal energy can be replaced by electromagnetic energy.

A standard process in heterogeneous photocatalysis is based on the photoexcitation of a suitable semiconducting system inducing the promotion of electrons in the conduction band (CB) and the formation of electron-holes (holes, h<sup>+</sup>) in the valence band (VB). The reductive and oxidative capacities of these photo-excited charge carriers respectively depend, as a first approximation, on the chemical potentials of CB and VB.

The materials that have so far dominated the field of environmental photocatalysis are based on titanium dioxide or other semiconductors with high band gap, whose excitation requires the use of UV radiation. In recent years an intense effort has been devoted to the search for innovative photocatalytic systems capable of working under visible light illumination. The approaches followed to this aim include the use of: i) small band gap semiconductors such as C<sub>3</sub>N<sub>4</sub> systems ii) semiconducting systems with band gap modified by the insertion of impurities; iii) coupled semiconductors reproducing either the so-called Z scheme of natural photosynthesis or the recently proposed S-scheme.

In the present contribution we will report about our experimental action that is devoted to individuate and prepare heterogeneous systems possibly active in visible light (VLA systems). Our work is based on a knowledge-based approach aiming to unravel the main phenomena occurring in a solid and at its interface. Electron Paramagnetic Resonance spectroscopy plays represents a fundamental, though not unique, tool in our activity. Different topics will be discussed including: i) photochemistry under visible light of wide gap pristine oxides; ii) photochemistry of oxides doped with rare earth ions; iii) systems based on oxide-oxide heterojunctions.

In the case of water photosplitting reactions the role of co-catalyst for hydrogen evolution (HER) based on earth abundant elements will be also mentioned.

### References

1. C. Gionco, M.C. Paganini, E. Giamello, R. Burgess, C. Di Valentin, G. Pacchioni, *J. Phys. Chem. Lett.*, **2014**, 5, 447-451
2. E. Cerrato, C. Gionco, M.C. Paganini, E. Giamello, E. Albanese, G. Pacchioni, *ACS Appl. Energy Mat.*, **2018**, 1, 4247-4260.

## The future energy system and its links via electrochemistry to the energy in molecules

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With the increasing addition of renewable energy generation, often in a decentral setting, our energy system is undergoing a fundamental change. Photovoltaic and wind become the cheapest source for energy in most places of the world, but due their volatility stabilization of the system and storage are the topics to solve. System modeling and the addition of battery capacities are required. This trend is increasing, nowadays the PV additions (100GW peak per year) exceed the sum of the additions in coal, gas and nuclear generation capacity. Electricity will be firstly used directly, i.e. in transport, heating ... wherever possible, with some short-term storage in batteries. Then we will see an increasing use of electricity to generate raw materials for the chemical industry and energy containing molecules to the petrochemical industry. Water electrolysis to  $H_2$  is a natural entry point of electricity in the chemical sector. Optimization of these processes need to be combined with capture of  $CO_2$  (at first from concentrated sources) and thermochemical reactions. Ammonia is also discussed as potential energy vector at places of cheap costs of renewables. The direct electrochemical  $CO_2$  conversions comes up and will compete as technological route, perhaps in the combination with Bioprocesses. One of the ultimate yardsticks is the overall efficiency/costs in the conversion chain. Strong research and industrial R&D are needed to optimize the needed technologies, that needs to be accompanied by precise engineering, measurement technology following strict rules to get comparability and the quest for finding the appropriate technology for a defined application.

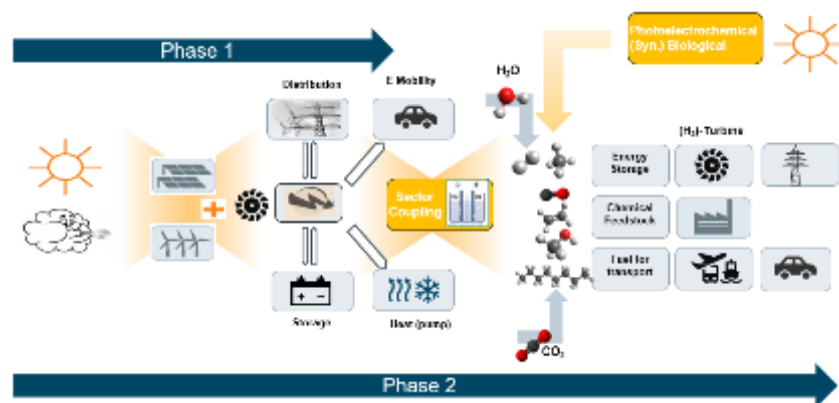


Figure 1: Two phase evolvement of the future energy system

## Nanocrystalline organic semiconductor photocatalysts – a dominance of oxygen reduction reactions

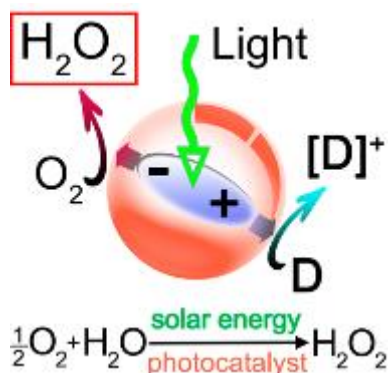
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Semiconductor-based catalysts can convert solar energy into chemical fuels such as hydrogen, hydrogen peroxide, or hydrocarbons produced via carbon dioxide reduction. Long overlooked due to stability concerns, some organic semiconductors have recently emerged as promising electrocatalysts and photocatalysts for operation in aqueous environments. Our attention has focused on nanocrystalline pigment-type organic semiconductors, which stand out due to stability and performance. We have found a high selectivity of organic semiconductors for oxygen reduction reactions, by both one-electron and two-electron pathways. The products of these reactions are superoxide or hydrogen peroxide. We find this occurs on numerous organic semiconductors and conducting polymers in a pH range from 1 to 12. We have found that while photogenerated electrons reduce oxygen, the fate of the holes represents a complex picture. When the nanocrystalline semiconductor is used as a photocathode and efficient p-type transport is available, photogenerated holes can easily be extracted to an external circuit. The possibilities of solar energy conversion into the high-energy molecule H<sub>2</sub>O<sub>2</sub> enabling carbon-neutral energy storage in liquid form will be covered. Organic semiconductors have potential to become a powerful class of intrinsic catalysts, tunable by molecular design.



### References

- Gryszel, M.; et al. Water-Soluble Organic Dyes as Molecular Photocatalysts for H<sub>2</sub>O<sub>2</sub> Evolution. *Adv. Sustain. Syst.* **2019**, *3*, 1900027.
- Warczak, M.; et al. Organic Semiconductor Perylenetetracarboxylic Diimide (PTCDI) Electrodes for Electrocatalytic Reduction of Oxygen to Hydrogen Peroxide. *Chem. Commun.* **2018**, *54*, 1960–1963.
- Gryszel, M.; et al. General Observation of Photocatalytic Oxygen Reduction to Hydrogen Peroxide by Organic Semiconductor Thin Films and Colloidal Crystals. *ACS Appl. Mater. Interfaces* **2018**, *10*, 13253–13257.
- Gryszel, M.; et al. Organic Heterojunction Photocathodes for Optimized Photoelectrochemical Hydrogen Peroxide Production. *J. Mater. Chem. A* **2018**, *6*, 24709–24716.
- Jakešová, M.; et al. Hydrogen-Bonded Organic Semiconductors as Stable Photoelectrocatalysts for Efficient Hydrogen Peroxide Photosynthesis. *Adv. Funct. Mater.* **2016**, *26*, 5248–5254.



## Thermochemical heat storage: issues, solutions and applications

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In the last years many countries have adopted energy transition laws with the aim of promoting the green growth. At different extent, the new legislation has strengthened countries' political strategy for a more effective contribution to energy independence, and for the reduction of greenhouse gas emissions that have a direct impact on global warming. In order to achieve the nationally announced targets (for France settled at 38% of its end-user heat consumption by 2030, as example), it is necessary, among other energy efficiency measures, to increase the effective use of renewable, excess and waste energy resources. The main barrier to their integration within buildings, industrial facilities, and heat distribution networks, is that their production timing, power, temperature level, or even location do not match the requirements of grids that are driven on-demand. Thermochemical heat storage is one of the more promising solutions to optimize the energy supply management. The main advantage of using this type of system is the possibility of storing heat during the period of maximum availability, and to release it when needed. The introduction of the present work presents a short case studies review based on a selection of representative applications in thermochemical heat storage by sorption of water on solid materials. The process is based on two phases, the dehydration of the material (charging step) and its hydration (releasing of the heat). The most investigated field is solar heat storage in individual buildings. Up today, the most advanced response to the heat and mass transfers issue in heat storage systems is connected to the storage materials. A particular focus will be put on the development of new storage materials, their characterization, implementation in prototypes and durability to hydration/dehydration cycling in real conditions (i.e. interaction with atmospheric pollutants)<sup>1</sup>. Examples, selected with respect to their potential of application to low-grade heat storage at industrial scale, and then reviewed with regard to their technology readiness level will be also briefly presented.

Last, an attempt to rationalize the conception of the most adapted process for a specific application; a decision-making approach will be presented, based on the identified trends, limits and challenges of the various technical solutions.

### References

1. S. Bennici et al., *RSER*. **2020**, *117*, Article 109473.

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## Design, synthesis and application of innovative organic and hybrid materials for emerging PV devices

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In the last decades, the demand for sustainable clean energy sources, particularly solar energy, has constantly raised. Even though the energy supplied by the sun radiation over one year is roughly 10,000 times higher than the world current rate of energy consumption, the state-of-art of the photovoltaic devices is not yet satisfactory because of low efficiency, high cost and/or limited scale. Therefore, the development of innovative materials should be tackled in order to improve the competitiveness of photovoltaic devices and make their commercialization feasible. Bearing this in mind, the scientific effort where focused on both Dye-Sensitized<sup>1</sup> and Perovskite Solar Cells<sup>2</sup>.

DSCs have attracted their attention since their discover in 1991, reaching efficiency close to 15%.<sup>3</sup> Yet, their commercialization is still in the early stage. This is partially ascribable to the relatively high cost and low sustainability of Platinum counter-electrode and to electrolyte-due stability issue. Some interesting approaches have been tested in order to replace the latter with a photoactive electrode. This will theoretically allow to construct tandem devices overcoming the S-Q limit. Yet, the obtainment of an effective device is limited by the poor photoconversion efficiency of the photocathode.<sup>4</sup> Throughout this contribution some innovative material will be proposed to obtain a perfect current matching between the photoanode and the photocathode. Additionally, new materials have been designed for application in water-based DSC. Water as electrolyte is a valuable approach to enhance both the sustainability and the long-term stability of DSC.

On the other hand, PSCs have shown outstanding photovoltaic performances since their first discovery, reaching PCE higher than 25%.<sup>5</sup> Yet, they heavily suffer for long-term instability being both the photoactive layer and the HTM degraded by moisture, oxygen, infiltration as well as prolonged exposition to UV radiation.<sup>2</sup> Straightforwardly, encapsulation of the device is strictly required for a forthcoming commercialization of this technology. Here, we present, for the first time, the use of thermosetting resins based on polyurethane as encapsulant for (flexible) device. This class of compound possesses some ideal features as high transmittance (above 90%), chemical inertness and good UV and thermal stability. Additionally, they are cost-effective, they do not require any time- or cost-demanding polymerization procedure, they are flexible and their mechanical and optical properties could be easily tuned by changing the precursors. Notably, the incapsulated cells retaining 94% of the initial PCE after more than 2500 hours.

### References

1. Bonomo et al. *J. Nanomater.* **2017**, 1–31.
2. Wang, R. et al. *Adv. Funct. Mater.* **2019**, 29, Article 1808843.
3. Mathew, S. et al. *Nat. Chem.* **2014**, 6, 242–247.
4. Bonomo, M. et al. *J. Electrochem. Soc.* **2017**, 164, 4, H137-H147.
5. <https://www.nrel.gov/pv/cell-efficiency.html>.

## Nickel-cobaltite Spinel Catalysts for Bifunctional Oxygen Electrodes

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Rechargeable alkaline metal–air batteries can be considered one of the most promising next energy storage systems owing to their extremely high energy densities. However, this kind of batteries requires very efficient and durable bifunctional electrocatalysts to accelerate the kinetics of oxygen reduction reaction (ORR), taking place during the discharge, and oxygen evolution reaction (OER), occurring during charging of the battery. In the last few years, research was focused on the development of highly efficient oxygen reduction/evolution catalysts based on transition metals, such as Co, Fe, Mn, La, etc, in the form of mixed oxides (perovskites, spinels, etc.), or advanced carbon materials. Co-based catalysts have been thoroughly investigated for the ORR/OER, and, usually,  $\text{Co}_3\text{O}_4$  is the most employed formulation. However, the electrical conductivity of bare  $\text{Co}_3\text{O}_4$  is not appropriate for the application in most of these devices. Ni and other transition metals can partially replace Co atoms in the  $\text{Co}_3\text{O}_4$  spinel structure, improving its electronic conductivity while promoting oxygen evolution. Another approach is to combine these oxides with carbon nanostructures, in particular graphitic ones, in order to maintain suitable stability under cycling operation. Recently, carbon nanofibers (CNF) synthesized by electrospinning, modified with a combination of cobalt oxide and metallic cobalt ( $\text{CoO-Co/CNF}$ )<sup>1</sup> or loaded with nickel and cobalt (both in the metallic and oxide forms)<sup>2</sup>, were investigated in our laboratories as bifunctional air electrodes showing good reversibility and stability. In the present work, the latter catalyst (NiCo-loaded CNFs<sup>2</sup>), after the electrospinning preparation, has been oxidized with the aim of synthesizing the pure spinel structure ( $\text{NiCo}_2\text{O}_4$ ) supported on CNFs. The electrochemical behavior of the spinel has been compared with the previously developed catalyst to elucidate the catalytic activity of the two systems for ORR and OER in relation with their physico-chemical properties.

### References

1. Alegre, C.; Busacca, C.; Di Blasi, O.; Antonucci, V.; Arico, A. S.; Di Blasi, A.; Baglio, V. *Journal of Power Sources* **2017**, *364*, 101-109.
2. Alegre, C.; Modica, E.; Di Blasi, A.; Di Blasi, O.; Busacca, C.; Ferraro, M.; Antonucci, V.; Arico, A. S.; Baglio, V. *Renewable Energy* **2018**, *125*, 250-259.

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## layered double hydroxides with a well-defined Me(II)/Me(III) ratio: New electrochemical synthesis and application for oxygen evolution reaction

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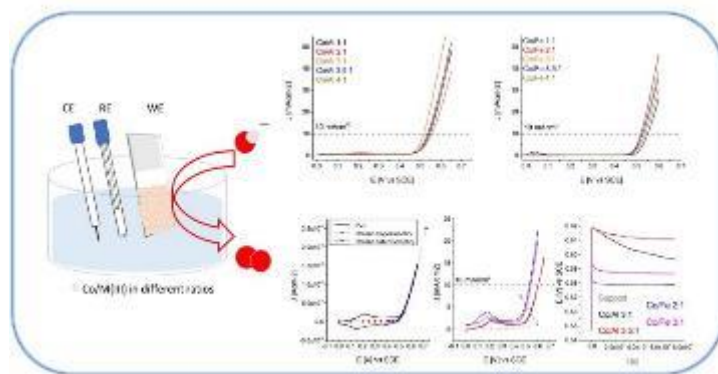
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The increasing global energy demand on energy grows and renewable resources are the only possible tools to rely for the future. The most relevant problem is that they tend to be intermittent and unpredictable. [1] As a result, there will be an increasing need to store this energy. Water electrolysis has drawn a lot of attention to store energy from renewables. In this scenario, layered double hydroxides (LDHs) containing redox active metals are promising materials. Cobalt and nickel based LDHs catalysts with iron and aluminum were synthesized by a newly developed electrochemical potentiodynamic method, able to finely control the composition of the obtained film for the first time [2,3]. The catalysts were characterized by a comprehensive combination of techniques and were evaluated for the oxygen evolution reaction (OER) on classically used rotating disk electrodes and on several stationary system. Carbonaceous and Ni based foils were employed to study the influence of the substrate on the catalytical performances and to evaluate long term stability. In all cases studied, an optimized catalyst was highlighted and the performances resulted highly competitive.



### References

1. I. Roger, M. A. Shipman and M.D. Symes, Nat. Rev. Chem. 1 (2017) art. no. 003.
2. E. Musella, I. Gualandi, E. Scavetta, A. Rivalta, E. Venuti, M. Christian, V. Morandi, A. Mullaliu, M. Giorgetti, and D. Tonelli, J. Mater. Chem. A, 7 (2019) 11241–11249.
3. E. Musella, I. Gualandi, E. Scavetta, M. Gazzano, A. Rivalta, E. Venuti, M. Christian, V. Morandi, and D. Tonelli accepted manuscript in Chem. – Eur. J. (DOI: 10.1002/chem.201903288)

## CeO<sub>2</sub> nanostructured BDD electrodes for CO<sub>2</sub> reduction

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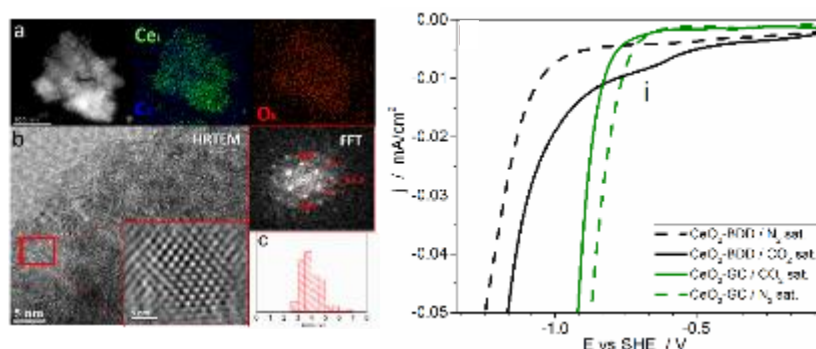
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To limit the concentration of greenhouse gases in the atmosphere, besides reducing the CO<sub>2</sub> emissions by increasing the efficiency of fossil fuels usage, various strategies for capturing and/or converting CO<sub>2</sub> are being studied and implemented [1]. A major contribution of electrochemical reduction reaction of CO<sub>2</sub> (CO<sub>2</sub>RR) processes to the limitation of CO<sub>2</sub> concentration in the atmosphere can be hardly envisaged in the short term. However, in a circular economy perspective, the electrochemical conversion of a waste like CO<sub>2</sub> to useful compounds to be used in industrial processes, as well as fuels, is an important goal that may be pursued by developing electrochemical reduction processes powered by green or renewable energy sources. Electrocatalysis play a fundamental role to reach, by means of lower energy routes, higher current densities close to equilibrium potential. Primarily, significant improvements of CO<sub>2</sub>RR are needed to overcome the slow reaction kinetics and the low efficiency of the process due to the parasitic hydrogen evolution reaction. We studied the electrochemical deposition of ceria and its application to electrocatalytic reduction of CO<sub>2</sub> in water. Ceria was deposited onto boron doped polycrystalline diamond (BDD) cathodes, through electrochemically induced precipitation from nitrate-based solutions. Morphology, thickness and composition of ceria films were controlled by acting on deposition parameters. Thin Ce(OH)<sub>3</sub>-free ceria films allowed CO<sub>2</sub> electrochemical reduction at overpotential below 50 mV, yielding formic acid with faradaic efficiency higher than 40% and stable performance during many hours. We propose a mechanism where ceria supplied CO<sub>2</sub> to the BDD electrode surface where H termination reduced CO<sub>2</sub> to formate ions, at low overpotentials [2].



### References

1. Mikkelsen, M. *Energy Environ. Sci.* **2010**, 3, 43–81.
2. Verlato, E. *J. Mat. Chem. A.* **2019**, 7, 17896–17905.

## Synthesis and characterization of Pt<sub>3</sub>Y alloyed NPS by Laser Ablation in Liquid and activity towards Oxygen Reduction Reaction

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According to Norskov d-band theory, Pt<sub>3</sub>Y alloy were predicted to be one of the most active catalyst for oxygen reduction reaction, positioned almost at the vertex of the Volcano plot reporting the Pt alloy catalytic behaviour [1]. The synthesis of Pt<sub>3</sub>Y alloy film or nanoparticle is for the most part restricted to UHV conditions, due to the high reactivity of yttrium which preferentially form Y<sub>2</sub>O<sub>3</sub>, so that a scalable synthesis of Pt<sub>3</sub>Y alloy is still missing. In this contribution the synthesis of Pt<sub>3</sub>Y alloyed NPs by laser ablation in liquid (LAL) is presented (Figure 1a). The alloyed component was evaluated by XPS analysis, which confirmed a Pt-Y ratio of *c.a.* 3 (Figure 1b). The XRD analysis show a mixture of Pt<sub>3</sub>Y and Pt<sub>2</sub>Y and the absence of Pt pure phases. The NPs were dimensionally separated obtaining PtY\_6h, PtY\_12 h and PtY\_R (residual). Pt<sub>3</sub>Y NPs are enveloped in a carbon shell that shield the metallic core and does not allow the material to be activated during the ORR tests. After the removal of the carbon shell by an electrochemical preconditioning, the electrochemical performances increase sensitively. PtY\_R shows a MA of 429 A g<sup>-1</sup>, a SA of 0.546 mA cm<sup>-2</sup> and a E<sub>1/2</sub> of 0.897 V vs. RHE (Figure 1c). It was found that the catalytic activity increases with the increasing of the particle dimension, that is reasonable to attest to a higher component to alloy in the particle [2,3].

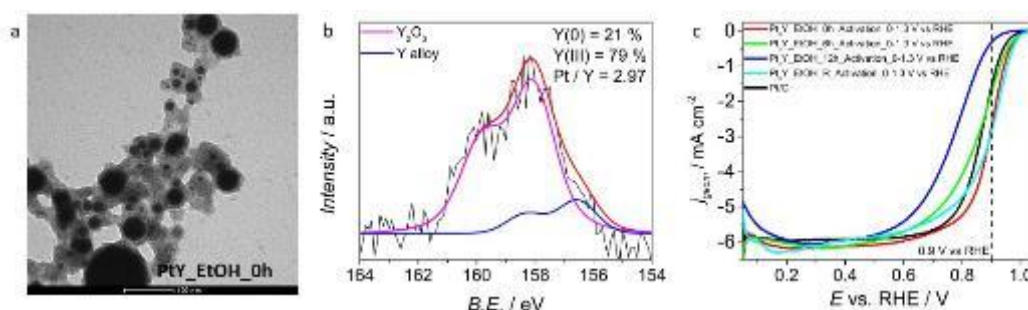


Figure 1: (a) TEM image of PtY\_EtOH. (b) XPS spectra of Y 3d for PtY\_EtOH (c) LSV with RDE recorded at 20 mV/s and  $\omega = 1600$  rpm in O<sub>2</sub> saturated HClO<sub>4</sub> 0.1 M electrolyte.

### References

1. J.-Y. Lin, C. Xi, Z. Li, Y. Feng, D.-Y. Wu, C.-K. Dong, P. Yao, H. Liu, X.-W. Du, Lattice-strained palladium nanoparticles as active catalysts for the oxygen reduction reaction, *Chem. Commun.* 55 (2019).
2. M. Censabella, V. Torrì, S. Boninelli, C. Bongiorno, M.G. Grimaldi, F. Ruffino, Laser ablation synthesis of mono- and bimetallic Pt and Pd nanoparticles and fabrication of Pt-Pd/Graphene nanocomposites, *Appl. Surf. Sci.* 475 (2019) 494–503.
3. R. Brandiele, V. Amendola, A. Guadagnini, G.A. Rizzi, D. Badocco, P. Pastore, A.A. Isse, C. Durante, A. Gennaro, Facile synthesis of Pd<sub>3</sub>Y alloy nanoparticles for electrocatalysis of the oxygen reduction reaction, *Electrochim. Acta.* 320 (2019) 134563.

## Electrocatalysts with a low Pt Loading for the Oxygen Reduction Reaction Comprising a Hierarchical Graphene-Based “Core” and a Carbon Nitride “Shell”

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State-of-the-art proton-exchange membrane fuel cells (PEMFCs) have begun to exit the research laboratories and are currently implemented in early products, that include both stationary systems (e.g., power plants for “zero-emission” houses) and light-duty vehicles. Despite these successes, PEMFCs still suffer from several drawbacks associated with the performance and the durability of the functional materials involved in their operation. One key issue affecting PEMFCs is the electrocatalyst (EC) that promotes the oxygen reduction reaction (ORR) at the PEMFC cathode. Indeed, to bestow the PEMFC a sufficient performance and durability, state-of-the-art ECs for the ORR must include a very high loading of platinum. Thus, to mitigate the risk to incur in supply bottlenecks, new and improved ECs with a low loading of Pt (“low-Pt”) must be developed.

An innovative approach to obtain advanced low-Pt ECs for the ORR exhibiting a performance and durability beyond the state of the art is to devise systems where the active sites are located on the surface of PtM<sub>x</sub> nanostructures. With respect to Pt NPs, in PtNi<sub>x</sub> nanostructures the utilization of Pt atoms is raised by up to *ca.* one order of magnitude. This allows for the maximization of the Pt availability for electrocatalytic purposes. Hence, the PEMFCs mounting the low-Pt ECs comprising the PtNi<sub>x</sub> nanostructures can achieve a specific power that is significantly larger than the 8 kW/g<sub>Pt</sub> target set by the Department of Energy of the U.S. Government for 2020.

In the proposed ECs the PtM<sub>x</sub> nanostructures are located on the surface of a support based on a “core” consisting of a combination of highly defected graphene nanoplatelets and carbon black NPs. Such hierarchical graphene-based (H-GR) “core” is covered by a carbon nitride (CN) “shell”, that is able to stabilize effectively the PtM<sub>x</sub> nanostructures by means of “coordination nests” consisting of C- and N- ligands. The present contribution compares the proposed low-Pt ECs with the state of the art and overviews the complex correlations that are established between: (i) the physicochemical properties of the low-Pt ECs (e.g., chemical composition, morphology and structure of both the active sites and of the support); (ii) the electrochemical performance, the reaction mechanism and the durability in the ORR; and finally (iii) the characteristic curve of the PEMFC mounting the proposed ECs as tested in operating conditions. The information thus obtained is then used to identify the most promising research approaches to pursue in order to devise next-generation low-Pt ORR ECs able to comply with the stringent requirements of tomorrow’s PEMFCs.

## Electrochemical Generation of Catalytically Active Cobalt Nanoparticles

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Currently the development of modern chemistry occurs in several priority areas, one of which is the development and use technology based on transition metal nanoparticles. These derivatives are widely applied in modern industry. First of all, this is due to specific properties of the nanoparticles and materials modified by them. At the present time possibilities of using metal nanoparticles in creating the new catalysts for a variety of industrial processes grow extensively. These systems obey the principles of self-assembly, which are used in a variety of technologies, applied to fabrication of microelectronic elements, sensoric and optical devices, synthesis of new materials with desired properties.<sup>1</sup> So, cobalt nanosized particles occupy a special place among known metal nanoparticles as they allow to create the catalysts, magnetic recording devices, composites, carriers of biological products.<sup>2</sup>

The majority of the methods of preparation of nanoparticles, especially physical methods, are energy consuming and require specialized equipment. Constraints of the methods related to difficulties in controlling the chemical composition of product, contamination of metal nanoparticles by initial reactants. Therefore, the development of research in this area requires new methods of preparation of nanoparticles. One perspective direction is an electrochemical method for the selectively generation of metal nanoparticles of a certain size with desired properties and catalytic activity.<sup>3</sup>

We have found that electrochemical reduction of coordinatively unsaturated cobalt dibromide 2,2'-bipyridine (bpy) complexes results in the formation of cobalt nanoparticles (CoNPs).<sup>4</sup> The process of the electrochemical generation of CoNPs was monitored by *in situ* EPR-spectroelectrochemistry where the signals of ferromagnetic resonance (FMR) have been observed for these species. According to small-angle X-ray scattering (SAXS) analysis the average diameter and average length of the formed cylindrical CoNP is varied from 9 to 10 nm and 30-32 nm, respectively, and correlates to the *g*-value and the broadness of the FMR signal observed by *in situ* EPR-spectroelectrochemistry during the electrochemical process.

### References

1. Zhang, J., Xu, J., Wang, Y., Xue, H., Pang, H. *Chem. Rec.* **2018**, *18*, 91-104.
2. Imadadulla, M., Nemaikal, M., Sannegowda, L. K. *New J. Chem.* **2018**, *42*, 11364-11372.
3. Schiavi, P. G., Altimari, P., Pagnanelli, F., Moscardini, E., Toro, L. *Chem. Eng. Trans.* **2015**, *43*, 673-678.
4. Khusnuriyalova, A. F., Petr, A., Gubaidullin, A. T., Sukhov, A. V., Morozov, V. I., Büchner, B., Kataev, V., Sinyashin, O. G., Yakhvarov, D. G. *Electrochim. Acta.* **2018**, *260*, 324-329.

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## Reuse of Zinc: from Galvanized Scrap to Galvanized Steel. The Role of Cathodic Plasma Electrolysis

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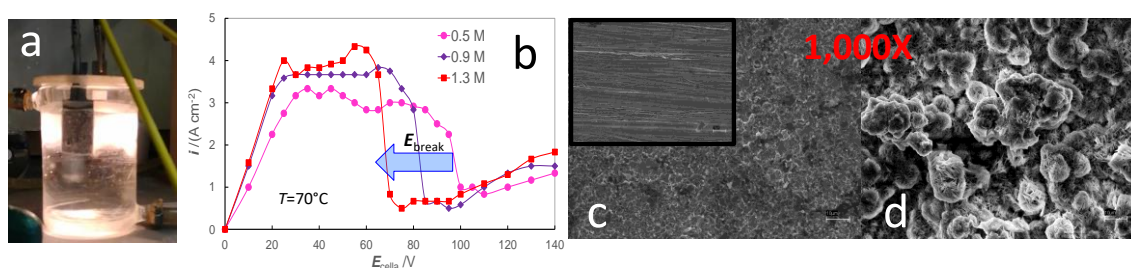
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Zinc is the fourth widely consumed metal in the world, with a global refined output of 15 Mt in 2018. Half of the production of zinc is employed to produce galvanized steel, largely used in automotive and construction sector. The strong link between zinc and steel continues also at their end-life cycles, in steel mills employing Electric Arc Furnace (EAF) for the production of secondary, recycled steel from mostly galvanized scraps. The Zn-rich powdery wastes from EAFs (4-8 Mt per year) represent a valuable source for secondary zinc production.

Driven by the Circular Economy paradigms, the aim of our current project is to demonstrate the feasibility of a hydrometallurgical process, based on the employment of Cathodic Plasma Electrolysis (CPE), for the *direct* production of galvanized steel using Zn-containing leachate solutions of the EAF dust. CPE is an electrochemical technique that, while working at atmospheric pressure and temperature, generates at the electrode surface a thin sheath of plasma (Fig. a) that assures peculiar properties to the treated sample. Its application ranges from surface cleaning/pre-treatment to coating deposition.<sup>1</sup>

In the present talk, some preliminary data will be discussed concerning the employment of CPE for both surface *pre-treatment* and *galvanizing* of steel in the form of plate and wire rod. Through a systematic study, electrolyte nature and concentration, temperature and applied potential have been identified as the most affecting operative parameters for both formation and stability of plasma (Fig. b). In optimized conditions, CPE carried out for 10-20 seconds in various blank solutions invariably showed a neat modification of the surface morphology (Fig. 1c) resulting into a neat increase of the surface roughness (from profilometry scans) of the sample, potentially useful to improve the adhesion of the zinc layer to be deposited. Concerning zinc electrodeposition, by exploiting design of experiment approach, many operative parameters were scanned to optimize uniformity, continuity and thickness of the resulting zinc layer (Fig. 1d).



### References

1. E. I. Meletis, X. Nie, F. L. Wang, J. C. Jiang, *Surf. Coat. Tech.* **2002**, *150*, 246-256.

*Acknowledgements:* This work was funded by SIAT-Società Italiana Acciai Trafilati S.p.A and Engitec TECHNOLOGIES S.p.A.

## Interplay Effects in Dye-Sensitized Photocatalytic Hydrogen Production

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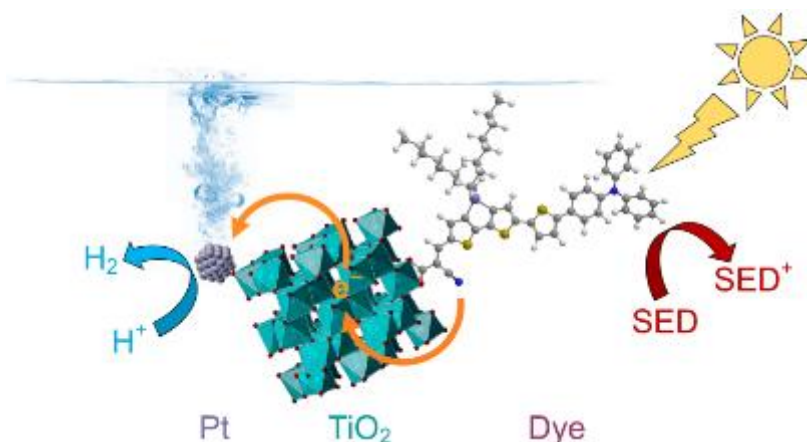
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Solar fuels production by so-called artificial photosynthetic processes is currently one of the most compelling research topics in the field of renewable energies. Visible light-driven hydrogen generation, in particular, is considered very promising since H<sub>2</sub> is an energy dense and carbon neutral fuel, which can be either burned or employed in fuel cells, producing only water as a by-product.<sup>1</sup> In recent years, our research group investigated several heterogeneous systems for the organic dye-sensitized photocatalytic production of hydrogen (Figure 1).<sup>2-4</sup> In this communication, we will discuss how modifying the hydrophobic/hydrophilic properties of the sensitizer can affect catalytic performances, and highlight how the interplay of all the components involved (photosensitizer, type of semiconductor, sacrificial electron donor) is crucial to maximize the light-to-fuel efficiency of the reaction.



### References

1. Zhang, X.; Peng T.; Song, S. *J. Mater. Chem. A* **2016**, *4*, 2365-2402.
2. Dessì, A. *et al. ChemSusChem* **2018**, *11*, 793-805.
3. Bettucci, O. *et al. ACS Appl. Energy Mater.* **2019**, *2*, 5600-5612.
4. Bartolini, M. *et al.*, manuscript in preparation.

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## Low cost NIR dyes for transparent Dye-Sensitized Solar Cells

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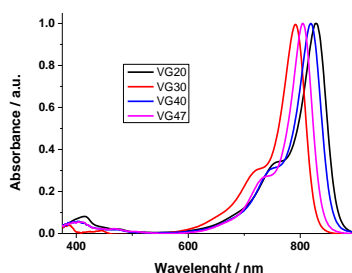
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Standard highly efficient colorful Dye-Sensitized Solar Cells (DSSCs) are mainly limited to 400-700 nm cut-off: this peculiarity restricts the short-circuit photocurrent density to ca. 20 mA/cm<sup>2</sup>.<sup>1</sup> NIR conversion, with the aim to widen solar harvesting and tune the color of final devices, is indubitably interesting, especially in BIPV applications. Our research group already developed several squaraine dyes, absorbing in the NIR region, for this purpose.<sup>2,3,4</sup> In this contribution we will present the design strategies, the main synthetic routes and the characterization on of a novel series of polymethine-based dyes. Their structure-properties relationships will be reviewed, highlighting the role of the molecule design on device properties: performances and transparencies among others. Specifically, their features have been tuned by using appropriate functional groups, diluted dye solutions and specific sensitizing conditions to promote the formation of a free self-assembled monolayer with the final goal to prepare transparent DSSCs with appealing performances and colors.



Absorption properties of different NIR dyes in solution

### References

1. Nazeeruddin, Md. K. Baranoff, E. Gratzel M. *Solar Energy* **2011**, 85,1172–1178.
2. Magistris, C.; Martiniani, S.; Barbero, N.; Park, J.; C. Benzi, C.; Anderson, A.; Law, C.; Barolo, C.; O'Regan, B. *Renewable Energy* **2013**, 60, 672–678.
3. Galliano, S.; Novelli, V.; Barbero, N.; Smarra, A.; Viscardi, G.; Borrelli, R.; Sauvage, F.; Barolo, C. *Energies* **2016**, 9, 486.
4. Bonomo, M.; Barbero, N.; Naponiello, G.; Giordano, M.; Danilo, D.; Barolo, C. *Frontiers in Chemistry* **2019**, 7, 99

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## Eco-friendly sugar-based natural deep eutectic solvent electrolyte solutions for dye-sensitized solar cells

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Among photovoltaics technologies, dye-sensitized solar cells (DSSCs) offer high conversion efficiencies (15% record efficiency) and low-cost manufacturing. Unfortunately, one of the major drawbacks in these record cells is the presence of toxic volatile organic solvents in the electrolyte.

To overcome this problem, we have successfully tested eco-friendly reaction media such as Deep Eutectic Solvents (DESs), made of two or three safe and cheap components which are able to express hydrogen-bond interactions with each other to form an eutectic mixture with a melting point much lower than either of the individual components. DESs are simple and low-cost to synthesize, do not need purification and they are usually biodegradable. One of the most common DES components, choline chloride (ChCl), is largely used as an additive for chicken feed. We have already tested both hydrophilic and hydrophobic DESs in DSSCs with promising results.<sup>1,2</sup>

In this study, we describe our results on DSSCs containing innovative sugar-based natural DES electrolytes, that is ChCl with different monosaccharides, sensitized with multi-branched phenothiazine dyes developed in our group, and characterized by the presence of an alkyl or a sugar substituent.<sup>3</sup> In particular, we have systematically varied the dye (alkyl functionality vs. sugar moiety), the co-adsorbent (chenodeoxycholic acid vs. glucuronic acid) and the monosaccharide present in the DES. In the end, these results are consistent with a cooperative interaction among all the components containing a sugar functionality leading to a performance boost.



### References

1. Boldrini, C. L.; Manfredi, N.; Perna, F. M.; Trifiletti, V.; Capriati, V.; Abboto, A. *Energy Technol.* **2017**, *5* (2), 345-353.
2. Boldrini, C. L.; Manfredi, N.; Perna, F. M.; Capriati, V.; Abboto, A. *Chem. Eur. J.* **2018**, *24* (67), 17656-17659.
3. Manfredi, N.; Cecconi, B.; Calabrese, V.; Minotti, A.; Peri, F.; Ruffo, R.; Monai, M.; Romero-Ocana, I.; Montini, T.; Fornasiero, P.; Abboto, A. *Chem. Commun.* **2016**, *52* (43), 6977-6980.

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## Half-sandwich Ir(III) complexes bearing pyridine-carboxamide ligands as efficient catalysts for formic acid dehydrogenation

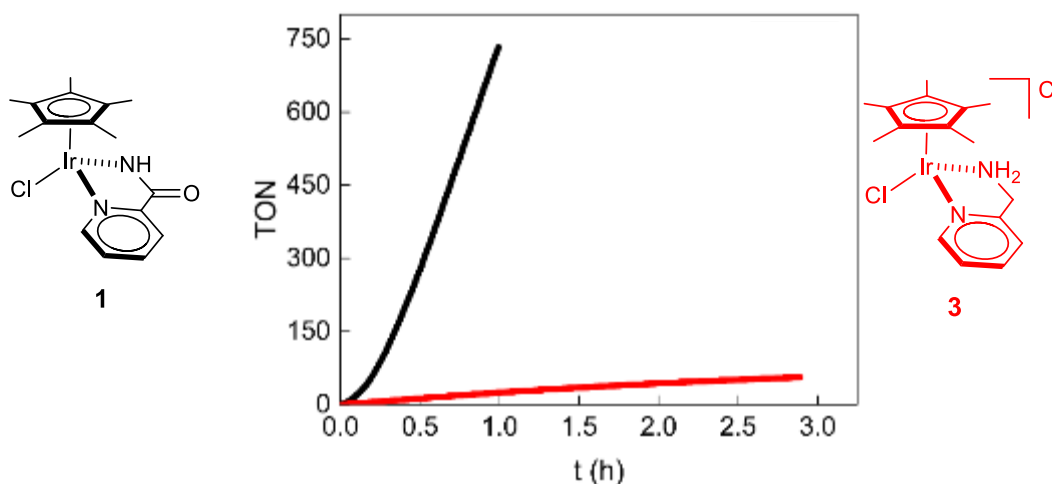
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Formic Acid (FA) has received significant attention as a promising hydrogen energy carrier due to its high volumetric capacity (53 g H<sub>2</sub>/L), low toxicity and flammability under ambient conditions.<sup>1</sup> Herein, it is shown that complexes [Cp\*Ir(R-pica)Cl] {R-pica = R-picolinamidate =  $\kappa^2$ -pyridine-2-carboxamide, ion(-1), **1** R = H and **2** R = Me} catalyse the liberation of H<sub>2</sub> from formic acid in water, with performances comparable with those of the best catalysts reported so far.<sup>3</sup> Furthermore, extensive NMR studies on complex **1** revealed several *in situ* modifications of the ancillary ligand under catalytic conditions, including hydrogenation of the amide moiety of the ancillary ligand leading to [Cp\*Ir(pyridin-2-ylmethanamine)Cl]Cl (**3**). The independently synthesized complex **3** is found to be active in FA hydrogenation, although with significantly lower performances with respect to **1**. Comparative kinetic studies revealed that the behaviour of the former catalyst is comparable to that of the latter species at long reaction times, providing a strong experimental evidence for amide hydrogenation of the ancillary ligand being the main decomposition route responsible for activity decay of **1**. DFT studies have been carried out to further elucidate this deactivation mechanism.



### References

1. Eppinger, J.; Huang, K-W *ACS Energy Lett.* **2017**, *2*, 188.
2. Mellmann, D.; Sponholz, P.; Junge, H.; Beller, M. *Chem. Soc. Rev.* **2016**, *45*, 3954.
3. Menendez Rodriguez, G.; Domestici, C.; Valentini, M.; Zuccaccia, C.; Macchioni, A. *Eur. J. Inorg. Chem.* **2018**, 2247

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## High optical efficiency of extended conjugated fluorescent organic compounds in acrylate polymer matrix

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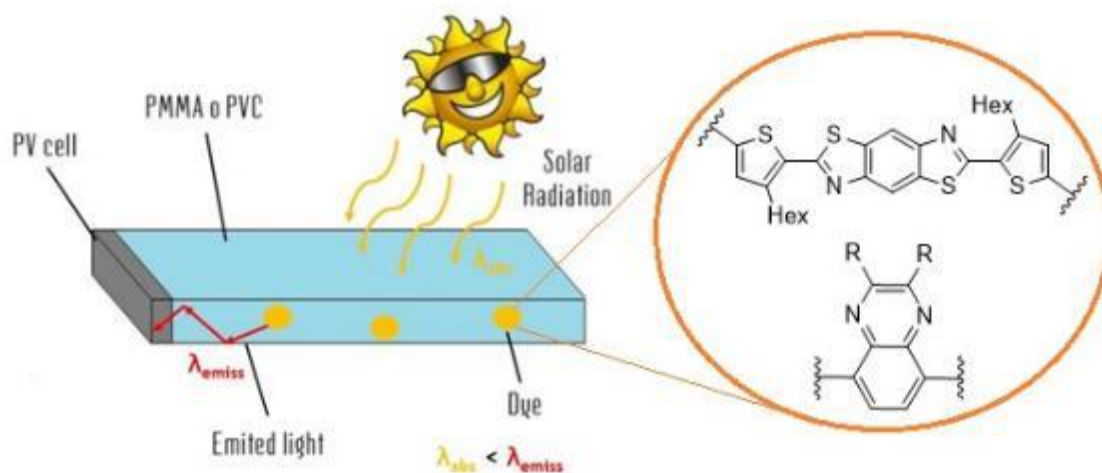
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Luminescent Solar Concentrators (LSCs) are optical devices based on a polymeric panel doped with a fluorophore, which is capable to improve the photovoltaic efficiency of a typical PV cell, at the edge of the panel, reducing the costs of installation and materials. Organic compounds will be promising dyes for LSC application for their versatile spectroscopic characteristics, depending on a specific structural design<sup>1</sup>.

This work is focused on fluorescent organic compounds with a typical conjugated D-A-D structure. New dyes were synthesized and characterized spectroscopically in solution and in polymer matrix, such as PMMA.

All the dyes showed good spectroscopic characteristics, in particular the optical efficiency which is in a range of 8-11% for all derivatives, higher than the typical commercial reference, Lumogen Red 305 (7.4%) at the same concentration (1.4%).



### References

1. Papucci, C. Eur. J. Org. Chem. **2018**, 20, 2657-2666

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## Improving the efficiencies of Fiber-Shaped Dye-Sensitized Solar Cells by using organic dyes

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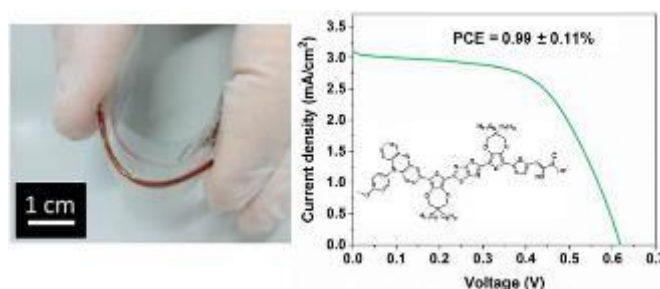
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Fiber-shaped dye-sensitized solar cells (DSSFs) have recently attracted increasing attention for the future of portable electronics and related fields such as smart textiles. This is due to their unique and promising advantages compared to the conventional planar structures: lightweight, easy integration into wearable and to a variety of curved surfaces (like our bodies). The three dimensional structure induces into DSSFs a new special features in light harvesting and charge transport overcoming the structural shortcomings of the common planar cells (harvesting solar radiation in 3D space). However, for flexible devices a crucial point in order to maintain devices performance and time stability is the adhesion of active layers during weaving operation. Moreover, for a complete DSSFs commercialization also the production costs must be reduced. In this work these issues are faced producing a thinner TiO<sub>2</sub> photoanode (5 μm) and replacing the traditional N719 Ru-based dye with a more efficient organic one. Three different thiazolo [5,4-*d*] thiazole-based organic dyes called TTZ3, TTZ5 and TTZ7<sup>[1]</sup>, capable of strongly absorb visible light were tested for the first time for this purpose. The mechanical properties of the thin film based photoanode were determined as well as the amount dyes adsorbed on the TiO<sub>2</sub> surface. The photovoltaic and electrochemical characterizations performed in different illumination conditions show better performance for all the devices based on organic sensitizers compared with the metallic one. TTZ7-based DSSFs reach the PCE of 0.99±0.11%, (J<sub>SC</sub> of 2.9±0.4 mA/cm<sup>2</sup>), while the N719-based ones produce PCE of 0.56±0.03%, (J<sub>SC</sub> of 1.6±0.1 mA/cm<sup>2</sup>). The best properties of the TTZ sensitizers were ascribed to their higher light harvesting capability that enhances the current density of the related devices<sup>[2]</sup>. These results show for the first time the superior efficiency of organic sensitizers instead of the metallic ones for DSSFs application. opening the possibility to develop efficient thin-film devices increasing the stability and reducing the production costs.



### References

1. Dessì, A. *RSC Adv.* **2015**, 5, 32657-32668.
2. Sangiorgi, N. *Sol.Energ.Mater.Sol.Cells* **2020**, 204, 110209-110217.

## Designing Layered Hybrid Perovskites with Tunable Band Gap and Enhanced Conductivity

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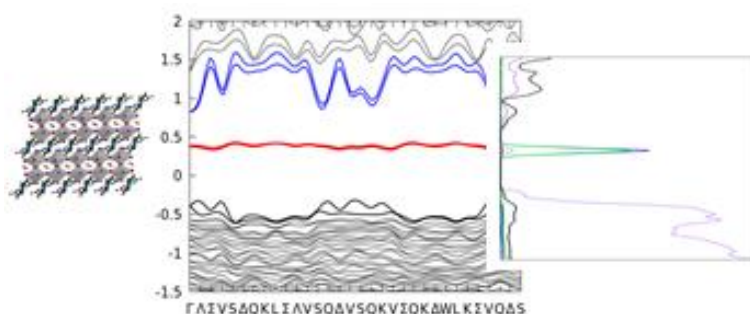
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The best PV performances obtained by hybrid organohalide perovskites come from systems with 3D structure, necessarily intercalated by small size organic cations: nonetheless, a large interest has grown recently for layered perovskites, with either pure 2D or mixed 2D/3D structures, which allow a much wider choice for the interlayer cations. [1]

We present DFT/GW theoretical models of layered hybrid perovskites, based either on Pb or Sn iodide sheets intercalated by large divalent organic cations. [2,3]

With a suitable choice of the intercalated cations, the perovskite band gap can be finely tuned (what is not feasible in 3D systems) allowing electronic transitions with energy in the optical/NIR region.

In addition, the presence of intragap electronic states (located on the organic layers) can enhance the electrical conductivity along the direction perpendicular to the lead halide sheets, especially in the quasi-2D systems. The low and anisotropic conductivity is one of the most serious limitations to the PV efficiency for the quasi-2D perovskites synthesized so far: we predict that using the proposed dications, possibly mixed with other mono- or di-valent organic cations, in the inter-slab region could actually improve the performance of such systems substantially.



### References

1. Petrus, M., et al. *Adv. Energy Mater.* **2017**, 7.
2. Fraccarollo, A.; Canti, L.; Marchese, L.; Cossi, M. *J. Chem. Phys.* **2017**, 146, 234703.
3. Fraccarollo, A.; Marchese, L.; Cossi, M. *J. Phys. Chem. C* **2018**, 122, 3677–3689.



## H<sub>2</sub>O<sub>2</sub> electrochemical production and sensing: a focus on updated research and applications

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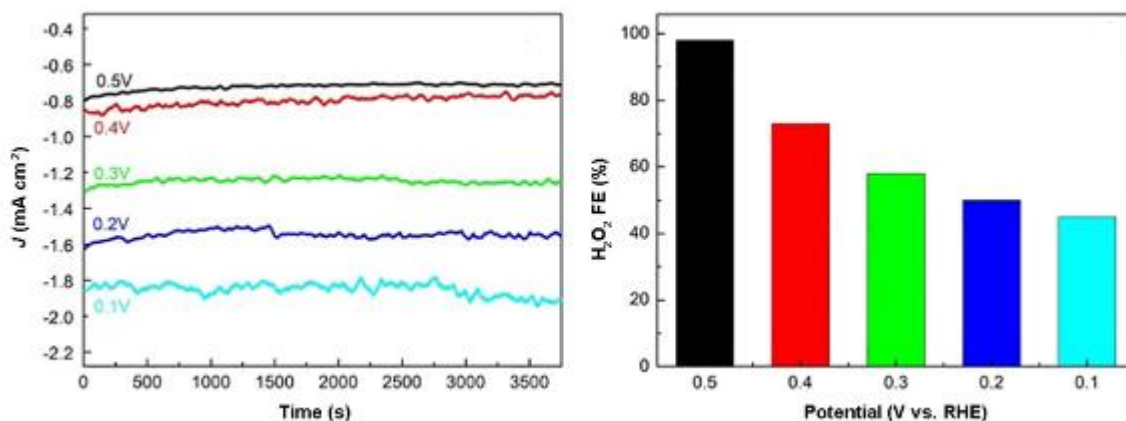
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Electrochemical oxygen reduction reaction (ORR) is a challenging approach for the sustainable production of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and it is also a reaction of relevance in fuel-cell applications. The versatility of hydrogen peroxide as a fine chemical for a wide range of applications justifies its heavy industrial production and the increasing interest in finding alternative low-cost and low-energy synthetic routes. Electrocatalytic processes exploiting the reduction of molecular O<sub>2</sub> are undoubtedly of high appeal, particularly if they can rely on electrocatalysts based on non-noble or metal-free materials. Recently, we report the outstanding electrocatalytic behaviour of a series of materials consisting of N-doped carbon shells enveloping Co core nanoparticles, which are able to generate H<sub>2</sub>O<sub>2</sub> with almost total current selectivity at very favourable potentials.<sup>1</sup> These materials are accessed through controlled pyrolysis implying an easy, inexpensive, and scalable preparative protocol.

On the other hand, the widespread industrial use of H<sub>2</sub>O<sub>2</sub> has induced great interest also in the development of new and more efficient electroactive materials for its detection. Inspired by the powerful proton-catalysed H<sub>2</sub>O<sub>2</sub> reduction mechanism of peroxidases, we have recently developed a well-defined and densely functionalized carboxylic graphene derivative that serves as a proton source and conductive electrode for binding and detecting H<sub>2</sub>O<sub>2</sub>.<sup>2</sup>



### References

1. Lenarda, A. et al.. *ChemSusChem*, **2019**, *12*, 1664-1672.
2. Lenarda, A. et al.. *ACS Omega*, **2019**, doi:10.1021/acsomega.9b02881. In press.

## Hierarchical nanostructures in multi-functional electrocatalysts for CO<sub>2</sub> conversion

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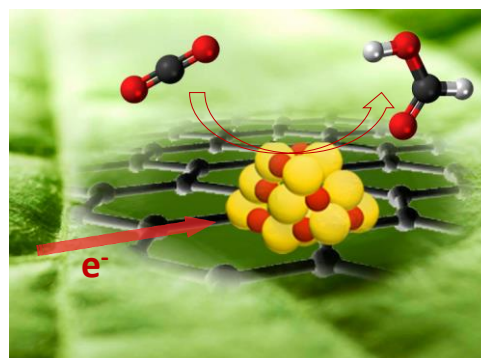
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CO<sub>2</sub> concentration in the atmosphere increased from 320 ppm in the early 60's, to more than 400 ppm in 2014, with an exponential trend never observed before. It is thus not surprisingly that recently a lot of efforts were focused in the research and improvement of new/existing materials, catalysts, methods, and technologies, able to capture and to convert CO<sub>2</sub> in useful products.[1] The design of new electrocatalysts that reduce CO<sub>2</sub> in a selective and efficient fashion is a key step for future exploitation of this technology.

Here we present how the combination of different building blocks in a single nanostructure might be a good strategy to achieve a good selectivity in the CO<sub>2</sub> reduction process.

Combining the unique physico-chemical properties of functionalized nanomaterials (such as carbon nanotubes and carbon nanohorns) and nanocrystalline cerium dioxide (CeO<sub>2</sub>) we revealed faradaic efficiency for formic acid production as high as 55% at an overpotential as low as 0.02V in acid solutions. These performances have been possible by the formation of partially reduced ceria (CeO<sub>2</sub>-X), responsible of an increased CO<sub>2</sub> adsorption and a more efficient electron transfer at the surface. [2] In the nanocomposite, where the nanomaterials are covered by nanoparticles of CeO<sub>2</sub>, the

oxide layer is thin enough to allow efficient charge transport through it and fast electron transfer at the surface where CO<sub>2</sub> is adsorbed. [3] The interconnection of the various components has been shown to be fundamental for the efficient CO<sub>2</sub> reduction to formic acid with this new metal-free nanocomposite, and opens new possibilities in the design of optimized electrocatalytic materials.



### References

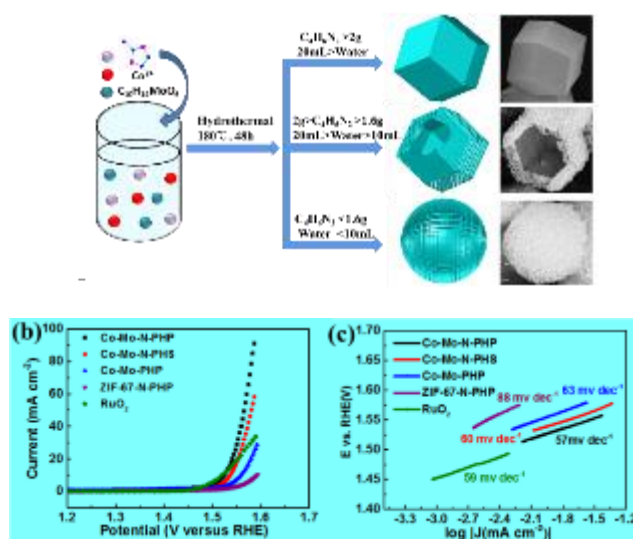
1. Armaroli N., Balzani V., *Angew. Chem. Int. Ed.* **2007**, *46*, 52-66.
2. Montini T., Melchionna M., Monai M., Fornasiero P., *Chem. Rev.* **2016**, *116*, 5987–6041
3. Valenti G., Boni A., Melchionna M., Cargnello M., Nasi L., Bertoni G., Gorte R. J., Marcaccio M., Rapino S., Bonchio M., et al., *Nat. Commun.* **2016**, *7*, 13549.

## Impact of morphology on the Oxygen Evolution Reaction of 3D Hollow Cobalt-Molybdenum Nitride

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Water splitting is an effective energy conversion process for replacing fossil fuels within a short time ideally resulting in zero pollution [1,2]. However, oxygen evolution reaction (OER) is the speed control step due to its tedious basic steps and sluggish kinetics [3]. In this work, we report a shape controlled 3D hollow Co-Mo hybridized binary catalyst via ZIF-67, which can be controlled by changing the contents of water and 2-methylimidazole. The binary catalyst can generate a particularly strong electron transfer between Co and Mo. The synergy between the morphology and composition of the Co-Mo polyhedrons binary heterostructure results in a remarkably high OER activity and stability. The optimal Cobalt-Molybdenum Nitride compound exhibits an attractive overall performance comprising an early onset at 1.46 V, an overpotential of 294 mV and achieves a current density of  $10 \text{ mA cm}^{-2}$ , and a Tafel slope of  $57 \text{ mV dec}^{-1}$ .



### References

1. Surname, M. *Angew. Chem., Int. Ed. Engl.* **1989**, 28, 322-325. I. Roger, M.A. Shipman, M.D. Symes, *Nat. Rev. Chem.* 1 (2017) 0003
2. A. Sivanantham, S. Shanmugam, *Appl. Catal. B: Environ.* 203 (2017) 485-493.
3. C.C.L. Mccrory, S. Jung, I.M. Ferrer, S.M. Chatman, J.C. Peters, T.F. Jaramillo, *J. Am. Chem. Soc.* 137 (2015) 4347-4357.

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## Effects of S-doped carbon support on Fe-N-C active site formation and activity versus oxygen reduction

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To promote the commercialization of proton exchange membrane fuel cell (PEMFC) the replacement of Pt-based catalysts with Pt-free catalysts (Non-PGM) is necessary. Doping of heteroatoms is an effective way to tune carbon structure, composition, porosity and electronic properties for enhancing electrochemical performance [1]. Specific surface area and microporous structure, which determine the accessibility of active sites and the transport of reagents and products, play important roles in enhancing the catalyst activity and stability. In Non-PGM two kinds of active sites, Fe-N<sub>x</sub> and N-functional groups, can usually be considered active towards 4 e<sup>-</sup> reduction of oxygen. Some studies have further demonstrated that multi-doped carbon matrix seems to be more effective in modifying carbons' electronic structure for enhancing electrochemical performance due to the synergetic effect arising from heteroatoms [1]. Sulfur has attracted particular interest due to its high synergetic effect with nitrogen [2]. In this work, the effects of S functional group content on the formation of Fe-N-C active site is considered. The catalysts were synthesized starting from a sulfur doped mesoporous carbon prepared by hard template and dibenzothiophene as organic precursor. It was found that the superficial nitrogen and iron fixation percentage increase at the increasing of the thiophenic functional group content. The materials were fully characterized by BET, XPS and XRD and the electrochemical characterization by RRDE confirms that the catalytic performances ( $E_{onset}$  and  $E_{1/2}$ ) versus ORR increases at the increasing of the initial sulfur content. The selectivity was found to be not affected by sulfur content, since the number of transferred electrons is 3.9 for all the investigated catalysts. The number of active sites (determined by nitrite stripping voltammetry) and the TOF number will be presented as a function of the initial sulfur content, graphitization degree, surface area and micro/mesopore ratio.

### References

1. X. Zhang, Y. Wang, Y. Du, M. Qing, F. Yu, Z.Q. Tian, P.K. Shen, , *Electrochim. Acta.*, 2019, 318, 272–280.
2. M. Guo, L. Wang, Y. Gao, G. Li, *Int. J. Hydrogen Energy.*, 2019, 44, 3625–3635.

## N-Doped Carbon Electrocatalyst for Oxygen Reduction with Zn Ion-Imprinted Active Sites

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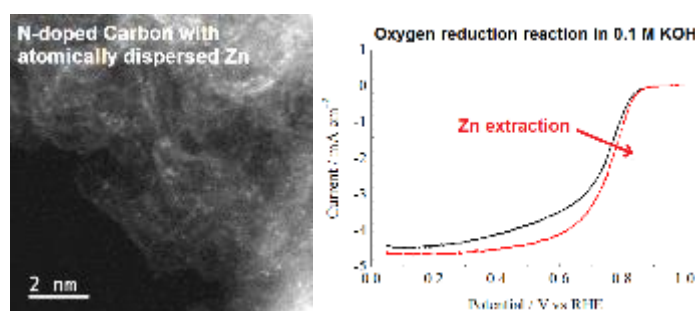
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For efficient transformation of chemical energy into electrical energy, hydrogen fuel cells require an effective electrocatalyst to facilitate the sluggish reduction of oxygen. As an alternative to scarce and expensive Pt-based catalysts, non-noble electrocatalysts are being developed and among them, nitrogen-doped carbons (NCs) are showing promising activity.[1] Due to the very complex structural and chemical properties of the materials in the diverse NC family, it is of great value to improve our understanding of their structure-activity relationship, especially identifying the nature of electrocatalytically active sites.[2] In this contribution, we will address the role of site-templating ions and the properties of imprinted sites in the NC structure.[3] We will demonstrate that an ionothermal synthesis in a Zn-containing salt melt produces a highly porous NC with atomically dispersed Zn<sup>2+</sup>. A study of the material structure (atomic-resolution scanning transmission microscopy, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy and nitrogen sorption porosimetry) together with its detailed electrochemical characterization in alkaline electrolyte (rotating (ring) disk electrode) showed that the Zn-binding sites exhibit a high ORR activity after the Zn ions have been extracted by acid. The structure and electrocatalytic behavior of such ion-imprinted active sites in NC materials will be discussed.



### References

1. Sarapu, A., Kibena-Pöldsepp, E., Borgheib, M., Tammeveski, K. *J. Mater. Chem. A* **2018**, 6, 776-804.
2. Chung, H.T., Cullen, D.A., Higgins, D., Sneed, B.T., Holby, E.F., More, K.L.; Zelenay, P. *Science* **2017**, 357, 479-484.
3. Menga, D., Ruiz-Zepeda, F., Moriau, L., Šala, M., Wagner, F., Koyutürk, B., Bele, M., Petek, U., Hodnik, N., Gaberšček, M., Fellingner, T.-P. *Adv. Energy Mater.* **2019**, 9, 1902412.

## Metal-doped organic conductive polymers for CO<sub>2</sub> reduction

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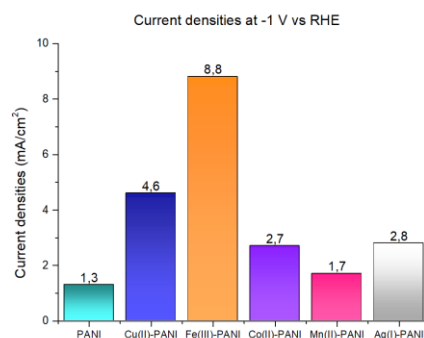
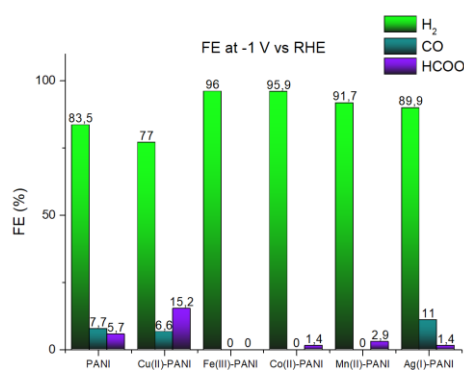
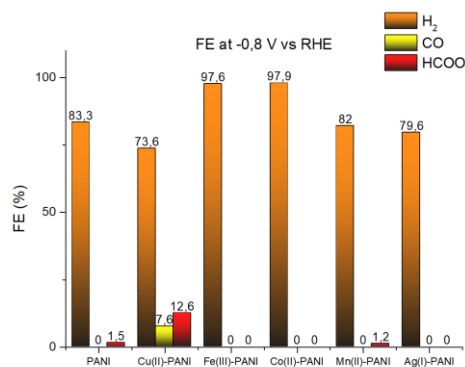
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Electrochemical reduction of carbon dioxide (CO<sub>2</sub>RR) into fuels is a promising technology, since it can potentially support all the alternative energy plants that result to be limited by territorial power distribution. In fact, the CO<sub>2</sub>RR allows the stocking of electrical energy in form of chemicals, which can overcome physical connection between the energy production situ with all the consumption sites in the territory [1,2] and thus help the alternative energy technology spread. The actual limiting factor in the CO<sub>2</sub>RR is still the absence of an electrocatalyst able to selectively convert CO<sub>2</sub> instead of H<sup>+</sup>, to have a narrow and controlled distribution of carbon products at great current densities and, possibly, to have a low price [3].

Polyaniline (PANI) based materials are cheap organic polymers able to conduct electrons through their widespread  $\pi$ -system. The behavior of the PANI in the CO<sub>2</sub>RR was analyzed. Several metal dopants, such as Cu<sup>II</sup>, Mn<sup>II</sup>, Co<sup>II</sup>, Fe<sup>III</sup> and Ag<sup>I</sup>, were also investigated in order to understand the doping effect on the activity and selectivity. Among these doped PANI, the Cu<sup>II</sup> one showed the best results: CO observed at more positive potential (-0.8 V vs RHE); current density increased by 2.6 times and faradic efficiency for formate enhanced from 5.7% to 15.2% with respect to the undoped PANI at -1.0 V vs RHE.



### References

1. Y. Cheng, *Small Methods*, 2019, 3, 1800440.
2. G. Kibria, *Adv. Mater.*, 2019, 31, 1807166.
3. A.D. Hadonko, *Nature Catalysis*, 2018, vol.1, 922–934

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## Electrochemomechanical Properties of Red Phosphorus with Lithium, Sodium and Potassium

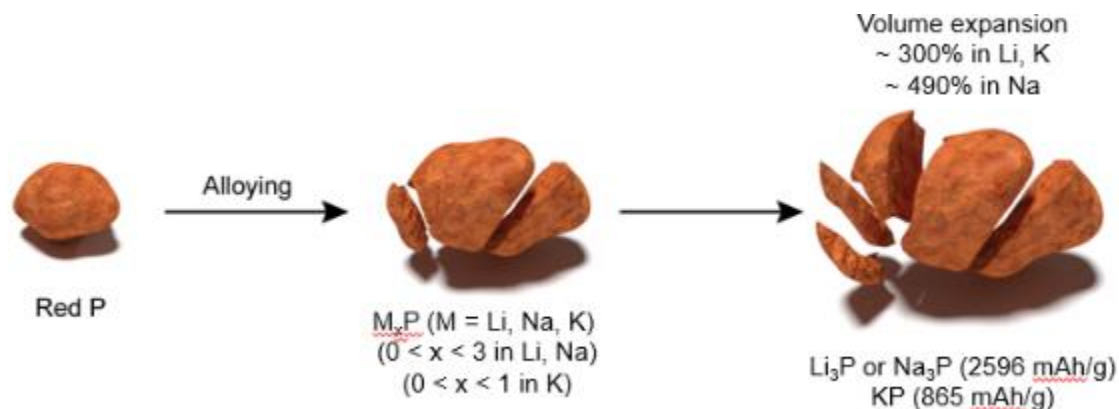
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Red phosphorus is a promising anode material thanks to its ability to form alloys with lithium, sodium and potassium, thus achieving high theoretical capacity (2596 mAh g<sup>-1</sup> with Li and Na and 865 mAh g<sup>-1</sup> with K). However, it suffers from its low electronic conductivity and a huge volume expansion that leads to the formation of stress with consequent fracture and pulverization of the particle. In this work, red phosphorus particles have been analyzed with in-situ TEM techniques in order to study the mechanism of the crack formation during the volume expansion with lithium, sodium and potassium. This experiment is coupled with computational modelling of the particles and the simulation of the diffusion of the ions through the particles to understand the development of stresses that can lead to the nucleation of the crack and the failure of the particle.



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## Transport properties and electrochemical performance of nanocomposite PEMs based on non-fluorinated polymers

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High proton conductivity and stability to the aggressive operation conditions are two of the main requirements for electrolyte membranes to be used in Proton Exchange Membrane Fuel Cell (PEMFC) devices. Despite perfluorosulfonic acid membranes represent the state of the art for fuel cell application, their use entails a large number of drawbacks that still limit the large-scale commercialization of such technology. Accordingly, the design and preparation of inexpensive and high-performing non-fluorinated ionomers has become the most compelling challenge of the recent years [1]. In this scenario, the low cost, large availability, biocompatibility and excellent film-forming ability, make Polysulfone (PSU), and in particular its sulfonated derivative (sPSU), one of the most promising material for PEM development. [2] This work focus on the recent advances in the development of sPSU-based electrolytes able to ensure adequate devices' performances and satisfactory thermo-mechanical resistance. The appropriate modifications of the polysulfone backbone are firstly proposed together with a systematic investigation of the structure-performance relationship. In this regard, the experimental data were elaborated to estimate the water distribution inside the prepared electrolyte and the number of water molecules per  $-\text{SO}_3\text{H}$  group with results that were in a very good agreement with the theoretical model obtained by theoretical simulation. Besides, the preparation of composite membranes through the incorporation of suitable inorganic-organic materials will be also discussed. In this context, the use of Nanoscale Ionic Materials (NIMs), consisting of a silica-core surface-functionalized with a large number of oligomeric chains terminating with  $-\text{SO}_3\text{H}$  ionic groups [3], is expected to enhance critical properties of the resulting electrolyte. Indeed, while the charged oligomeric corona allows to generate a well-connected path for proton conduction, especially under drastic conditions, the silica core further improves the thermal and mechanical stability of the final composite membranes. Finally, NMR spectroscopy has been employed to study the molecular dynamics (water and protons) in such kind of systems through the direct measurements of the self-diffusion coefficients (PFG-method) and the relaxation times ( $T_1$  and  $T_2$ ) [4]. The ion diffusivity studies, together with electrochemical characterizations, as a function of  $T$  and  $\text{RH}$ , can allow to comprehend the relationship between architecture, dimensionality, chemical structure of ionomers and nanofillers and the physicochemical properties of the resulting electrolytes.

### References

1. Kraysberg A., Ein-Eli, Y. *Energy Fuels*, **2014**, 28, 7303–7330
2. Zhu, Y., Manthiram, A. *Journal of Power Sources*. **2011**, 196, 7481–7487.
3. L.G. Boutsika, A. Enotiadis, I. Nicotera, C. Simari, G. Charalambopoulou, E.P. Giannelis, T. Steriotis. *Int. J. Hydr. En.* **2016**, 41, 22406–22414.
4. Suarez, S., Greenbaum, S. *Chem Rec.* **2010**, 10, 377-393.

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## Towards a critical evaluation of electrocatalyst stability

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As a result of the energy transition and electrification of the chemical industry, electrocatalytic conversions will play an important role in the near future. Electrocatalytic conversion of e.g. carbon dioxide (CO<sub>2</sub>R) has shown great potential for storing electrical energy in fuels and chemicals. Research in this field has mainly focused on catalyst development aimed at high activity and selectivity. Although significant progress has been made in understanding the CO<sub>2</sub>R reaction,<sup>[1]</sup> for a CO<sub>2</sub>R technology to have a sustainable impact on society and environment, industrial realization is ultimately required, and hence the emphasis of CO<sub>2</sub>R research will gradually shift towards upscaling and improving electrocatalyst stability.<sup>[2,3]</sup>

There is no unambiguous definition reported for electrocatalyst stability to date. A measure for stability generally accepted in the literature is the operational time for which a certain value of the faradaic efficiency (FE) remains approximately constant. In this work,<sup>[4]</sup> we take CO<sub>2</sub>R as an example to highlight important pitfalls and hidden ambiguities caused by improper experimental/mathematical procedures related to FE calculation. We complement recent works on experimental procedures for CO<sub>2</sub>R,<sup>[5,6]</sup> by demonstrating and critically discussing the impact of data averaging, sampling frequency and the effect of temporal evolution of the product yield and current density on the FE. The way in which data are averaged, may lead to incorrect and unrealistic values for the FE that usually stay unnoticed. Additionally, systematic experimental errors (e.g. poor mixing) can be identified by discrimination in data averaging procedures. Depending on the frequency of sample collection, important information may be masked or interpreted differently. Therefore, it is crucial for researchers in the field to be aware of these extrinsic effects, leading to misinterpretation of electrocatalyst stability.<sup>[4]</sup>

In this work we also discuss alternatives for a better assessment of electrocatalyst stability and based on commonly occurring trends (product, current, FE vs. time), possible degradation mechanisms of the catalyst are highlighted. Depending on the catalyst and process conditions, different degradation mechanisms may occur e.g. poisoning by impurities in the electrolyte or CO, detachment of active species from the support, chemical/mechanical degradation of catalyst, etc. The type of degradation may be revealed by a careful analysis of aforementioned parameters. The insights obtained in this work provide new tools to better evaluate electrocatalyst stability and consequently improve the electrocatalyst or process conditions for durable performance not only for CO<sub>2</sub>R but other electrocatalytic reactions as well.<sup>[4]</sup>

### References

1. Y. Y. Birdja et al., *Nat. Energy*, 2019, 4, 732-745
2. H. R. M. Jhong et al., *Curr. Opin. Chem. Eng.* 2013, 2, 191-199
3. O. Gutiérrez Sánchez, Y. Y. Birdja et al., *Curr. Opin. Green and Sust. Chem.* 2019, 16: 47-56
4. Y. Y. Birdja et al., submitted 2019
5. E. L. Clark et al., *ACS Catal.* 2018, 8, 6560-6570
6. J. E. Pander et al., *Catal. Sci. Technol.*, 2017,7, 5820-5832

## Ultrafast Transient Absorption Spectroscopy vs. Photoelectrochemical Performance of WO<sub>3</sub>/BiVO<sub>4</sub> Photoanodes

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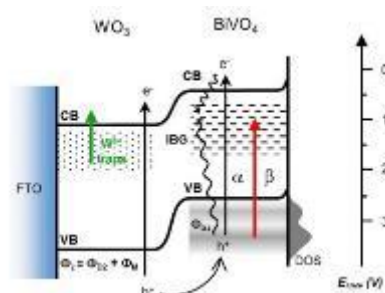
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Efficient photoanodes can be obtained by combining bismuth vanadate with tungsten trioxide in a WO<sub>3</sub>/BiVO<sub>4</sub> heterojunction, where electrons photoexcited in BiVO<sub>4</sub> can be injected into WO<sub>3</sub>, thus merging the excellent visible light harvesting properties of BiVO<sub>4</sub> with the superior conductivity of WO<sub>3</sub> [1] for water splitting applications. The WO<sub>3</sub>/BiVO<sub>4</sub> system has been investigated through femtosecond transient absorption (fs-TA) spectroscopy in the visible range, by comparing the dynamics of the signal ascribed to trapped holes in BiVO<sub>4</sub> alone with that in the coupled system [1,2]. Under selective BiVO<sub>4</sub> excitation, electron transfer from photoexcited BiVO<sub>4</sub> to WO<sub>3</sub> occurs immediately after excitation, as demonstrated by the increase of the trapped holes' lifetime in BiVO<sub>4</sub> [2] and confirmed by directly tracking electron transfer processes by TA mid infrared spectroscopy in the picosecond to microsecond time range [3]. On the other hand, a recombination channel opens when both oxides are simultaneously excited [2], evidenced by a shorter lifetime of trapped holes in BiVO<sub>4</sub>. PEC measurements reveal the implication of these wavelength-dependent ultrafast interactions on the performance of WO<sub>3</sub>/BiVO<sub>4</sub> heterojunction photoanodes [2].

*In operando* photoelectrochemical conditions, i.e. under an applied anodic potential, the photoinduced charge carrier dynamics in the WO<sub>3</sub>/BiVO<sub>4</sub> system is dominated by the interfacial electric field arising from the band energy offset of the two oxides and by the bias-dependent alteration of intra band gap states in BiVO<sub>4</sub>, which were evidenced by electrochromic measurements [4]. Both these effects contribute to the accumulation of surface trapped holes in BiVO<sub>4</sub>, which are beneficial for water oxidation [4].



### References

1. Grigioni, I.; Stamplecoskie, K. G.; Selli, E.; Kamat, P. V. *J. Phys. Chem. C* **2015**, *119*, 20792-20800.
2. Grigioni, I.; Stamplecoskie, K. G.; Jara, D. H.; Dozzi, M. V.; Oriana, A.; Cerullo, G.; Kamat, P. V.; Selli, E. *ACS Energy Lett.* **2017**, *2*, 1362-1367.
3. Grigioni, I.; Abdellah, M.; Corti, A.; Dozzi, M. V.; Hammarström, L.; Selli, E. *J. Am. Chem. Soc.* **2018**, *140*, 14042-14045.
4. Grigioni, I.; Ganzer, L.; Camargo, F. V. A.; Bozzini, B.; Cerullo, G.; Selli, E. *ACS Energy Lett.* **2019**, *4*, 2213-2219.

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## Photocatalytic routes in the water oxidation reaction

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Artificial photosynthesis aims at the conversion of solar light into chemical energy, and is thus considered a promising route towards the production of renewable fuels.<sup>1</sup> Following bioinspired guidelines, typical photosynthetic schemes require the integration of different functional modules for light harvesting and charge separation, with catalytic redox routines for the activation of small molecules such as water and carbon dioxide.

In this communication, photocatalytic processes for the water oxidation reaction will be presented; in particular, a focus will be given on mechanistic aspects dealing with intermediates characterization, electron transfer dynamics, photon management for high quantum efficiency.<sup>2-3</sup>

Perspectives towards the development of photoelectrochemical devices will be finally discussed,<sup>4</sup> together with a more recent approach aimed at the application of photosynthetic schemes for the preparation of fine chemicals.

### References

1. Sartorel, A.; Bonchio, M.; Campagna, S.; Scandola, F. *Chem. Soc. Rev.*, **2013**, *42*, 2262-2280.
2. Volpato, G. A.; Bonetto, A.; Marcomini, A.; Mialane, P.; Bonchio, M.; Natali, M.; Sartorel, A. *Sustain. Energy Fuels* **2018**, *2*, 1951 – 1956.
3. Volpe, A.; Tubaro, C.; Natali, M.; Sartorel, A.; Brudvig, G. W.; Bonchio, M. *Inorg. Chem.* **2020**, doi:10.1021/acs.inorgchem.9b02531.
4. M. Bonchio, M.; Syrgiannis, Z.; Burian, M.; Marino, N.; Pizzolato, E.; Dirian, K.; Rigodanza, F.; Volpato, G. A.; La Ganga, G.; Demitri, N.; Berardi, S.; Amenitsch, H.; Guldi, D. M.; Caramori, S.; Bignozzi, C. A.; Sartorel, A.; Prato, M. *Nat. Chem.*, **2019**, *11*, 146-153.

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## Strategies for the development of efficient Ir-based water oxidation catalysts

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Over the last decade, the search for efficient water oxidation catalysts (WOCs) has sparked.<sup>[1]</sup> Arguably, WOCs based on noble metals, especially Ru and Ir, have shown the most promising performances by far. Therefore, along with the development of earth abundant metal systems, many efforts are currently devoted to the optimization of exceedingly active Ru/Ir-catalysts in a ‘noble metal atom economy’ fashion, that is, trying to maximize performance while minimizing the utilization of such precious elements.<sup>[2]</sup> To this end, a first possible strategy consists in the exploitation of molecular catalysts, which ideally guarantee 100% active sites and the possibility to boost activity by proper tailoring the ancillary ligands. Furthermore, molecular WOCs can be heterogenized on suitable supports, providing additional advantages, for instance, with respect to recoverability and recyclability. Finally, it is conceivable to develop robust heterogeneous WOCs in which the Ru/Ir centers are dispersed in layered and cheap inorganic materials, in order to maximize the accessibility of the active metal centers with respect to more classical systems like bulk or nanometric IrO<sub>2</sub>.

Our group has been exploring all these three approaches to catalysts development and some representative, recent examples will be described in this presentation. In particular, two novel dinuclear Ir complexes, bearing EDTA or EDTMP ligands (Figure 1a), and their TiO<sub>2</sub>-supported analogues will serve as exemplifying cases for molecular and heterogenized WOCs, respectively. Additionally, highly efficient and recyclable Ir-doped layered double hydroxides (Ir-LDH; Figure 1b) will be presented as suitable and economic heterogeneous WOCs.<sup>[3]</sup>

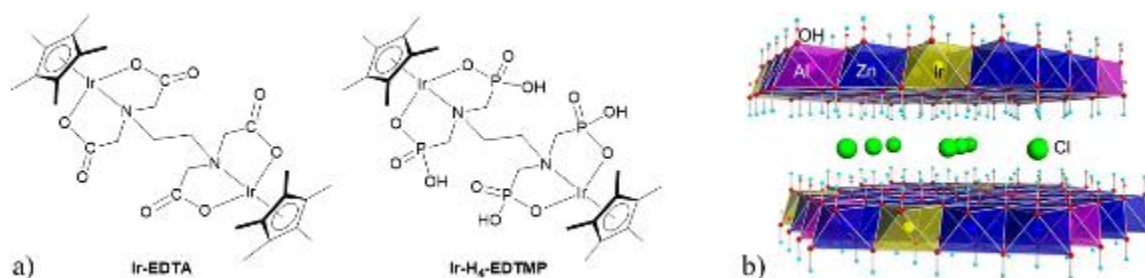


Figure 1. a) Dinuclear Ir-complexes with EDTA and EDTMP ligands; b) Pictorial representation of Ir-LDH.

### References

1. J. Li, R. Güttinger, R. Moré, F. Song, W. Wan, G. R. Patzke, *Chem. Soc. Rev.* 2017, 46, 6124-6147.
2. Macchioni, *Eur. J. Inorg. Chem.* 2019, 2019, 7–17; b) M. Ledendecker, S. Geiger, K. Hengge, J. Lim, S. Cherevko, A. M. Mingers, D. Göhl, G. V. Fortunato, D. Jalalpoor, F. Schüth, C. Scheu, K. J. J. Mayrhofer, *Nano Res.* 2019, 12, 2275–2280.
3. L. Fagiolari, A. Scafuri, F. Costantino, R. Vivani, M. Nocchetti, A. Macchioni, *ChemPlusChem* 2016, 81, 1060–1063.

## Self-Pressurized H<sub>2</sub> Production From the Electrochemical Reforming of Ethanol at 150 °C

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The aqueous electrochemistry above 100°C is a relatively unexplored field because requires dedicated electrochemical cells. <sup>[1]</sup> Here we report one of the first examples of an electrochemical autoclave employed in the electrooxidation of ethanol at 150°C in alkaline media. These operating conditions make the alkaline solution in the autoclave very aggressive to catalysts including noble metals like Pt and Pd. <sup>[2]</sup> For this reason we synthesized a highly active and stable ethanol oxidation catalyst (PdCoNi<sub>foam</sub>) composed of Pd nanoparticles supported on nanostructured Co oxide structures grown on nickel foam. Treatment with phosphorous vapors at high temperature yields a thin coating of phosphate that confers enhanced stability to the electrode in the hot KOH solution at pH 14 for ethanol electrooxidation. A combination of scanning electron microscopy (energy dispersive X-ray spectroscopy) and X-ray photoelectron spectroscopy reveal a 3D nano-flake surface with an external layer of phosphates that prevents Pd dissolution (figure 1). The PdCoP@Ni<sub>foam</sub> resulting catalyst was employed as anode in an ethanol electrochemical reforming cell at 150 °C with self-pressurization of the H<sub>2</sub> produced by the electrochemical reaction; the H<sub>2</sub> self-pressurization is safe since no O<sub>2</sub> is evolved during EtOH reforming. <sup>[3]</sup>

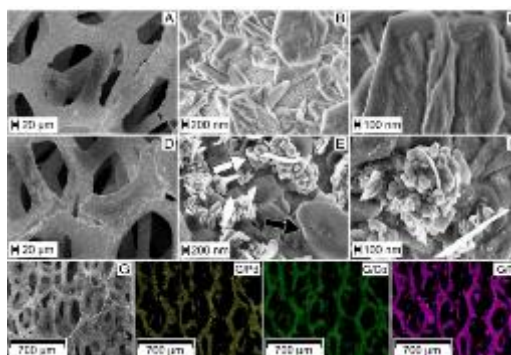


Fig.1 (A,B,C) SEM images of the PdCo@Ni foam precursor. (D,E,F) SEM images of the PdCoP@Ni foam catalyst. (G) SEM image of the sample region investigated with EDS analysis.

### References

1. Macdonald, D.D. *Corrosion*. **1978**, *34*, 75-84.
2. Cerevko, S. et al. *Electrocatalysis*. **2018**, *9*, 153-161
3. Pagliaro, M.V. *Catalysis*. **Accepted article**.

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## Copper Phorphyrin – Carbon Nitride Hybrid for the Photoelectroreduction of CO<sub>2</sub> to CO and Formate

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The production of low-carbon fuels through the electroreduction of CO<sub>2</sub> assisted by the solar light supposes a sustainable energy strategy to fight against the climate change. However, for the development of this technology, more efficient, stable and selective photoelectrocatalysts are needed.<sup>1</sup> To this end, we have developed a new type of hybrid material consisting of a copper-porphyrin (CuPor) embedded into the 2D polymeric structure of carbon nitride (gCN). In this way, we exploit the catalytic activity of the metal centre and the light-harvesting of gCN. The synthesis method and the materials studied in this work have never been reported in the literature.

Many techniques have been used to determine the morphological, structural, chemical and optical properties of these new material. FTIR and XRD confirmed the formation of gCN and that the addition of the Cu-porphyrin into the gCN matrix do not alter its structure. TEM showed that both gCN and CuPor/gCN have the same 2D structure. *Ex situ* EXAFS measurements showed that the Cu-porphyrin maintains its geometry when it is included into the gCN matrix. XPS showed a slightly different Cu 2p spectrum for CuPor/gCN, respect to that for CuPor, which could be attributed to a change of the electronic environment of the metal when is introduced in the polymeric matrix. Finally, UV-Vis diffuse reflectance spectroscopy showed that CuPor/gCN adsorbs in the visible and UV range.

In addition, we have studied the photoelectrocatalytic activity of these materials toward the CO<sub>2</sub> reduction by conventional electrochemical techniques (cyclic and linear voltammeteries) under dark and illumination conditions. The results show that CuPor/gCN is able to reduce CO<sub>2</sub> and that the activity is enhanced by the light. Recently, we have started to investigate these materials by *in situ* differential electrochemical mass spectroscopy (DEMS) in order to determine the products obtained as a function of the potential. The results obtained up to now show that gCN is not able to reduce CO<sub>2</sub> (in the potential range studied) since H<sub>2</sub> was the only product detected. However, CO and formate, as well as H<sub>2</sub>, were obtained on CuPor/gCN, confirming its ability to reduce CO<sub>2</sub>.

### References

1. Birdja, Y. Y.; Pérez-Gallent, E.; Figueiredo, M. C.; Göttle, A. J.; Calle-Vallejo, F.; Koper, M. T. M.; *Nature Energy* **2019**, *4*, 732-745.

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## Use of reducible metal oxides in CO<sub>2</sub> conversion to formic acid

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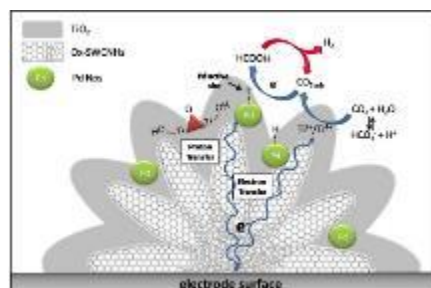
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Electrocatalytic hydrogenation of CO<sub>2</sub> to formic acid (HCO<sub>2</sub>H) is a central strategy for quickening the transition to carbon-neutral energy schemes. Recently, CO<sub>2</sub> electrohydrogenation to HCOOH could be achieved by Pd-based electrocatalysts supported on carbon, with the active species being an *in-situ* formed Pd hydride.<sup>1</sup> We have demonstrated that interfacing reducible metal oxides such as TiO<sub>2</sub> and CeO<sub>2</sub> with carbon nanostructures (CNS) is a valuable approach to mediate electron transfer processes at the carbon-metal oxide junction, favouring formation of metal-hydride species that can catalyze the electrohydrogenation to HCO<sub>2</sub>H at low overpotentials, while controlling the H<sub>2</sub>O/CO<sub>2</sub> binding equilibria. As a result, the reduction of CO<sub>2</sub> proceeds with excellent selectivity, decreasing the extent of the competing Hydrogen Evolution Process (HER). In the case of TiO<sub>2</sub>, a ternary hybrid consisting of carbon nanohorns/Pd@TiO<sub>2</sub> was assembled with a task specific design that set a state-of-the-art in the CO<sub>2</sub> reduction to HCOOH,<sup>2</sup> while in the case of CeO<sub>2</sub>, combination with carbon nanotubes allows the system to be highly performant even without inclusion of any noble metal.<sup>3</sup> The talk aims at critically discuss the relevant structural features of these materials, provide perspectives that could inspire future research on CO<sub>2</sub> reduction to make new breakthroughs.



### References

1. Min, X. and Kanan, M. W. *J. Am. Chem. Soc.* **2015**, *137*, 4701-4708.
2. Melchionna, M., Bracamonte, V., Giuliani, A., Nasi, L., Montini, T., Tavagnacco, C., Bonchio, M., Fornasiero, P., Prato, M. *Energ. Environ. Sci.*, **2018**, *11*, 1571-1580.
3. Unpublished Results.

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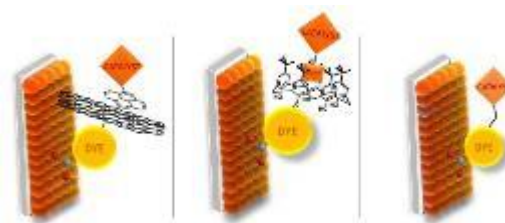
## Design Of Organic Based Photosystems For Photoelectrochemical Production Of Solar Fuels

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Nowadays, scientists are looking for a solution to contrast the high CO<sub>2</sub> emissions due to the extreme use of fossil fuels. The best one is to employ hydrogen whose combustion generates only water. Nevertheless, today hydrogen is mainly produced by the steam reforming reaction that produces also CO<sub>2</sub> as a by-product. The only way to achieve sustainability is to produce hydrogen in a cleaner way. In this scenario, PhotoElectrochemical Cells (PEC) could be a choice using only solar radiation, water and carbon dioxide, they can produce molecular oxygen, hydrogen and, hydrocarbons, mimicking the natural photosynthesis. A PEC is composed of two electrodes, soaked in an aqueous media in two different half-cells and connected by an external circuit. In the aqueous media, a water oxidation catalyst (WOC) or a hydrogen evolution catalyst are dissolved. The electrodes are p-type and n-type semiconductors (SC), both dye-sensitized (e.g by organic molecules) to enhance light harvesting in the visible region. Therefore, the irradiated dye has the strategic task of generating the hole/electrons couple and ensuring the charge transfer from the water oxidation catalyst into the SC conduction band. Organic dyes with their interesting characteristics as easy synthesis, low cost, and abundance of precursors have been playing an emerging role as light harvester in photocatalysis and PEC.<sup>1-5</sup> We decided to functionalize various organic push-pull dyes to exploit different types of interaction with the catalyst. In this way, it is possible to obtain the highest light harvesting and a faster charge transfer. In this work, we investigated three different types of interaction between dye and catalyst: in the first series, a graphene layer functionalizes the sensitizer,<sup>6</sup> and in this way it can perform  $\pi$ - $\pi$  stacking interaction with a suitable catalyst; in the second series the dye was functionalized with a calixarene ring to exploit host-guest interaction with the WOC; in the end we studied the interaction by covalent bond.

In this case, the donor moiety of the sensitizer is covalently linked with a ligand of the WOC, which is typically a ruthenium complex. This type of interaction guarantees greater stability with the aim of obtaining a real artificial photosystem.



### References

1. Cecconi, B.; Manfredi, N.; Ruffo, R.; Montini, T.; Romero-Ocana, I.; Fornasiero, P.; Abboto, A. *ChemSusChem* **2015**, *8*, 4216-28.
2. Manfredi, N.; Cecconi, B.; Calabrese, V.; Minotti, A.; Peri, F.; Ruffo, R.; Monai, M.; Romero-Ocana, I.; Montini, T.; Fornasiero, P.; Abboto, A. *Chem. Commun.* **2016**, *52*, 6977-80.
3. Manfredi, N.; Monai, M.; Montini, T.; Peri, F.; De Angelis, F.; Fornasiero, P.; Abboto, A. *ACS Energy Letters* **2017**, *3*, 85-91.
4. Manfredi, N.; Monai, M.; Montini, T.; Salamone, M.; Ruffo, R.; Fornasiero, P.; Abboto, A. *Sustainable Energy Fuels* **2017**, *1*, 694-698.
5. Decavoli, C.; Boldrini, C. L.; Manfredi, N.; Abboto, A. *Rendiconti Lincei. Scienze Fisiche e Naturali* **2019**.
6. Gatti, T.; Manfredi, N.; Boldrini, C.; Lamberti, F.; Abboto, A.; Menna, E. *Carbon* **2017**, *115*, 746-753.

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## Cerium doped transition metal oxides as visible light photoactive interfaces

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Among the semiconductors employed in photocatalytic reactions, transition metal oxides play a paramount role due to their qualities in term of stability in various media often accompanied by low or reasonable cost. The search for innovative materials in these field is oriented to select systems having a suitable electronic structure capable of harvesting solar light (which means essentially visible light) and excellent potentials to perform the desired redox process. This is practically impossible to be found in a unique system. Solid materials with large band gap values correspond, in principle, to good reduction and oxidative potentials but inevitably, to perform the charge separation, need high energy photons. On the other hand semiconductors with smaller band gap value, compatible with visible light absorption, may have unsatisfactory potentials for both reduction and oxidation. A possibility to overcome this drawback consists in modifying a semiconductor with relatively large band gap in order to make possible the absorption of visible light or to generate active interfaces between different materials. In the first case we analyzed the spectroscopic and photocatalytic properties induced by engineering the band gap of ZrO<sub>2</sub> showing how using low energy photons it is possible to observe charge separation and photocatalytic activity in spite of the relatively large band gap value of the oxide (5eV).[1] In another case we used zinc oxide (ZnO) that could be considered as an alternative to TiO<sub>2</sub> in photo-catalysis [2]. In particular, the photocatalytic activity of ZnO can be significantly enhanced by doping with lanthanide ions having 4f<sup>x</sup> configuration. The (Ce<sup>3+</sup>/Ce<sup>4+</sup>) redox pair could act as an electron scavenger that traps the bulk electrons in semiconductor modifying the band gap [3]. On the basis of the above concerns, the features of Ce doped ZnO and Ce doped ZrO<sub>2</sub> nanoparticles will be described. The prepared materials were characterized by different techniques and their photo-activity in the visible range was tested. The working hypothesis is that the two materials reacts differently toward doping and both are sensitive to visible light irradiation even working in a different way. In the case of ZnO it is very important the role of the CeO<sub>2</sub>/ZnO interfaces, while in the case of zirconia, cerium generates a solid solution with the matrix. These phenomena have been investigated by means of several methods. A specific EPR-based approach allowed to monitor and quantify the charge separation following the formation of holes in the valence band (VB) of the two materials. DFT calculations provide a rational for some of the observed phenomena [4].

### References

1. Gionco C., Paganini M.C., Giamello E., Burgess R., Di Valentin C., Pacchioni G., *J Phys.Chem.Lett*, **2014**, *5*, 447-451.
2. Li P., Wei Z., Wu T., Peng Q., Li Y., *J. Am. Chem. Soc.*, 2011, 133 5660-5663.
3. Teh C.M., Mohamed A.R., *J. Alloys Compd.*, 2011, 509, 1648-1660
4. Cerrato E., Gionco C., Paganini M.C., Giamello E., Albanese E., Pacchioni G., *ACS Appl. Energy Mater.* 2018, *1*, 4247–4260.

## **All-inorganic perovskite for photo-electrochemical CO<sub>2</sub> reduction**

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The dependence from fossil fuels in daily life is still increasing nowadays, bringing to severe issues in terms of environment pollution, public health and limited availability. For this reason it is important to consider alternative way of fuel production. One interesting option is to use renewable solar energy to convert CO<sub>2</sub> in chemicals or solar fuels through photo-electrocatalytic process. To reach this objective, the present study considers an all-inorganic perovskites (CsPbBr<sub>3</sub>), well known for its properties in harvest sunlight and long-hole diffusion, to be used in a photo-electrochemical device (PEC). The material was studied from the synthesis to the morphological and electrochemical point of view and then tested in PEC to assess the CO<sub>2</sub> conversion. The results reported a good activity of the compound towards the production of oxalic acid even if they confirmed its substantial instability in aqueous environment. Different strategies to overcome this issue were considered and thoroughly analyzed. As a results, the stability of CsPbBr<sub>3</sub> was substantially increased.

## Fast screening for N<sub>2</sub>RR catalytic activity with RRDE analysis

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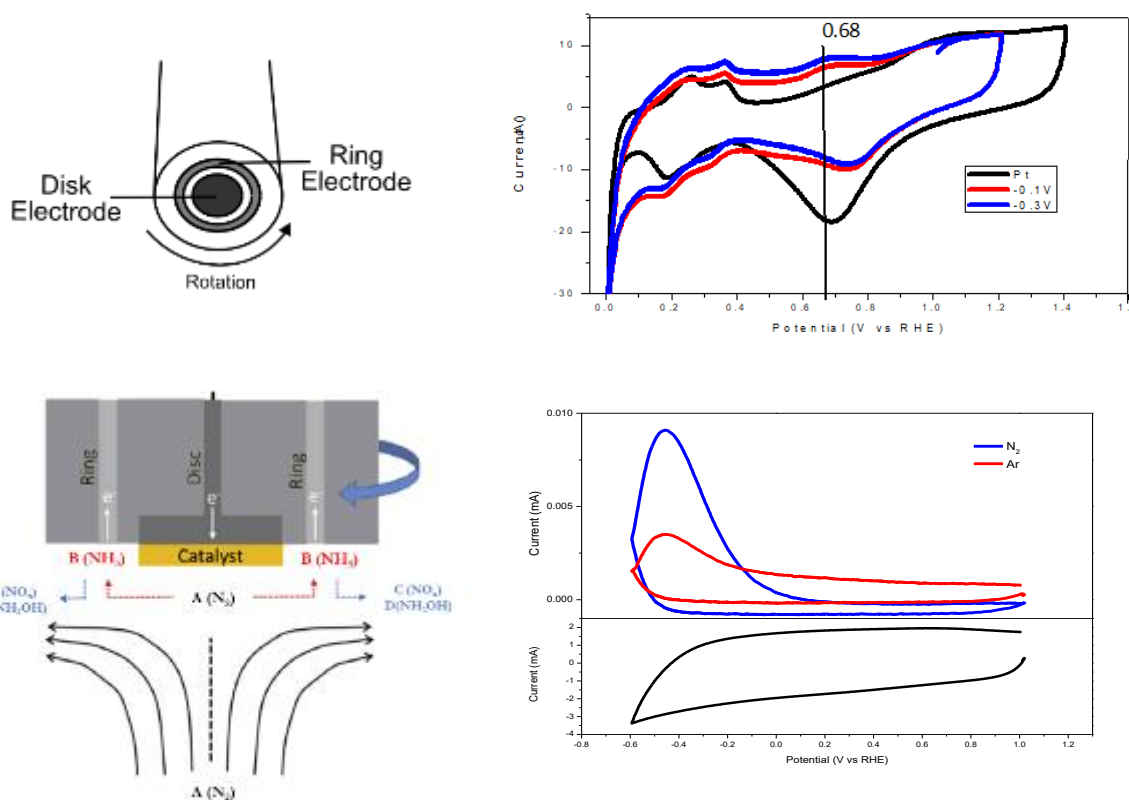
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RRDE analysis has been extensively used to study ORR processes, while its adoption for CO<sub>2</sub>RR and N<sub>2</sub>RR has lacked behind due to inherit technical complications<sup>[1,2]</sup>. Nitrogen reduction offers a unique case to develop a method for the evaluation of new materials, both because of the novelty of this reaction and the difficulties of current methods in obtaining meaningful results not biased from environmental contamination<sup>[3]</sup>.

From a preliminary study<sup>[4]</sup>, alkaline electrolytes (pH>10) appear to be optimal for the detection of ammonia on the platinum ring electrode. Other variables, such as rotation speed, scan rate and ring potentials, were optimized to create a robust procedure for a fast and reliable determination of potentials of interest for ammonia production.

This method abides to all checks necessary in the N<sub>2</sub>RR catalysts evaluation, recently summed up by Andersen *et al.*<sup>[3]</sup>, and takes advantage of a well-studied electrochemical technique that can detect and identify even traces of ammonia.



### References

1. Lates, V. et al., *Electrochim. Acta*, **2014**, 128, 75-84
2. Zhu, X. et al., *Electrochim. Acta* **2018**, 283, 1037-1044.
3. Andersen, S.Z. et al., *Nature* **2019**, 570, 504-508.
4. Marinčić, L. et al., *J Appl Electrochem* **1978**, 8, 333.

## Exploring the Flatland of 2D materials by Electrochemical STM: visualization of active sites in *operando* conditions

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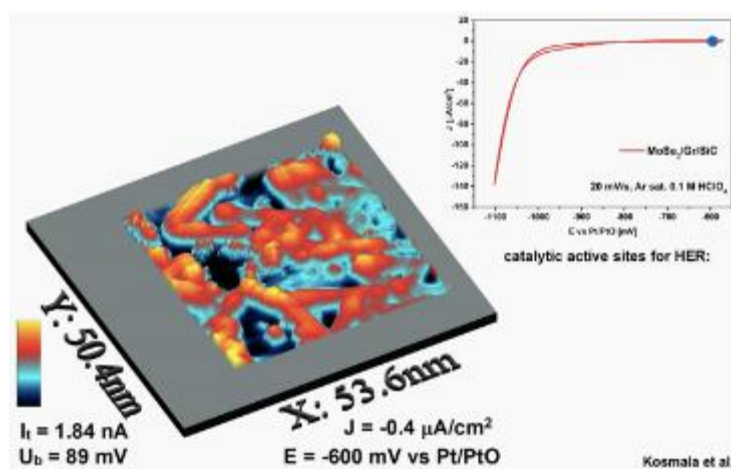
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2D materials such as chemically modified graphenes, transition metal dichalcogenides, layered double hydroxide to name only a few, are having a huge impact on electrocatalysis providing materials with outstanding activity for a variety of reactions.[1]

However, despite the intense research efforts in this field, a clear identification of the real active sites in many reactions remains a great challenge, given the necessity to employ *spatially and structurally sensitive techniques* in *operando* conditions (i.e. during the application of an electrochemical potential in the presence of an electrolyte).

Here we present an innovative approach to the study of 2D materials by using electrochemical Scanning tunneling microscopy. As demonstrated by a seminal paper,[2] this technique allows identifying the presence of catalytic processes *at the nanoscale* by observing a typical noise in the tunneling current, which is due to instantaneous variations of the tunneling junction.

By using special model systems consisting of CVD grown transition metal dichalcogenides thin films (MoSe<sub>2</sub> and WSe<sub>2</sub>), we achieved even *atomic resolution* during the hydrogen evolution reactions. This allowed us to distinguish the chemical activity of several chemical and morphological features such as single atom vacancies, step edges, and even exotic line defects such as metallic twin boundaries.[3]



### References

1. X. Chia, X., Pumera, M. *Nature Catalysis* **2018**, 10, 909-921
2. Pfisterer, J.H., Liang, Y., Schneider, O. and Bandarenka, A.S., *Nature*, **2017**, 549, 74.
3. Kosmala, T., H. Coy-Diaz, Komsa, H.-P., Ma, Y., Krashenninnikov, A., Batzill, M. Agnoli S. *Advanced Energy Materials* **2018** 180031

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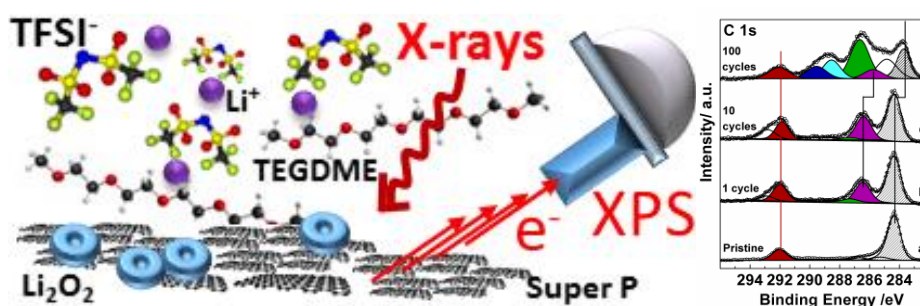
## Unravelling the surface chemistry of electrodes for Li-O<sub>2</sub> cells by means of X-ray photoelectron spectroscopy

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Li-air cells are at the cutting edge among the devices for energy storage [1]. The electrode reactions, called Oxygen Reduction Reaction (ORR) and Oxygen Evolution Reaction (OER), occur on discharge and charge at the triple interface O<sub>2</sub>/cathode/electrolyte. We recently demonstrated how this electrified interface can be successfully investigated by means of a surface-oriented multi-technique approach, where X-ray photoelectron spectroscopy is thoroughly applied [2,3]. The unrivalled sensitivity to the chemical environment of surface atoms and species is here particularly suitable to shed light on the mutual interplay among the actors involved in the oxygen electrode reactions, such as solvent, Li salt, highly reactive Li species (LiO<sub>2</sub>, Li<sub>2</sub>O<sub>2</sub>), electrode surface and undesired degradation products, etc..

We have recently reported that the long-term fading of performance of Li-air cells assembled with a carbon cathode and an ether-based electrolyte (TEGDME) is due to the carbon paper and/or the TEGDME chemical instability [2,3]. In the search for a stable cathode material for Li-air cells, our experimental activity has then been focused on carbon-free electrodes, based on novel M<sup>n+</sup>-doped NiCo<sub>2</sub>O<sub>4</sub>@Ni (M<sup>n+</sup> = Cr<sup>3+</sup>, Cu<sup>+</sup>, Zn<sup>2+</sup> etc.) materials [4]. We report here some examples of how XPS helps address the fate of electrochemically generated species and their evolution during the lifecycle of the cell.



### References

1. Feng, N., He, P., Zhou, H. *Adv. Energy Mater.* **2016**, 6, 1-24.
2. Carboni, M., Brutti, S., Marrani, A.G., *ACS Appl. Mater. Interfaces* **2015**, 7, 21751-21762.
3. Giacco, D., Carboni, M., Brutti, S., Marrani, A.G., *ACS Appl. Mater. Interfaces*, **2017**, 9, 31710-31720.
4. Giacco, D., Marrani, A.G., Brutti, S., *Materials Letters* **2018**, 224, 113-117.

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## Recent advances in (photo)electrochemical *operando* X-ray absorption spectroscopy. Analysis on time- and space-resolution

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A deep understanding of reaction mechanisms is required for the rational design of catalysts by better defining structure/activity relations.

Operando (or *quasi-operando*) X-ray absorption spectroscopy (XAS) represents one of the most powerful available techniques to study the fine structure and the behavior of electrode and photoelectrode materials [1].

During the last years, we have been developing new methods and experimental approaches to better fit the capabilities of XAS in (photo)electrochemistry. Among these, Fixed Energy X-Ray Absorption Voltammetry (FEXRAV) represents a novel tool for fast and easy preliminary characterization of electrodes and photoelectrodes. It consists in recording the absorption coefficient at a fixed energy while varying at will the electrode potential. Still, FEXRAV gives important information by itself and can serve as a preliminary screening of the potential window or for choosing the best experimental conditions for a better targeted XAS analysis. This led to new insights in the mechanisms of the oxygen evolution reaction [2,3].

Other time-resolved techniques will be described, including those based on energy dispersion [4], and the overview is completed by considering time-resolved studies on photoelectrodes [5,6,7].

Thanks to the intrinsic element selectivity of XAS, this technique becomes a powerful “microscope” to selectively study specific positions within highly complex semiconductor/overlayer/electrolyte systems.

### References

1. Minguzzi, A., Ghigna, P. in *Electroanalytical Chemistry: A Series of Advances*, **2017**, Vol 27
2. Minguzzi, A. *Chem. Sci.* **2014**, *5*, 3591.
3. Minguzzi, A. *ACS Catalysis*, **2015**, *5*, 5104
4. Rondinini, S. *Electrochim. Acta*, **2016**, *212*, 247.
5. Fracchia, M. *Surfaces*, **2018**, *1*, 138
6. Minguzzi, A. *Phys. Chem. Chem. Phys.*, **2017**, *19*, 5715.
7. Fracchia, M. *Electrochim. Acta*, **2019**, *320*, 134561

## Co-doped reduced graphene oxide as novel electrocatalyst for the oxygen and carbon dioxide reduction reaction.

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In recent years, the negative impact of anthropogenic CO<sub>2</sub> emissions on our planet's climate has motivated a progressive transition from a global energy scenario heavily reliant on fossil fuels to one based on environmentally benign, renewable energy sources. Consequently, the past decade has seen considerable growth in the development of materials for fuel cell electrodes that consume H<sub>2</sub> and O<sub>2</sub> as sustainable technologies<sup>1</sup>. Therefore electrochemical reactions such as oxygen reduction reaction (ORR) in these energy converting systems are becoming increasingly important<sup>1</sup>. However, while the long-term solution is abandoning fossil fuels for renewable sources, it has been shown<sup>2</sup> that in the short-to-medium term conventional fuels will still be used and CO<sub>2</sub> emissions will have to be compensated for. To this aim, one of the most interesting strategies is the electroreduction of captured CO<sub>2</sub> (CO<sub>2</sub>RR) to value-added fuels and chemicals.

Although very promising, these technologies based on electrochemical reduction reactions still face several challenges, due to the high reaction barriers, slow kinetics and low selectivity towards a specific target product. To tackle these problems, in the last decade a growing theoretical effort has been focused on the quantum modelling of materials and reaction mechanisms in electrochemical cells and, more recently, on CO<sub>2</sub> and O<sub>2</sub> electroreduction in some specific systems. Herein we present the recent progress of co-doped reduced graphene oxide and its role in electrochemical reduction reactions, such as ORR and CO<sub>2</sub>RR. Carbon-based materials are very cheap and have good electric properties, but they hardly show low onset potential and high efficiency, yet. Doping rGO with metal ions has shown to be an effective way to tune its electronic properties and catalytic activity. We employed Density Functional Theory (DFT) calculations to predict realistic structures of metal-containing rGO co-doped with nitrogen atoms. In particular, we considered several model host-systems involving N-graphitic, N-pyridinic and N-pyrrolic-like which may eventually coordinate metal (M) ions (M=Mn, Mg, Co, Ni, Zn, Cu etc.). We investigated how the properties of rGO depend on the type of doping elements and identify the most active catalytic sites. Further we identified the reaction steps that lead from CO<sub>2</sub> to the specific final product (value-added chemicals such as formic acid, carbon monoxide, synthetic gas and methanol) or from O<sub>2</sub> to H<sub>2</sub>O, calculating key quantities, such as reaction barriers and onset potentials, that allow to propose a rational design of new catalysts to be subsequently implemented and tested experimentally.

### References

1. Chu, S., Majumdar, A., *Nature*, **2012**, 488, 294-303.
2. [www.weforum.org/agenda/2017/10/fossil-fuels-will-dominate-energy-in-2040/](http://www.weforum.org/agenda/2017/10/fossil-fuels-will-dominate-energy-in-2040/).

## Surface Engineering of MoS<sub>2</sub> with Tailored Functional Groups: a Rational Design of Heterogeneous Catalysts for Renewable Energy Applications

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Transition Metal Dichalcogenides (TMDCs) have attracted huge attention in the last decade due to their promising applications in several fields of heterogeneous catalysis. In particular, structural and electronic properties of MoS<sub>2</sub> have boosted its application in various electrocatalytic processes at the heart of renewable energy technology (*i.e.* Hydrogen Evolution and Oxygen Reduction Reactions) as a valuable and cheap alternative to the benchmark Pt-based catalysts.<sup>1</sup> Many strategies have been developed to date to enhance the poor electrochemical activity of pristine MoS<sub>2</sub>.<sup>1</sup> Among them, doping and chemical modification of the surface/edges of MoS<sub>2</sub> nanosheets with light heteroatoms (*i.e.* O, N, P) have remarkably enhanced their efficiency.<sup>2</sup> However, despite of great research efforts, preparing tailored hetero-doped MoS<sub>2</sub> samples through a rational bottom-up synthesis of novel "hybrid" composites, still remains a challenging matter in the field of catalysis and material science. Covalent decoration of MoS<sub>2</sub> flakes with selected organic groups could represent a convenient way to meet with this challenging issue. Although several MoS<sub>2</sub> functionalization strategies have been reported, effective and easy tunable protocols for its surface decoration are still lacking.<sup>3</sup> On this ground, we developed a convenient and highly efficient methodology for the anchoring of aryl-azido groups to MoS<sub>2</sub> nanosheets. Their subsequent post-synthetic modification *via* "click chemistry" with terminal acetylenes has been used to generate homo- and hetero-decorated MoS<sub>2</sub> flakes.<sup>4</sup> As a further step-forward towards the simple and versatile MoS<sub>2</sub> engineering, a new functionalization strategy based on the single-step anchoring of differently substituted epoxyde derivatives has been settled up.<sup>5</sup> Overall, these studies represent a milestone towards the fine tuning of TMDCs chemico-physical and electronic properties, thus prompting their use in the field of renewable energy technology.

### References

1. Jayabal, S., Saranya, G., Wu, J., Liu, Y., Geng, D., Meng, X. *J. Mater. Chem. A*, **2017**, 5, 24540.
2. a) Huang, X., Leng, M., Xiao, W., Li, M., Ding, J., Tan, T. L., Xue, J. *Adv. Funct. Mater.*, **2017**, 27, 1604943;  
b) Huang, H., Feng, X., Du, C., Wu, S., Song, W. *J. Mater. Chem. A*, **2015**, 3, 16050; c) Xiao, W., Liu, P., Zhang, J., Song, W., Feng, Y.P., Gao, D. *Adv. Energy Mater.* **2017**, 7, 1602086
3. Chen, X., McDonald, A.R., *Adv. Mater.*, **2016**, 28, 5738-5746
4. Tuci, G., Mosconi, D., Rossin, A., Luconi, L., Agnoli, S., Righetto, M., Pham-Huu, C., Ba, H., Cicchi, S., Granozzi, G., Giambastiani, G. *Chem. Mater.*, **2018**, 30, 8257-8269.
6. Tuci, G., Mosconi, D., Granozzi, G., Giambastiani, G. *et al. manuscript in preparation*

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## Mixed 1T-2H MoS<sub>2</sub> nanoflakes electrodes for Li-ion supercapacitors and electrocatalyst for HER.

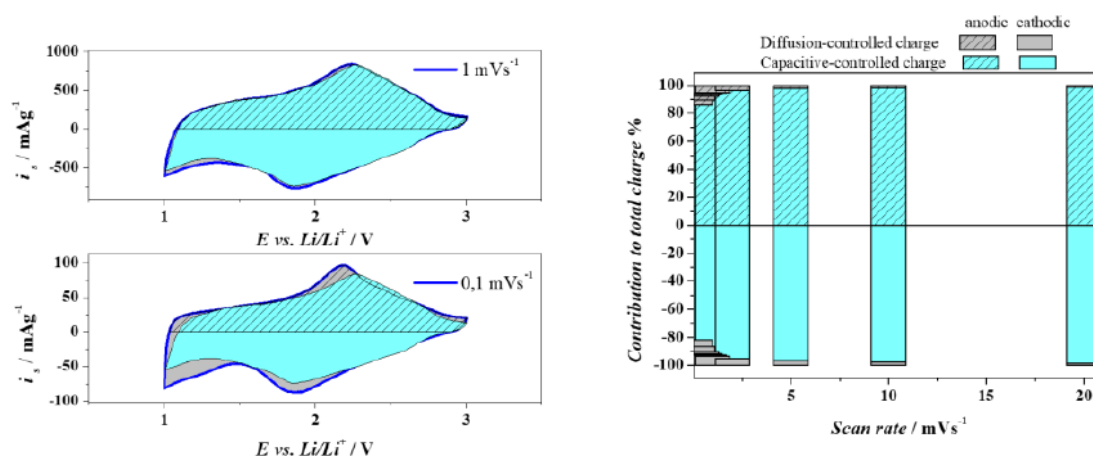
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Molybdenum disulfide (MoS<sub>2</sub>) is a layered transition-metal dichalcogenide which has attracted great interest as material for energy conversion and storage. MoS<sub>2</sub> exists in three different polymorphs that are the stable 2H, the meta-stable 1T and 3R with the possibility of obtaining 2D nanostructures. Herein, we report the synthesis and characterization of a few-layer hybrid material containing both metallic 1T and semiconducting 2H phases (1T-2H MoS<sub>2</sub> nanoflakes) obtained with phosphomolybdic acid and L-cysteine in one-pot hydrothermal synthesis. Morphological and structural characterizations are presented and compared to commercially available 2H-MoS<sub>2</sub> powders. The thermal conversion of the 1T-2H MoS<sub>2</sub> on fully 2H MoS<sub>2</sub> is studied by means of X-ray Photoelectron Spectroscopy due to the possibility to quantify the relative amount of 1T and 2H phase and maintaining the same morphology. This conversion allows to appreciate the superior properties of the 1T-2H mixed phases as catalyst for hydrogen evolution reaction (HER) and as electrode material in both aqueous and Li ion supercapacitors. In order to enhance the capacitive proprieties of the mixed phases, the 1T-2H nanoflakes were finely alternated to reduced graphene oxide (rGO) sheets by obtaining a tridimensional matrix of rGO-MoS<sub>2</sub>. This co-synthesis allowed to increase the cycling life and stability of aqueous supercapacitors.



### References:

1. M. Acerce, D. Voiry, M. Chhowalla. *Nature Nanotechnology*. **2015**, 10, 4, 313-318.
2. J.B. Cook, H. Kim, T.C. Lin, C. Lai, B. Dunn, S.H. Tolbert. *Adv. Energy Mater.* **2017**, 7, 2, 1601283.
3. J.A. Gigot, M. Fontana, M. Serrapede, M. Castellino, S. Bianco, M. Armandi, B. Bonelli, C.F. Pirri, E. Tresso, P. Rivolo. *ACS Appl. Mater. Interfaces*. **2016**, 8, 48, 32842-32852.

## Tunable optical absorption and charge separation in black/blue phosphorene interfaces

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Single layer black and blue phosphorenes possess largely different electronic and optical properties that can yield interesting features when these two materials are stacked in a van der Waals heterostructure. By employing *ab initio* techniques, we devise an almost strain-free heterostructure and investigate its electronic properties within the  $G_0W_0$  approximation. An intrinsic type-II band alignment with an indirect gap of 2.09 eV is found. The application of mild strain on the supercell results in a direct bandgap at the  $\Gamma$  point. Optical properties are then studied by solving the Bethe-Salpeter equation and reveal that the strain induces an almost complete separation of the optically excited holes and electrons between the two layers. This peculiar characteristic, together with the position of the excitonic peak in the visible spectrum, points out that this structure can be very promising for several applications in optoelectronics, photovoltaics and photocatalysis.

## Laser-induced graphene as active materials for energy storage into flexible and stretchable micro-supercapacitors

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Graphene and graphene-like materials have been intensively studied in the field of electrochemical energy storage, and in the last three years the research focus has been broadened on new layered 2D-materials, such as MoS<sub>2</sub> and other transition metal dichalcogenides. Recently, laser-induced graphene (LIG) has been proposed as an efficient active material for flexible supercapacitor (SC) electrodes. This material consists of a 3D network of multilayer graphene obtained by a laser writing process on polymer surface during which the sp<sup>3</sup>-carbon atoms in the polymer are photothermally converted to sp<sup>2</sup>-carbon atoms. Herein we are reporting a rapid one-pot synthesis of MoS<sub>2</sub>-decorated laser induced graphene by direct writing of polymeric foils. By covering the polymer surface with a layer of MoS<sub>2</sub> dispersion before processing, it is possible to obtain an in-situ decoration of porous graphene network during laser writing, enabling both electric double layer and pseudo-capacitance behavior (Figure 1).[1] Additionally, a simple method to transfer the LIG porous layer obtained onto polyimide sheet to a transparent and elastomeric substrate (PDMS) is proposed.[2] Additional results have been achieved in order to exploit the elastomeric nature of the host matrix allowing high deformation-tolerance of the fabricated devices opening the way to the development of stretchable and wearable energy storage sources.

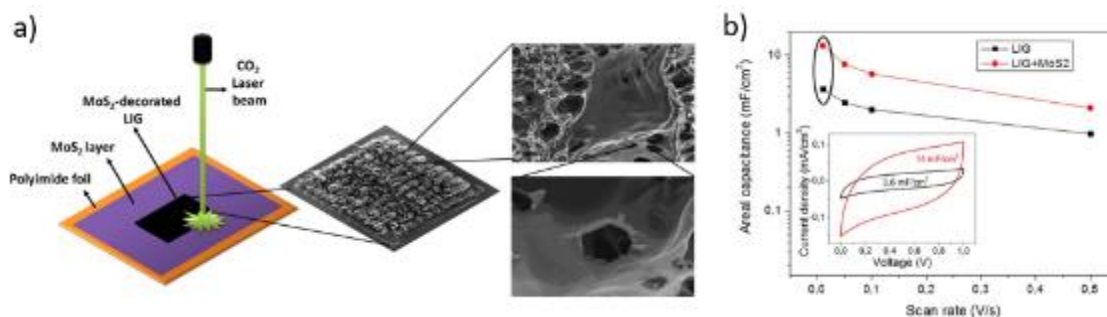


Figure 1. Scheme of the fabrication process of the laser-induced graphene decorated by MoS<sub>2</sub> flakes together with electron microscope images (a) and its electrochemical performances in aqueous based electrolyte (b).

### References

1. Clerici F. et al., *ACS applied materials & interfaces* **2016**, 8, 10459.
2. Lamberti A. et al., *Advanced Energy Materials* **2016**, 6, 1600050.

## Novel approaches for the application of electrodeposited silicon anodes for lithium ion batteries

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The growing demand of energy storage devices with high energy density led to an explosion of research on new electrode materials for Lithium-Ion-batteries (LIBs). Electrodeposited silicon has turned out to be a very promising material, since it can be directly deposited on a current collector. However, its drastic volume change of more than 300% during lithiation is still a big challenge [1].

To buffer this strong volume expansion and the accompanied mechanical stress, we applied porous copper as a substrate for the electrodeposition of silicon. A copper and nickel foils were used for comparison. Figure 1 shows the results of the galvanostatic cycling of the thus prepared electrodes in half-cells. Within a few cycles the coulombic efficiency (CE) reached almost 100%, when porous copper is used as current collector, while on the flat substrates showed a maximum efficiency of about 98%. Rate capability experiments, however, showed that the porous structure suffers more from increasing the C-rate, which is mainly due to the restricted diffusion of the lithium ions into the pores of the substrate. The superior performance of this material can be also seen by the full recovery of the capacity, when the C-rate is turned back to C/10 again. Apart from the substrate the electrolyte for silicon deposition plays a significant role on the stability and behavior as anode, as it can change the composition of the silicon layer. In order to clarify the effect of electrolyte, we investigated two different electrolyte systems on basis of an ionic liquid (IL) and sulfolane, by means of electrochemical quartz crystal microbalance (EQCM). The data display a smooth silicon film with only minor impurities for the sulfolane electrolyte. The high damping in case of the IL suggests the formation of a rough and/or viscoelastic layer.

XPS measurements exhibit a considerable amount of C, N and S in the deposits when the IL was used for electrodeposition.

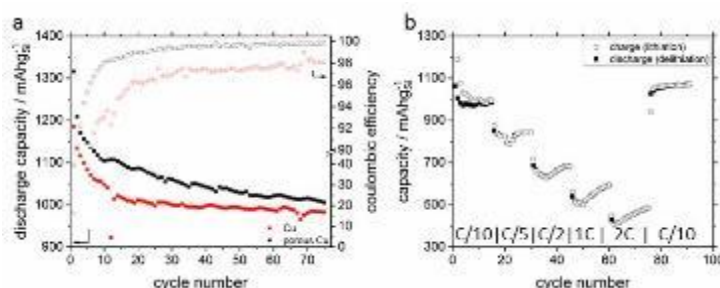


Figure 2: Galvanostatic cycling of electrodeposited silicon from 0.5 M  $\text{SiCl}_4$  dissolved in sulfolane in 1:1 EC/DMC with 10 vol.% FEC and 1 M  $\text{LiPF}_6$ . (a) Cycling rate C/5 on Cu (red) and porous Cu (black), (b) rate-capability test on porous Cu.

### References

1. Obrovac, M. N., *Chem. Rev.*, **2014**, *114*(23), 11444-11502

## Enhancing Performance and Stability of Nanocomposite Alloying Anodes for Li-ion Batteries

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The development of Li-ion technology has allowed the portable electronics revolution and is now fostering the widespread diffusion of hybrid and electrical vehicles (xEV). However, the increasing demand in energy density requests for a breakthrough in active materials for Li storage. High-capacity anode materials, relying on mechanisms alternative to intercalation such as alloying or conversion, have been investigated for several years, but severe limitations arise from lack of cycle-over-cycle efficiency, because of relevant structural and interfacial rearrangements upon prolonged Li uptake/release cycles [1]. In this context, the use of nanocomposite active materials and the optimization of electrode and electrolyte formulations are among the more efficient strategies to enhance structural, morphological and interfacial stability and thus electrochemical performance.

We present here how the combined use of tailored nanometer morphologies, efficient binders and optimized electrolytes strongly enhance performance and stability of anodes based on Si and Sn, yielding capacity values as high as 1000 mAh g<sup>-1</sup> and outstanding cycling stability.

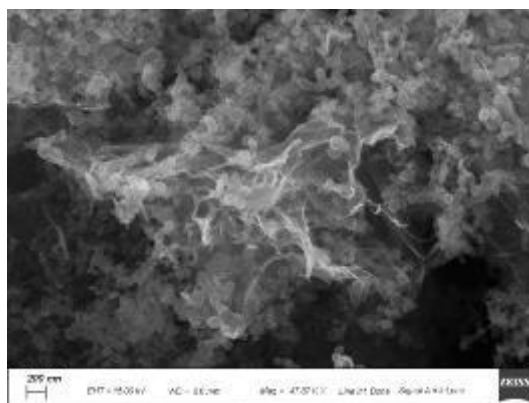


Figure 1. SEM image of active Si embedded in a nanosize inorganic matrix.

### References

1. Obrovac, M.N., Chevrier, V.L. *Chem. Rev.* **2014**, 114, 11444-11502.

## Iodoaluminate Ionic Liquid Electrolytes for Advanced Multivalent Twin Metals Secondary Batteries

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Recent advances in technological fields such as portable electronic devices, automotive, load levelling and peak shaving have resulted in an urgent need of new and improved energy conversion and storage systems.

Magnesium secondary batteries, first proposed in the late 1990s [1], demonstrate intrinsic advantages over other competing technologies (e.g., Li secondary batteries); thus, they are promising candidates for energy conversion and storage. Early Mg secondary batteries comprised of a metallic magnesium anode, a composite cathode and a polymer electrolyte (e.g. polyethylene glycol with  $\delta$ -MgCl<sub>2</sub> salt) [2]. Subsequent electrolytes based on Grignard and other organo-Mg compounds were studied [3]. Nevertheless, these electrolytes suffer from several drawbacks associated with their low chemical stability, high vapor pressure and flammability. In order to overcome these drawbacks, the use of ionic liquids (ILs) as a solvent for stable Mg-ion source precursors was proposed [4-6].

Here we present a new room-temperature ionic liquid synthesized by reacting 1-ethyl-3-methylimidazolium iodide with aluminum iodide.  $\delta$ -MgI<sub>2</sub> is used as the magnesium source to obtain a family of Mg<sup>2+</sup> conducting electrolytes with the general formula [EMImI/(AlI<sub>3</sub>)]/( $\delta$ -MgI<sub>2</sub>)<sub>x</sub> (0 ≤ x ≤ 0.023).  $\delta$ -MgI<sub>2</sub> is a highly disordered form of MgI<sub>2</sub> synthesized by reacting metallic Mg with n-iodobutane [7].

The chemical composition of the samples was determined by ICP-AES and microanalysis. Their thermal stability and transitions were studied by differential scanning calorimetry (DSC). The applicability of the [EMImI/(AlI<sub>3</sub>)]/( $\delta$ -MgI<sub>2</sub>)<sub>x</sub> electrolytes in prototype cells was evaluated by studying the conductivity of the materials as well as the electrochemical performance in terms of Mg-Al deposition/stripping, Coulombic efficiency, and exchange current density.

### References

1. Di Noto, V.; Fauri, M. Magnesium-based Primary (Non Rechargeable) and Secondary (Rechargeable) Batteries. *PCT/EP00/07221*, **1999**.
2. Di Noto, V.; Lavina, S.; Longo, D.; Vidali, M. *Electrochim. Acta* **1998**, 43, 1225-1237.
3. Liebenow, C.; Yang, Z.; Lobitz, P. *Electrochem. Commun.* **2000**, 2, 641-645.
4. Bertasi, F., Hettige, C., Sepehr, F., Bogle, X., Pagot, G., Vezzù, K., Negro, E., Paddison, S.J., Greenbaum, S.G., Vittadello, M., Di Noto, V. *ChemSusChem* **2015**, 8, 3069-3076.
5. Bertasi, F., Sepehr, F., Pagot, G., Paddison, S.J., Di Noto, V. *Adv. Funct. Mater.* **2016**, 26, 4860-4865.
6. Pagot, G., Bertasi, F., Vezzù, K., Sepehr, F., Luo, X., Nawn, G., Negro, E., Paddison, S.J., Di Noto, V. *Electrochim. Acta* **2017**, 246, 914-923.
7. Vittadello, M.; Stallworth, P. E.; Alamgir, F. M.; Suarez, S.; Abbrent, S.; Drain, C. M.; Di Noto, V.; Greenbaum, S. G. *Inorg. Chim. Acta* **2006**, 359, 2513-2518.

## C-encapsulated T-Nb<sub>2</sub>O<sub>5</sub> nanocrystals for high performance Li- and Na-ion batteries

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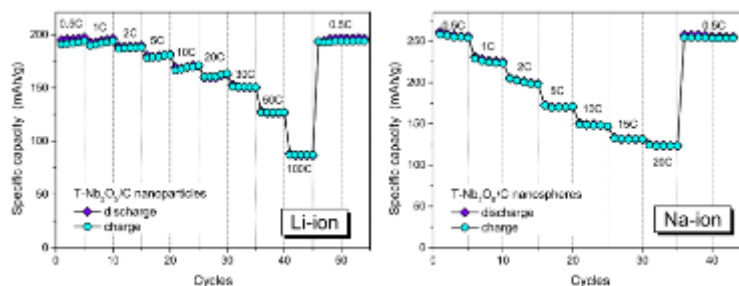
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This contribution [1] presents an effective route, based on a two-step process to synthesise carbon-encapsulated metal oxide nanocrystals (NCs). The first step consists of the solvothermal reaction of a metal precursor with acetophenone to simultaneously produce metal oxide NCs and an organic carbon precursor homogeneously coating their surface, thus limiting their growth and preventing their agglomeration. The second step consists in the heat treatment to increase the crystallinity degree of the metal oxide NCs and carbonize the organic carbon precursor.

The case of carbon-encapsulated orthorhombic niobium oxide (T-Nb<sub>2</sub>O<sub>5</sub>/C) NCs is here considered as an example and it is shown that the C content and size of the T-Nb<sub>2</sub>O<sub>5</sub> NCs can be controlled, while the morphology of the T-Nb<sub>2</sub>O<sub>5</sub>/C nanostructures produced can be varied via the addition of assembly promoting agents. This enables tuning and optimization of their properties, as demonstrated by utilizing the produced T-Nb<sub>2</sub>O<sub>5</sub>/C nanocomposites as active anode materials in Li- and Na-ion batteries.

The nanomaterials prepared under optimized conditions exhibit excellent high rate performance, delivering a specific capacity of ~90 mAh/g at 100 C rate in a Li-ion electrolyte and ~125 mAh/g at 20 C rate in a Na-ion electrolyte [1].



### References

1. Han X., Russo P.A., Goubard-Bretesché N., Patanè S., Santangelo S., Zhang R., Pinna N. *Adv. Energy Mater.* **2019**, *9*, 1902813–1902813

*Acknowledgements:* This work was partially funded by the Italian Ministry of Education, University and Research (MIUR) through the PRIN project 2017MCEEY4, TRUST (TowaRds sUstainable, high-performing, all-solid-state Sodium-ion baTteries).

## Functionalization of ionic liquid-based electrolytes for advanced lithium ion batteries

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Li-ion batteries (LIBs) have been recognized as powerful energy storage devices having appealing energy density and long cycle life. Because of the exponential growth in the energy density of LIBs, there is a growing demand for improving the safety of LIBs. Electrolyte solutions are traditionally composed of flammable organic solvents that add safety concern to LIBs.[1] Ionic liquids (ILs) are promising alternative components in the electrolytes because they greatly improve the thermal stability of electrolytes and also suppress the decomposition of electrolytes by forming solid electrolyte interface (SEI) on anode surfaces. Generally, ILs are used in designing electrolytes in three ways: (1) as an electrolyte itself (IL-Li salt system), (2) as a majority component in electrolytes, or (3) as an additive for electrolytes. The former two classes show an advantage in self-extinguishing property but have a disadvantage in ionic conductivity, while the last one exhibits a compromising property between these.

With respect to the design of ILs, we have reported outstanding properties of ether-functionalized cations such as a reduced crystallinity at lower temperatures and a high dissociation ability in variable electrolytes. In this study, the cations were combined with imide- or borate-anions, and the resulting ILs were assessed as an electrolyte itself or as an additive for battery grade electrolytes. The effects of the use of ILs on thermal and electrochemical properties, including the crystallinity, electrochemical stability window, interface characteristics towards carbon-based and lithium electrodes were analyzed.[2] By taking these results into account, the functions allocated to the cations and to the anions will be summarized.

### References

1. “Recommendations on the Transport of Dangerous Goods”, the United Nation.
2. Navarra, M.A.; Fujimura, K.; Sgambetterra, M.; Tsurumaki, A.; Panero, S.; Nakamura, N.; Ohno, H.; Scrosati, B.; *Chem. Sus. Chem.* **2017**, *10*, 2496–2504; Tsurumaki, A.; Branchi, M.; Rigano, A.; Poiana, R.; Panero, S.; Navarra, M.A.; *Electrochim. Acta*, **2019**, *315*, 17-23.

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## Quantitative Lithiation of Graphite Anode in Li ion Batteries: an *in situ* Electron Paramagnetic Resonance Study

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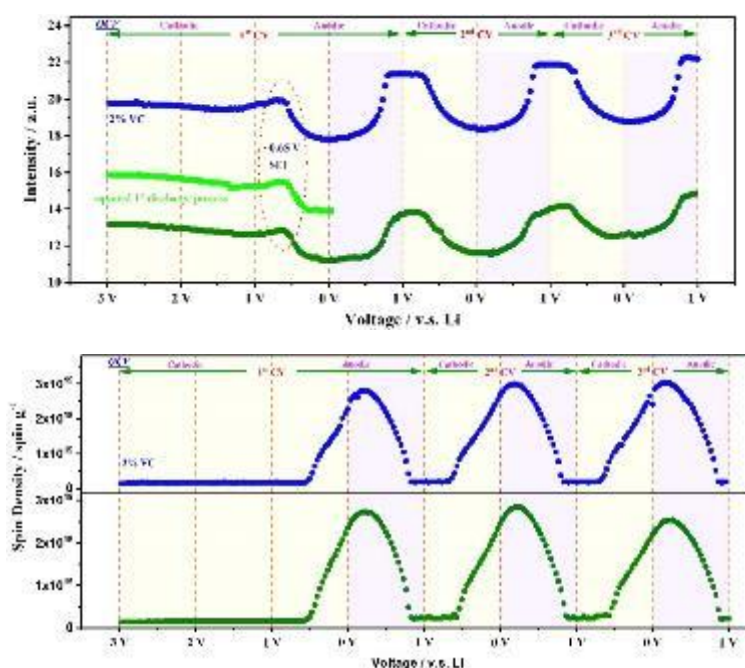
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An *in situ* electrochemical for electron paramagnetic resonance (EPR) spectroscopy cell has been built to study the graphite anode of Lithium ion batteries. The changes in conductivity of the anode due to the lithiation/de-lithiation ( $\text{Li}_x\text{C}_6$ ,  $0 \leq x \leq 1$ ) process and also the solid electrolyte interphase (SEI) formation was monitored via the quality factor (Q) change during cyclic voltammetry (CV). The  $\text{Li}^+$  ions intercalation and de-intercalation into the graphite structure was quantitated via the EPR spin density change with potential. Lithium dendrite or “dead lithium” formation at the graphite anode could also be detected by the EPR signal intensity change; vinylene carbonate (VC) additives inhibited the formation of dendrites.



### References:

1. Wang, B. *Angew. Chem. Commun.* **2018**, *54*, 3827-3380.
2. Wandt, P. J. *Mater. Today* **2018**, *21*, 231-240.
3. Wang, B. *Angew. J. Electroanal. Chem.* **1995**, *397*, 315-319.

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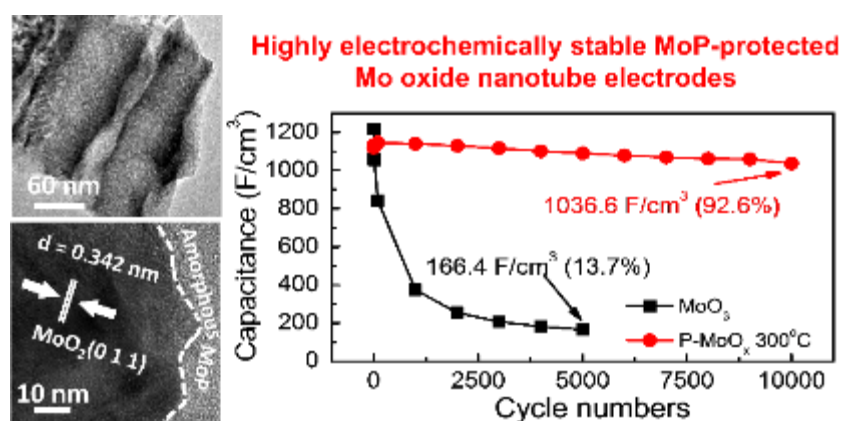
## High Efficient Nanotubes Arrays Supercapacitors Electrodes Enabled by Engineered MoO<sub>x</sub>/MoP Heterostructure

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Recently, molybdenum oxide have received attention owing to their unique chemical and physical properties and the resulting high potential in energy conversion and storage (such as battery, supercapacitor).<sup>1</sup> However, the poor conductivity and poor stability of pure Mo oxide limits the practical application. The formation of one dimensional nanoporous materials, especially heterostructure nanotubes have been proved effective way to overcome these shortage.<sup>2-4</sup> Here, we report the fabrication of one dimension molybdenum oxide nanotube arrays by anodization. Following, the amorphous MoP protective shell on Mo oxide nanotube heterostructure structure can be transformed by partially phosphidation on as-formed molybdenum oxide nanotubes. The protective of MoP shell not only overcome the limitations in capacitive performance caused by the relatively poor conductivity but also stabilized Mo oxide nanotube array for long-term cycling.



### References

1. X. Hu, W. Zhang, X. Liu, Y. Mei, Y. Huang, *Chem. Soc. Rev.* **2015**, 44, 2376.
2. Q. Wei, F. Xiong, S. Tan, L. Huang, E. H. Lan, B. Dunn, L. Mai, *Adv. Mater.* **2017**, 29, 1602300.
3. B. Jin, X. Zhou, L. Huang, M. Lickleder, M. Yang, and P. Schmuki, *Angew. Chem. Int. Ed.*, **2016**, 55, 12252–12256.
4. B. Jin, S. Hajazi, H. Chu, S. Mohajernia, N. T. Nguyen, M. Yang, M. Altomare, and P. Schmuki, *Applied Materials Today*, **2019**, 17, 227-235.

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## Are renewable-based processes economically sustainable today? The case of H<sub>2</sub> production and distributed energy cogeneration from bioethanol

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The possibility to obtain chemicals and/or fuels from renewable sources is an attractive option in order to develop an integrated biorefinery concept. Bioethanol can be a suitable starting material for the production of H<sub>2</sub> as fuel or syngas. Hydrogen is considered as future energy vector that can meet the ever growing world energy demand in a clean and sustainable way.

In this work, the centralized production of pure hydrogen from bioethanol was investigated using the process simulation software AspenONE Engineering Suite<sup>®</sup>. After designing the process and the implementation of kinetic expressions based on experimental data collected in our lab for the steam reforming of bioethanol, an economic evaluation and sensitivity analysis were carried out, assessing conventional economic indicators such as the net present value (NPV), internal rate of return (IRR) and pay-out period of the plant. In particular, three scenarios were studied by changing the fuel of the furnace that heats up the ethanol steam reformer, *i.e.* the main energy input, using methane, ethanol or part of the produced hydrogen. Heat integration was also optimised for the best scenario.

Sensitivity analysis was applied to investigate the economic performance of bioethanol steam reforming under different circumstances, changing feedstock cost, hydrogen selling price, taxes and capital expenditure (CAPEX). The results highlight the advantages and drawbacks of the process on a large scale (mass flow rate of bioethanol 40,000 ton year<sup>-1</sup>) for pure hydrogen production from bioethanol. The higher return is achieved when using methane as auxiliary fuel. The process was strongly OPEX sensitive and very tightly correlated to the bioethanol cost and hydrogen selling price.

This case was compared with the use of bioethanol in a distributed heat and power cogeneration system, where the cost determining item was as expected the fuel cell, together with the H<sub>2</sub> purification section.

In all the cases, the possibility to operate with less expensive, diluted bioethanol streams was investigated.

### References

1. Compagnoni M., Mostafavi E., Tripodi A., Mahinpey N., Rossetti I., *Energy&Fuels* **2017**, *31*, 2988–12996.
2. Mattos L.V., Jacobs G., Davis B.H., Noronha F.B., *Chem. Rev.* **2012**, *112*, 4094–4123.

## Eumelanin as Novel (Bio)Material for Energy Applications ?

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Eumelanin is an ubiquitous natural pigment responsible for the pigmentation of many plants and animals and men, whose electrical properties have been studied since the 1960's. Based on its charge carrier transport properties, chelating properties, biodegradability and intrinsic biocompatibility, eumelanin stands today as a unique source of inspiration for the design and implementation of soft biocompatible multifunctional materials for organic bioelectronics.<sup>1</sup>

The hydration dependent electrical conductivity of eumelanin, once studied in the frame of amorphous semiconductivity, is now interpreted in the perspective of a mixed ionic-electronic conductivity.<sup>2</sup> Eumelanin also exhibits strong affinity toward transition metal ions susceptible of redox transition in biological environments.<sup>3</sup>

Eumelanin based application in batteries,<sup>4</sup> photocatalysis,<sup>5</sup> supercapacitors,<sup>6</sup> etc., will be addressed here along with representative examples of structure-property function relationships, fundamental tailoring strategies, pigment processing and the balance of ionic-electronic processes eumelanin-based hybrids to orient ongoing efforts toward innovative eumelanin-based technology for energy applications.

### References

1. Barra, M.; Bonadies, I.; Carfagna, C.; Cassinese, A.; Cimino, F.; Crescenzi, O.; Criscuolo, V.; Marco, D.; Maglione, M. G.; Manini, P.; Migliaccio, L.; Musto, A.; Napolitano, A.; Navarra, A.; Panzella, L.; Parisi, S.; Pezzella, A.; Prontera, C. T.; Tassini, P., *Mrs Advances* **2016**, *1*, 3801-3810.
2. Wunsche, J.; Deng, Y. X.; Kumar, P.; Di Mauro, E.; Josberger, E.; Sayago, J.; Pezzella, A.; Soavi, F.; Cicoira, F.; Rolandi, M.; Santato, C., *Chem. Mater.* **2015**, *27*, 436-442.
3. d'Ischia, M.; Wakamatsu, K.; Napolitano, A.; Briganti, S.; Garcia-Borrón, J. C.; Kovacs, D.; Meredith, P.; Pezzella, A.; Picardo, M.; Sarna, T.; Simon, J. D.; Ito, S., *Pigment Cell & Melanoma Research* **2013**, *26*, 616-633.
4. Kim, Y. J.; Khetan, A.; Wu, W.; Chun, S. E.; Viswanathan, V.; Whitacre, J. F.; Bettinger, C. J., *Adv. Mater.* **2016**, *28*, 3173-3180.
5. Migliaccio, L.; Gryszel, M.; Derek, V.; Pezzella, A.; Glowacki, E. D., *Materials Horizons* **2018**, *5*, 984-990.
6. Kumar, P.; Di Mauro, E.; Zhang, S. M.; Pezzella, A.; Soavi, F.; Santato, C.; Cicoira, F., *Journal of Materials Chemistry C* **2016**, *4*, 9516-9525.

## Flowable semi-solid electrodes enable a concept for battery sustainability

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The battery market is rapidly increasing. The electric vehicle market alone has grown to over 2 million vehicles sold by 2016,<sup>1</sup> projecting a need of 200,000 tonnes of lithium-ion battery cathode material annually by 2020.<sup>2</sup> As a result, sustainability of batteries has raised concerns which is driving interest in end-of-life scenarios of spent batteries as well as recyclability. Indeed, the new large-scale and long-term European research initiative Battery 2030+ pays special attention to recyclability and circular economy (Figure 1a).

In contrast to redox flow batteries, the active energy storage materials in static batteries, e.g. Li-ion and Ni-MH batteries, are fixed onto the current collectors, which hinders the recyclability of the battery. On the other hand, flowable semi-solid electrodes containing a suspension of Li-ion or Na-ion intercalation materials and conductive additive have been used in redox flow batteries.<sup>3,4</sup>

In this contribution, the concept of injectable batteries based on semi-solid electrode will be introduced to increase the sustainability of batteries (Figure 1b). It will be shown that the use of flowable semi-solid electrodes enables direct recycling of active materials. Additional benefits that this concept offers, e.g. increased areal capacity and reuse of non-active materials, will also be demonstrated and discussed.

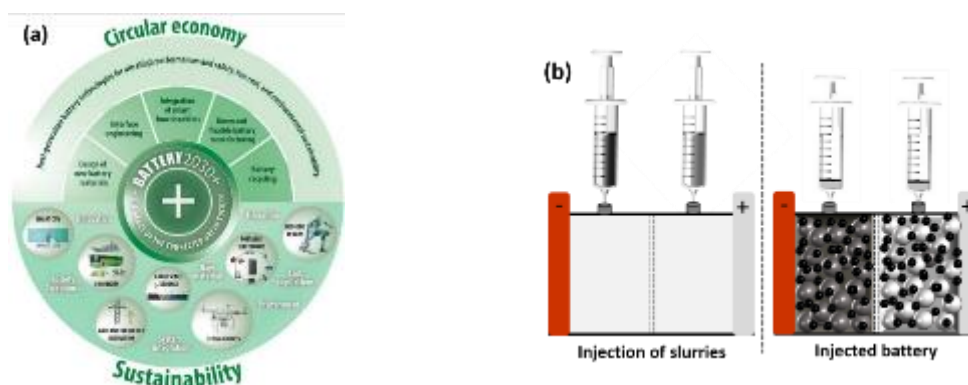


Figure 1. (a) Scheme illustrating the pillars of the new large-scale and long-term European research initiative Battery 2030+. (b) Concept of injectable battery based on semi-solid electrodes

### References

1. Global EV Outlook 2017: Two Million and Counting (International Energy Agency, Clean Energy Ministerial & Electric Vehicles Initiative, 2017).
2. J. Ayre. GM aiming for 500,000 'new energy vehicle' sales per year by 2025. Clean Technica (2017) <https://cleantechnica.com/2017/07/10/gm-aiming-500000-new-energy-vehicle-sales-per-year-2025>.
3. M. Duduta, B.Y. Ho, V.C. Wood, P. Limthongkul, V.E. Brunini, W.C. Carter, Y.-M. Chiang, *Adv. Energy Mater.* **2011**, 1, 511.
4. E. Ventosa, D. Buchholz, S. Klink, C. Flox, L.G. Chagas, C. Vaalma, W. Schuhmann, S. Passerini, J.R. Morante, *Chem. Commun.* **2015**, 51, 7298

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## H<sub>2</sub> purification through BaCe<sub>0.65</sub>Zr<sub>0.20</sub>Y<sub>0.15</sub>O<sub>3-Δ</sub>-Ce<sub>0.85</sub>Gd<sub>0.15</sub>O<sub>2-Δ</sub> ceramic dual-phase membrane

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BaCe<sub>0.65</sub>Zr<sub>0.20</sub>Y<sub>0.15</sub>O<sub>3-δ</sub>-Ce<sub>0.85</sub>Gd<sub>0.15</sub>O<sub>2-δ</sub> (BCZ20Y15-GDC15) dual-phase material is currently one of the most promising dense ceramic membrane for H<sub>2</sub> separation and purification at T > 600 °C. Indeed, this composite material reached H<sub>2</sub> permeability values among the highest ever reported for mixed protonic and electronic conductor (MIEC) membranes ( $\geq 0.3 \text{ mL} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$  at 750°C).<sup>1, 2</sup> A selective H<sub>2</sub> separation and purification is allowed through BCZ20Y15-GDC15 membrane by incorporating it into the crystal structure of its constituents as charge protonic defects and electrons/holes that are transported to the opposite side of the membrane under a H<sub>2</sub> partial pressure gradient, thus providing a non-galvanic separation, *i.e.* without external power.<sup>3</sup> Besides the H<sub>2</sub> permeability performances, it shows also a good chemical stability under harsh reducing conditions and under CO<sub>2</sub>- and H<sub>2</sub>S- containing atmospheres.<sup>5, 6</sup> This talk provides a comprehensive overview of the recent results reached by our group in such MIEC material for H<sub>2</sub> separation. The preparation method, hydrogen permeability and long-term stability of the BCZ20Y15-GDC15 composite system under reducing harsh environments will be discussed. *In-situ* synchrotron XRD analyses under H<sub>2</sub> atmospheres will be also shown.

### References

1. E. Rebollo, *Et al.*, *Energy Environ. Sci.*, **2015**, 8, 3675.
2. D. Montaleone, *Et al.*, *J. Mater. Chem. A*, **2018**, 6, 15718.
3. H. Wang, *Et al.*, *J. Ind. Eng. Chem.*, 2018, **60**, 297.
4. C. Mortalò, *Et al.*, *Materials Today Energy* 13 (**2019**) 331.
5. C. Mortalò, *Et al.*, *J. Membr. Sci.*, 2018, **564**, 123.

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## Life Cycle Assessment of Perovskite Solar Cells technology: environmental profile harmonization of the manufacturing process

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The main priority of the H2020 Programme of the European Commission for “Secure, Clean and Efficient Energy” is the development of low-carbon technologies for energy generation, storage and management. In this context, the application of Life Cycle Assessment (LCA) methodology is crucial to support the design and optimization of innovative and sustainable technologies, and to foresee their role in future energy scenarios, even prior to their industrialization. LCA allows for a comprehensive evaluation of the investigated system by integrating resource and energy efficiency optimization, critical raw materials analysis and future impact assessment scenarios, if used to its fullest potential.

In this work, we present the harmonization of LCA studies available in the literature focusing on Perovskite Solar Cells (PSCs) to evaluate the environmental profile of the fabrication of this new promising class of devices. The high-power conversion efficiency records obtained for PSCs have led to great expectations for this technology as a promising future market competitor of the conventional silicon-based photovoltaics.

The outcomes of this analysis allow to outline which are the environmental hotspots of the PSCs manufacturing process, and to identify the material and energy flows that mostly contribute to the technology profile in terms of environmental impact.

### References

1. Maranghi S., Parisi M.L., Basosi R., Sinicropi A., *Energies* **2019**, 12, 3746
2. Parisi ML, Maranghi S, Vesce L, Di Carlo A, Sinicropi A, Basosi R. *Renew. Sustain. Energy. Rev.* (under review)
3. Arvidsson R., Tillman A.M., Sandén B.A., Janssen M., Nordelöf A., Kushnir D., Molander S. *J. Ind. Ecol.* **2018**, 22:1286–1294
4. Cucurachi S., Van Der Giesen C., Guinée J. *Procedia CIRP* **2018**, 69:463–468
5. Parisi ML, Maranghi S, Basosi R. *Renew. Sustain. Energy Rev.*, **2014**, 39:124–138

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## Conversion of grape marc residue into biochar for soil amendment in a circular economy approach

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**Introduction** - In France, the wine industry leads to the production of 850 000 tons of raw grape marc each year. Among this huge amount of wastes, 25 500 tons come from the Alsace region (north-east of France) where grape marc is mostly valorised by distillation to extract ethanol (IFV, 2013). The residual biomass corresponds to exhausted grape marc, which is usually used as biofuel. An interesting alternative to this issue is to transform this biomass into biochar, after pyrolysis, and to use it as fertiliser. By this way, it is possible to obtain a negative carbon balance, and also to generate carbon sequestration. This study has been done in the frame of a territory circular economy (Ferjani, 2019), at the level of a small a French department (68 – Haut Rhin). A batch of exhausted grape marc coming from a distillery was sampled and analysed. The grape pulp and pips fraction were selected to produce a biochar at different temperature. These biochars were used as fertilisers for the growth of ray-grass.

Three different biochars were produced with yields of 78.50, 46.96 and 35.43 %wt at 300, 400 and 500°C respectively. By increasing the pyrolysis temperature, the structural and textural properties of the biochars were modified. Increasing the temperature lead to an increase of the porosity of the biochar (ultramicroporosity).

These biochars were used as fertilisers for the growth of a model plant : Ray grass (see Figure 1). The K content of the different biochars was selected to calculate the quantity of biochar to add to each pot (200 unities of K<sub>2</sub>O/ha), which corresponds to 1.10 %wt, 1.64 %wt and 2.17 %wt for biochars produced at 300, 400 and 500°C respectively. The analyse of the different cuts (after 4 and 8 weeks of growing) showed that K and P were bio-available and allowed the plant growth without difference compared to reference samples fed with mineral solution containing KNO<sub>3</sub>. The best results were obtained with the biochar produced at 500°C, Ray grass yield was slightly higher than with the different references and the use of this biochar led to soil alkalisation. The suppressive effect of the biochars was also evaluated. A low pyrolysis temperature (300°C) leads to the absence of bacteria growth, due to the presence of aromatic molecules.

This study has shown that exhausted grape marc can be transformed into biochar to be used as fertilizer for soil if the pyrolysis temperature is close to 500°C. The main advantages are the limitation of chemicals to fertilize the soil, the sequestration of carbon and the management of short circuit operation.

### References

1. A. Ibn Ferjani et al., *RSER*. **2019**, *107*, 425-433.

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## Biomass derived carbon and water in salt electrolyte for green supercapacitor

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Supercapacitors (SC) are playing a central role in the transition to a green economy based on renewable energy sources and electric vehicles. The exponentially growing market of supercapacitor requires to replace flammable, volatile and toxic chemicals such as acetonitrile by cheap and environmentally friendly components.

Therefore, valuable strategies are the use of aqueous electrolytes and bioderived components such as biochar-based carbon that enable the valorization of wastes in a circular economy approach. Here we report about a physicochemical study and preliminary electrochemical characterization of a supercapacitor based on Argan fruit shell derived carbon electrode and a non-toxic super-concentrated aqueous electrolyte, i.e. a Water In Salt (WIS) solution of ammonium acetate.

Indeed, the utilization of WIS enables high voltage which are the main limitation of aqueous based electrolyte.

To prove the practical applicability of this kind of electrolyte, electrochemical measure at into a wide range of temperatures (from -10 °C to 80°C), have been performed. This preliminary work aims at paving the way towards the design of novel green SCs based on non-dangerous aqueous based electrolyte and sustainable carbon sources.

### References

1. Wen Jun Xie; Zhen Zhang; Yi Quin Gao, J. Phis. Chem, 2016, 120, 2343-2351
2. Zhujie Li et al., J. Phis. Chem, 2018, 122, 23917-23924
3. Maria R. Lukatskaya et al., Energy Environ. Sci., 2018, 11, 2876-2883
4. Dahbi M, J. Mater. Chem. A. 5 (2017) 9917–9928
5. Chafik, WO/2012/050411, (2012)
6. Boujibar, J Environmental Chemical Engineering 6 (2018) 1995–2002

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## Renewable electricity generated utilising benign redox-couples through thermoelectrochemistry

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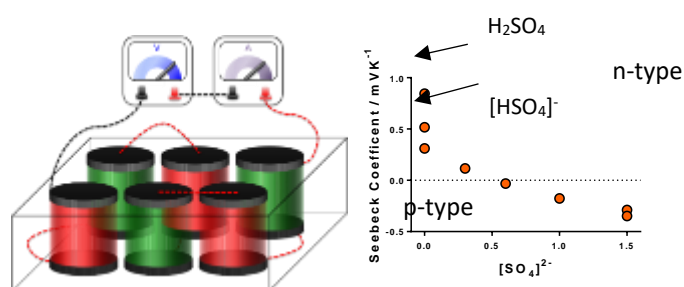
Despite our clear awareness that the demand for global energy from non-renewable sources is unsustainable, two-thirds of all generated energy is still lost as waste heat. Notably, thermoelectrochemistry is a simple method of converting thermal energy to electrical energy.[1] It is a liquid analogue to solid-state thermoelectrics.

An ideal thermoelectrochemical device has two redox couples; one with a positive Seebeck coefficient (how many volts are generated per Kelvin temperature difference across the two electrodes;  $\text{V K}^{-1}$ ), the other with a negative Seebeck coefficient. Here a positive sign indicates that the hotter electrode acts as the cathode; negative indicates anode. This allows cells to be wired electrically in-series to boost voltage, without introducing thermal short-circuits between electrodes (*cf.* Fig. 1 (left)).

The  $[\text{Fe}(\text{CN})_6]^{4-/3-}$  redox couple has a relatively high Seebeck coefficient of  $-1.4 \text{ mV K}^{-1}$ . [1] Recently, we have also investigated the  $\text{Fe}^{3+/2+}$  redox couple; through careful control of the anion and pH, a record high Seebeck coefficient of  $+1.4 \text{ mV K}^{-1}$  was achieved; [2] this will be discussed in the first half of this presentation.

Thus, single devices with multiple cells can be prepared, half containing the  $[\text{Fe}(\text{CN})_6]^{4-/3-}$  redox couple, half the  $\text{Fe}^{3+/2+}$  redox couple, and generate volts from minor temperature gradients. But this has one major flaw; if these solutions are mixed and heated, they can generate lethal quantities of HCN gas.

To overcome this, we have recently demonstrated that by controlling the ratio of  $\text{Fe} : \text{SO}_4^{2-}$  in the iron (II/III) sulphate system, these systems can have either positive or negative Seebeck coefficients (Fig. 1 (right)). [3] Thus the second half of this presentation will describe how entire thermoelectrochemical devices can be constructed from benign, cheap and abundant iron and sodium sulphate. Furthermore, they will still generate thermogalvanic power, even if 'accidentally' mixed and heated.



**Fig. 3** – Figure denoting (left) the transition from n-type to p-type  $\text{FeSO}_4$  thermoelectrochemical cell with increasing  $[\text{SO}_4]^{2-}$ , (right) figure showing how n- and p-type thermocells can be utilised electrically in-parallel to increase voltage output.

### References

1. Alzahrani, HAH, Buckingham, M. A., Aldous, L. *et al. Electrochem. Commun.*, 2019, 102, 41-45.
2. Buckingham, M. A., Marken, F., Aldous, L. *Sustain. Energy Fuels*, 2018, 2, 2717-2726. [a 2018 Sustainable Energy and Fuels HOT Article]
3. Buckingham, M. A., Aldous, L. *Submitted*.

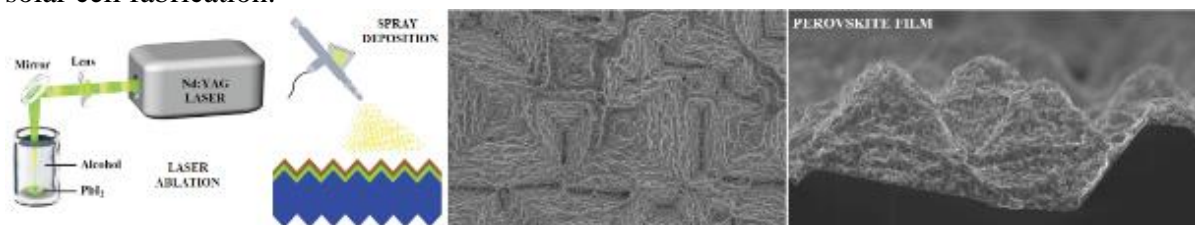
## Eco-friendly spray deposition of perovskite films on macro-scale textured surfaces

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Perovskite-silicon monolithic tandem solar cells are a promising technology to overcome the limits of single junction devices to provide sustainable energy for the future global energy-demand. This technology is quickly developing at the lab scale as proved by the remarkable power conversion efficiencies (PCE) obtained by different laboratories. However, to fully disclose its potential, the perovskite-silicon tandem needs to scale up in size, matching the standards of solar cells manufacturing. The current fabrication of many lab-scaled tandems relies on techniques that are not suitable for large-scale production, such as spin coating the perovskite top-absorber on polished-flat silicon bottom cell. In this work we combine two industrially-established technologies - laser ablation and spray coating - to deposit wide band gap (1.68 eV) perovskites on pyramidal-textured surfaces typical of commercial silicon solar cells. The main advantage of laser ablation is the synthesis of PbI<sub>2</sub> nanocrystals in alcoholic solutions, which greatly simplify the spraying deposition. Indeed, with our technology we use only environmental-friendly solvents, taking the distance from the widely used and toxic dimethylformamide-based lead solutions. Our spray-casted perovskite morphology covers uniformly the silicon texturing, showing the potential of this technique for scalable wet processing of perovskites on rough substrates, such as for low-cost perovskite/silicon tandem solar cell fabrication.



### References

1. V. Amendola, S. Polizzi, M. Meneghetti, *J. Phys. Chem. B* **2006**, *110*, 7232.
2. F. Lamberti, L. Litti, M. De Bastiani, R. Sorrentino, M. Gandini, M. Meneghetti, A. Petrozza, *Adv. Energy Mater.* **2017**, *7*, 1601703.
3. A. Rizzo, F. Lamberti, M. Buonomo, N. Wrachien, L. Torto, N. Lago, S. Sansoni, R. Pilot, M. Prato, N. Michieli, M. Meneghetti, G. Meneghesso, A. Cester, *Sol. Energy Mater. Sol. Cells* **2019**, *189*, 43.
4. E. Aydin, J. Troughton, M. De Bastiani, E. Ugur, M. Sajjad, A. Alzahrani, M. Neophytou, U. Schwingenschlögl, F. Laquai, D. Baran, S. De Wolf, *ACS Appl. Energy Mater.* **2018**, *1*, 6227.
5. E. Aydin, M. De Bastiani, X. Yang, M. Sajjad, F. Aljamaan, Y. Smirnov, M. N. Hedhili, W. Liu, T. G. Allen, L. Xu, E. Van Kerschaver, M. Morales-Masis, U. Schwingenschlögl, S. De Wolf, *Adv. Funct. Mater.* **2019**, *29*, 1.
6. Z. Li, T. R. Klei, D. H. Ki, M. Yan, J. J. Berry, M. F. A. M. van Hest and K. Zhu, *Nat. Rev. Mater.* **2018**, *3*, 18017.
7. D. A. Jacobs, M. Langenhorst, F. Sahli, B. S. Richards, T. P. White, C. Ballif, K. R. Catchpole and U. W. Paetzold, *J. Phys. Chem. Lett.* **2019**, *10*, 3159–3170

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## The golden fig: a combined study of the plasmonic gold effect with a natural dye in DSSC

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The plasmonic effect of gold nanoparticles when embedded in the TiO<sub>2</sub> substrate of a Dye Sensitized Solar Cells (DSSC) has been widely investigated [1] and this is still catching the attention of the scientific community [2]. DSSC is a PV technology extensively studied for easy fabrication, transparency and weak dependence from the incident angle. Dye, the characterizing material for DSSC technology, is adsorbed on TiO<sub>2</sub> layer. Doping TiO<sub>2</sub> layer with Au nanoparticles increases the power conversion efficiency (PCE) of the cell by improving the current. Besides optimizing the Au nanoparticles procedure of conglomeration in TiO<sub>2</sub> (inset fig. 1), we test and compare this effect between artificial ruthenium dye, N719, and a natural dye, the Sicilian fig [3]. The efficiency raise has been appreciated with both dyes, starting from 9.96 % reaching 10.83 % of PCE with N719, and doubling the PCE with the fig pigments (from 1 % w/o Au to 2 % with Au). Measuring the natural-dye device with UV-LED, an overall efficiency of 15 % was achieved (fig. 1). In order to scale up, works are in progress to realize a natural dye module with Z series connection.

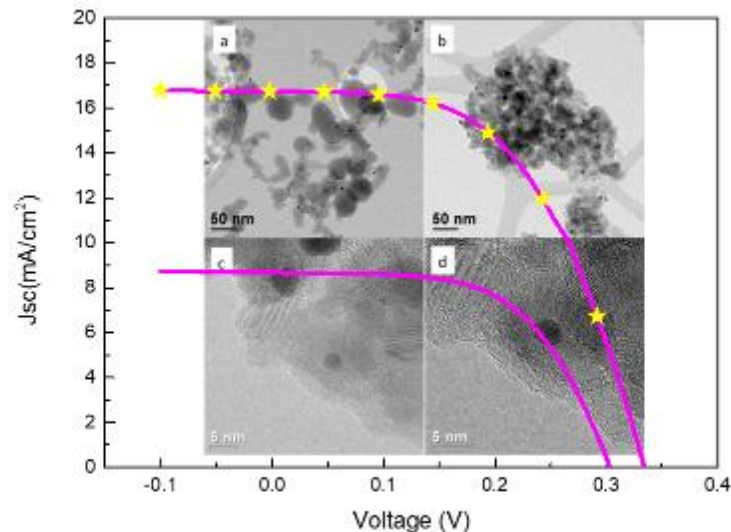


Fig. 1. – JV curves of Sicilian fig dye DSSC (red line) and Sicilian fig dye DSSC in Au@TiO<sub>2</sub> (blue line with yellow stars), measured under UV LED. Inset: TEM images of the Au@TiO<sub>2</sub> nanoparticles: a) before calcination b) after calcination at different magnification; in c) and d) atomic plane fringes of a gold nanoparticle are visible.

### References

1. Y. Li, H. Wang, Q. Feng, G. Zhou, Z. Wang. Gold nanoparticles inlaid TiO<sub>2</sub> photoanodes: a superior candidate for high-efficiency dye-sensitized solar cells. *Energy Environ. Sci.*, 2013, 6, 2156.
2. A. K. Ali, S. Erten-Ela, K. I. Hassoon, Ç. Ela. Plasmonic enhancement as selective scattering of gold nanoparticles based dye sensitized solar cells. *Thin Solid Films.*, 2019, 671.
3. G. Calogero, A. Bartolotta, G. Di Marco, A. Di Carlo, F. Bonaccorso. Vegetable-based Dye-Sensitized Solar Cells. *Chemical Society Reviews*, 2015, 44 (10), 3244-3294.

## Charge recombination dynamics in Perovskite based devices: a guide to correlate steady-state and dynamic measurements

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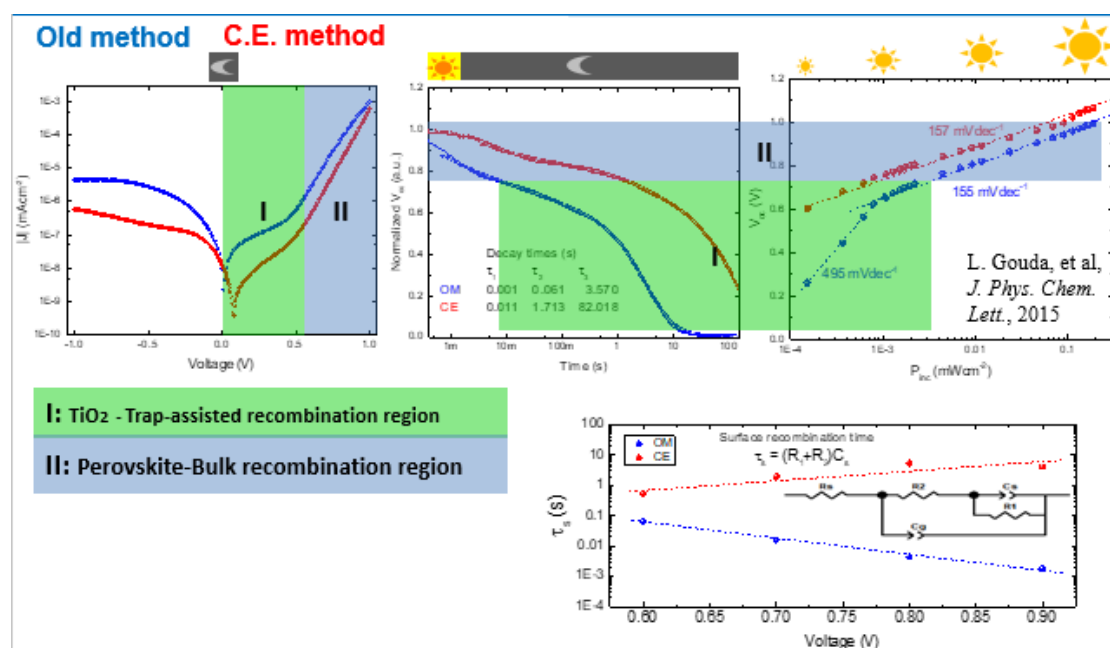
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Steady-state and dynamic electro-optical tests on hybrid organic-inorganic photovoltaic devices, when properly performed, can give advanced knowledge on physical parameters like charge carrier diffusion length [1] or recombination times at the active layer/selective contact interface [2-5].

The goal of this talk is to propose good practices in order to properly correlate information from steady-state and small-high perturbation dynamic tests (TPV, photo-CELIV, charge extraction, EIS, etc.). We developed a reliable analysis to investigate charge carrier recombination dynamics by quantifying ideality factor, recombination time and trap-filled limited region. Case studies on direct mesoscopic structure (NIP) of perovskite-based device will be reported.



Dark JV, Transient Voc, SUN-Voc and Impedance analysis used to investigate surface recombination mechanisms.

### References

1. Cinà, L. *Energies* 9.9 (2016): 686.
2. Yaghoobi Nia, N. *Nano Energy* ACCEPTED
3. Salamandra, L. *Organic Electronics* 69 (2019): 220-226.
4. Cacovich, S. *Nanoscale* 9.14 (2017): 4700-4706.

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## Understanding the role of hydrogenation on the performance of ZnFe<sub>2</sub>O<sub>4</sub> photoanodes for water oxidation

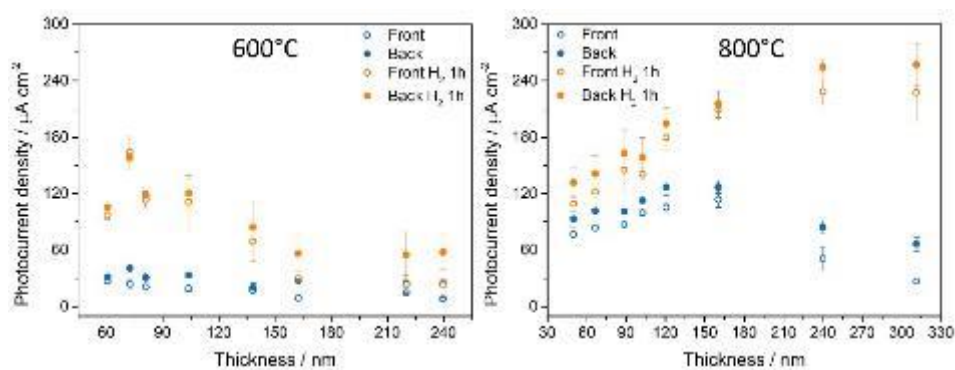
A. Polo<sup>a</sup>, F. A. Boudoire<sup>b</sup>, C. R. J. Lhermitte<sup>b</sup>, N. Guijarro<sup>b</sup>, P. A. Schouwink<sup>b</sup>, M. V. Dozzi<sup>a</sup>, K. Sivula<sup>b</sup>

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The increasing need for renewable energy sources has opened the route to the research of novel materials able to exploit most of the visible radiation coming from the Sun. ZnFe<sub>2</sub>O<sub>4</sub> (ZFO) spinel ferrites have emerged thanks to their relatively narrow band gap ( $E_g^i = 2.0$  eV,  $E_g^d = 2.3$  eV) as well as remarkable thermal and chemical stability [1,2]. In a previous study [2], the photoelectrochemical (PEC) performance of hydrogenated ZFO nanorods films acting as photoanodes for water oxidation was found to be greatly affected by the selected annealing temperature. In this work, the interplay between hydrogen incorporation, acting as n-type dopant, and annealing temperature has been thoroughly investigated on ZFO films with flat morphology selected as ideal models. Two series of electrodes were synthesized through single step spin coating deposition starting from differently concentrated precursor solutions, followed by annealing at 600°C or 800°C. The resulting samples underwent a post-synthesis hydrogen treatment at mild conditions and were finally tested as photoanodes for water splitting in 1.0 M NaOH electrolyte either before or after hydrogenation. As shown in Fig. 1, reporting the photocurrent density values obtained at 1.6 V vs RHE for the two series of films annealed at the two temperatures, the synergistic effect between the higher crystallinity of the electrodes annealed at 800°C and hydrogen treatment allows to exploit a larger film thickness for light absorption, leading to the maximum PEC performance. This was ascribed to an increased charge separation upon hydrogenation of the material, despite the increase of surface trap states affecting the holes injection efficiency at the film/electrolyte interface, as proved by EIS analyses.



**Fig. 1** Photocurrent density values at 1.6 V vs RHE as a function of film thickness for all investigated films.

### References

1. Guijarro, N. *et al. Sustainable Energy Fuels* **2018**, 10, 103-117.
2. Zhu, R. J. *et al. Adv. Mater.* **2018**, 30, 1801612.

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## Hematite nanostructures: An old material for a new story. Simultaneous photoelectrochemical oxidation of benzylamine and hydrogen production through Ti doping

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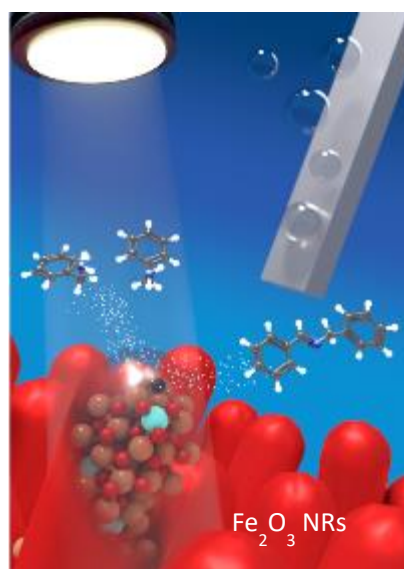
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The production of hydrogen through the photoinduced water splitting process has been a scientific dream for long, but its application is yet to be effective. The limits are mainly related to the slow kinetics of the oxygen evolution reaction, due to its multi-electron character. Since the aim of the process is mostly the production of hydrogen, an effective workaround might be to replace the conventional water oxidation path with the oxidation of an organic compound to a molecule of industrial or pharmaceutical value, in order to exploit the full potential of the photocatalytic process. In this study, the photoelectrochemical oxidation of Benzylamine to N-

benzylidenebenzylamine<sup>1</sup> and the simultaneous production of hydrogen in acidic media has been achieved upon irradiation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) photoanodes, with only 0.3V of applied external bias<sup>2</sup>.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanostructured thin films have been grown on FTO substrates through a high throughput, extremely cheap hydrothermal technique, allowing for full catalyst recyclability and extremely trivial product workup. The electrodes display elevated IPCE up to 550 nm and good stability under anodic polarization. In addition, the morphology and the Ti substitutional doping of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanostructured photoanodes has been optimized, producing photo-currents as high as 1.2 mA/cm<sup>2</sup> at 1.0V vs SHE and unitary faradaic efficiency for the organic oxidation reaction.



### References

1. H. Liu, C. Xu, D. Li, and H.-L. Jiang, *Angew. Chemie Int. Ed.* 57, 5379 (2018).
2. R. Mazzaro, S. Boscolo Bibi, M. Natali, G. Bergamini, V. Morandi, P. Ceroni and A. Vomiero, *Nano Energy*, 2019, 61, 36–46.

## Indium promoted Cu/SiO<sub>2</sub> catalyst for improved hydrogen productivity in the steam reforming of methanol

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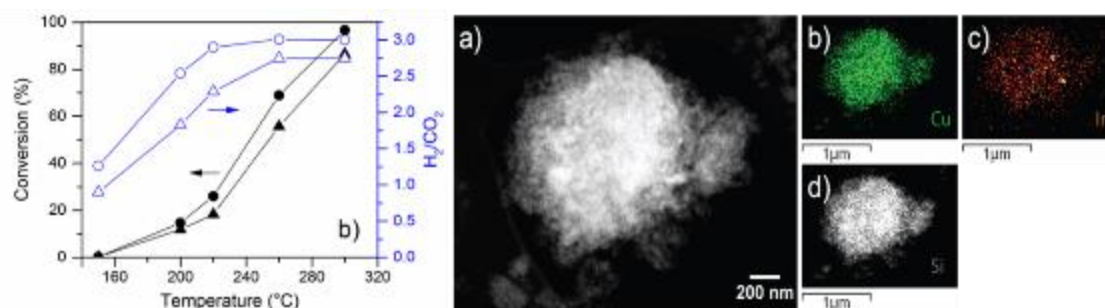
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The use In as an effective promoter for the methanol steam reforming (MSR) reaction with Pt or Pd supported catalysts is well known [1]. The M-In interactions play a crucial role for the improvement of the H<sub>2</sub> and CO<sub>2</sub> selectivity, as well as CO suppression. However, the high cost of these noble metals is an important penalty for the development of new catalysts for sustainable hydrogen production. Alternatively, Matsumura et al. reported Cu-In catalysts for MSR at different In loadings showing a high stability in reaction conditions together with a dramatic loss of activity due to the deactivation of the Cu active phase by indium oxide [2]. We report herein the synthesis of a silica-supported Cu-In bimetallic catalyst by urea-assisted co-precipitation of the metal precursors. By this approach Cu exposure was preserved due to the small size of the Cu nanoparticles (2.5 nm) and to the homogeneous dispersion of the indium oxide phase. The Cu-In/SiO<sub>2</sub> catalyst promoted the MSR by producing an almost stoichiometric hydrogen stream (H<sub>2</sub>/CO<sub>2</sub> molar ratio of 3) already at reaction temperatures as low as 220 °C. For comparison, at the same conditions, the Cu/SiO<sub>2</sub> catalysts exhibited a lower H<sub>2</sub> selectivity (H<sub>2</sub>/CO<sub>2</sub> molar ratio of 2.7). A series of characterization tools, including XPS, XRPD and HRTEM-EDX along with H<sub>2</sub>-TPR, CO-TPR and N<sub>2</sub>O titrations, allowed us to unravel the superior performance of this Cu-In catalyst.



**Figure 1.** Left side: Effect of the temperature on the activity between 150 °C and 300 °C with Cu/SiO<sub>2</sub> (triangles) and Cu<sub>1</sub>In<sub>1</sub>/SiO<sub>2</sub> (circle). Right side: STEM measurements of Cu<sub>1</sub>In<sub>1</sub>/SiO<sub>2</sub>: a) HAADF image of a catalyst grain; b-d) STEM-EDX mapping of the catalyst showing the copper and indium dispersion.

### References

- See as example: Barbosa, R.; Papaefthimiou, V.; Law, J.; Teschner, D.; Hävecker, M.; Knop-Gericke, A.; Zapf, R.; Kolb, G.; Schlögl, R.; Zafeiratos, S. *J. Phys. Chem. C*, **2013**, 117, 6143-6150.
- Matsumura, Y.; Ishibe, H. *J. Power Sources* **2012**, 209, 72-80.

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## **All-in-one catalytic sites for the methanol steam reforming as electron-poor copper nanoparticles on amorphous zirconia-silica**

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Copper on zirconia catalysts are a benchmark for the methanol steam reforming reaction (MSR) because of the simultaneous presence of  $\text{Cu}^0$  and  $\text{Cu}^+$  sites responsible for the molecular hydrogen formation and intermediates dehydrogenation, respectively, the latter being adsorbed on the zirconia support [1]. A system so conceived, although active, is intrinsically limited as copper does not participate to all the reaction steps. By means of *in-situ* XRPD, XPS and FT-IR analyses, we found that by adding a specific amount of silica (10 wt.%) in the zirconia support, the copper reduction is inhibited and leads to nanoparticles in the range of 2-3 nm. Such small nanoparticles are in the metallic state but feature a markedly electron-poor surface on which methanol preferentially adsorbs. This catalyst showed a hydrogen productivity almost four times higher than a classical zirconia-supported catalyst because both the dehydrogenation of the intermediates and the subsequent molecular hydrogen evolution are carried out by the same site. The drawback of having different adsorption sites and two distinct  $\text{Cu}^0$  and  $\text{Cu}^+$  sites is thus overcome thanks to this *all-in-one* catalytic site and the amount of copper actually participating to all the reaction is maximized [2].

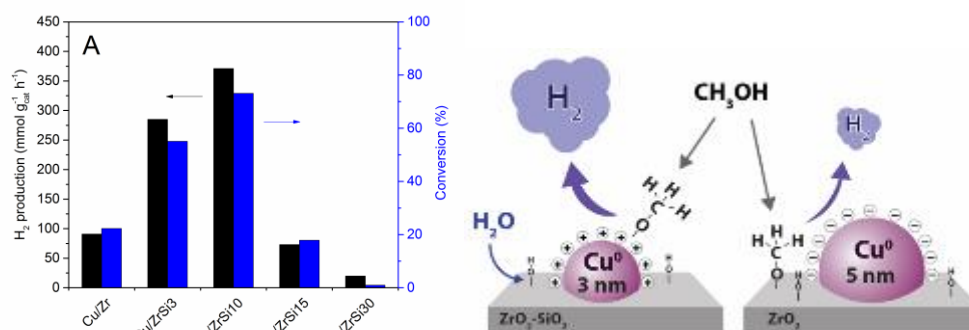


Figure 1. Catalytic activity reported as hydrogen productivity and methanol conversion of all the catalysts (left) and sketch of the impact of the so-called electron-poor nanoparticles over the MSR reaction compared to a classical zirconia-supported catalyst (right).

### References

- Yong, S.T.; Ooi, C.W.; Chai, S.P.; Wu, X.S. *Int. J. Hydrogen Energ.* **2013**, *38*, 9541-9552.
- Bossola, F.; Scotti, N.; Somodi, F.; Coduri, M.; Evangelisti, C.; Dal Santo, V. *Appl. Catal. B: Environ.* **2019**, *258*, 118016.

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## Water-gas shift membrane reactor and steam reforming membrane reactor for pure hydrogen production

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Small-scale delocalized H<sub>2</sub> production with integrated separation will play a fundamental role in the development of a circular economy based on hydrogen. Though, the integration between small-scale production and separation has to be improved. For this reason, this work evaluated the use of Pd-based, H<sub>2</sub>-selective membrane reactors (MBR) in two different configurations. At first, H<sub>2</sub> was produced in a fixed bed reactor through methane oxy-reforming (OR)<sup>1</sup> followed by a membrane reactor unit where the water gas shift (WGS) reaction and hydrogen separation occurred.

Further intensification was carried out by performing the steam reforming reaction inside the membrane reactor. The process temperature was lowered to 400-450°C as higher values would damage the Pd layer. Although this affects the steam reforming thermodynamics, high conversions were obtained due to the equilibrium-shift effect.

Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> and ZrO<sub>2</sub> supports obtained by microemulsion synthesis<sup>1,2</sup> were employed in this work. They displayed peculiar properties: (i) the obtainment of the desired Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> phase; (ii) and of tetragonal ZrO<sub>2</sub>; (iii) the production of a mesoporous materials characterized by small and round particles. High and stable conversions were obtained in the oxy-reforming, using a Rh-Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> catalyst. The obtained stream was fed to the water gas shift membrane reactor, filled with Pt-Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>. Comparing the results with those of a water gas shift fixed bed reactor, it was observed that methanation reaction was suppressed, H<sub>2</sub> was purified, and its production increased in the MBR.

The process was further intensified by loading Rh-ZrO<sub>2</sub> onto the membrane charging the membrane with a Rh-ZrO<sub>2</sub>. Steam reforming was then directly performed in the membrane at 400 or 450°C. The MBR allowed to obtain high methane conversion and hydrogen recovery was obtained due to the high permeability of the membrane that shifted the equilibrium due to H<sub>2</sub> removal. Noteworthy, the methane conversion was higher than the equilibrium conversion of a fixed bed reactor (figure 1).

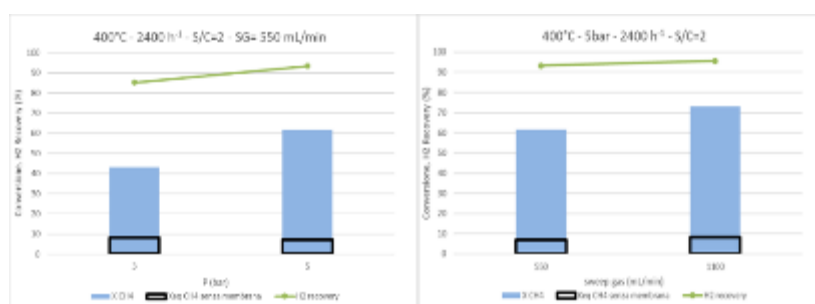


Figure 1: Pressure (left) and sweep gas (right) effect on experimental and equilibrium CH<sub>4</sub> conversion and H<sub>2</sub> recovery at 400°C in a membrane reactor charged with Rh-ZrO<sub>2</sub>.

### References

- Basile, F. et al. *Journal of the European Ceramic Society* **2019**, 39, 41-52.
- Martínez-Arias, A. et al., *Langmuir*, **1999**, 15, 4796

## Electrochemical Methods as a Green Way for Synthesis of Organometallic and Organophosphorus Compounds

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The development of modern chemistry proceeds in various priority directions focused on creation and design of new ecologically friendly methods for preparation of different organic and organoelement compounds and materials bearing practically useful chemical and physical properties. A combination of synthetic methods with electrochemical techniques can be considered as a new powerful tool for preparation of various biologically active compounds, ligands for transition metal catalysts and new types of mono- and polynuclear complexes and clusters. The mild conditions, single-stage process, cyclic regeneration of the catalyst, convenient and relatively inexpensive form of the energy used are main advantages of the electrochemical methods.

Herein, we present our recent results obtained by using of the synthetic electrochemical techniques towards preparation and investigation of the properties of various types of organometallic and organophosphorus species,<sup>1,2</sup> including the reactions involving high reactive phosphine oxide H<sub>3</sub>PO,<sup>3</sup> which is very promising intermediate for synthetic organophosphorus chemistry, synthesis and investigation of the electrochemical behavior of organonickel complexes bearing carbon-nickel sigma-bond<sup>4,5</sup> and unsymmetrical pincer-type ligands,<sup>6</sup> obtaining of the magnetically active binuclear nickel<sup>7</sup> and cobalt<sup>8</sup> complexes. Recent application of the electrochemical methods involves generation and *in situ* observation of superparamagnetic cobalt, nickel and iron nanoparticles.<sup>9</sup>

### References

1. Gafurov, Z. N., Sinyashin, O. G., Yakhvarov, D. G. *Pure Appl. Chem.* **2017**, *89*, 1089-1103.
2. Gafurov, Z. N., Kagilev, A. A., Kantyukov, A. O., Sinyashin, O. G., Yakhvarov, D. G. *Pure Appl. Chem.* **2019**, *91*, 797-810.
3. Yakhvarov, D., Caporali, M., Gonsalvi, L., Latypov, Sh., Mirabello, V., Rizvanov, I., Sinyashin, O., Stoppioni, P., Peruzzini, M., Schipper, W. *Angew. Chem. Int. Ed.* **2011**, *50*, 5370-5373.
4. Yakhvarov, D. G., Khusnuriyalova, A. F., Sinyashin, O. G. *Organometallics.* **2014**, *33*, 4574-4589.
5. Yakhvarov, D. G., Petr, A., Kataev, V., Büchner, B., Gómez-Ruiz, S., Hey-Hawkins, E., Kvashennikova, S. V., Ganushevich, Yu. S., Morozov, V. I., Sinyashin, O. G. *J. Organomet. Chem.* **2014**, *750*, 59-64.
6. Luconi, L., Garino, C., Vioglio, P. C., Gobetto, R., Chierotti, M. R., Yakhvarov, D., Gafurov, Z. N., Morozov, I. Sakhapov, V., Rossin, A., Giambastiani, G. *ACS Omega.* **2019**, *4*, 1118-1129.
7. Yakhvarov, D., Trofimova, E., Sinyashin, O., Kataeva, O., Lönnecke, P., Hey-Hawkins, E., Petr, A., Krupskaya, Yu., Kataev, V., Klingeler, R., Büchner, B. *Inorg. Chem.* **2011**, *50*, 4553-4558.
8. Yakhvarov, D. G., Trofimova, E. A., Dobrynin, A. B., Gerasimova, T. P., Katsyuba, S. A., Sinyashin, O. G. *Mendeleev Commun.* **2015**, *25*, 27-28.
9. Khusnuriyalova, A. F., Petr, A., Gubaidullin, A. T., Sukhov, A. V., Morozov, V. I., Büchner, B., Kataev, V., Sinyashin, O. G., Yakhvarov, D. G. *Electrochim. Acta.* **2018**, *260*, 324-329.

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## H<sub>2</sub> production and levulinic acid hydrogenation to GVL using the co-produced formic acid as H<sub>2</sub> source

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Levulinic acid (LA) is a useful platform molecule to produce green chemicals and it is produced from cellulose by acidic-hydrolysis together with formic acid (FA). Moreover,  $\gamma$ -valerolactone (GVL) can be produced by consecutive hydrogenation and dehydration of LA. The H<sub>2</sub> reagent for the LA hydrogenation needed in GVL synthesis can be obtained by decomposition of FA. The goal was to study the catalytic upgrading of a levulinic acid-formic acid mixture. Ni based and NiCu-based catalysts were synthesized. Best results were obtained with an ex-hydrotalcite Ni<sub>24</sub>Mg<sub>56</sub>Al<sub>20</sub> mixed oxide. The hydrotalcite precursor allowed a high dispersion of Ni and the high Mg/Al ratio provided a basic support with high surface area. Calcination of the hydrotalcite at 650°C gave a mixed oxide. This was then reduced to produce the final catalyst which was characterized by means of XRD and Temperature Programmed Reduction.

The tests were performed in an autoclave under autogenous conditions and products were analysed by GC (gas phase), HPLC (liquid phase) and GC-MS (product identification). FA decomposition was first tested and confronted with blank tests, that showed the Ni-based catalyst gave H<sub>2</sub> and CO<sub>2</sub> by FA decomposition at low temperatures, while the blank test did not provide significant FA conversions in the same conditions. Having identified the appropriate conditions for the FA decomposition, tests with a formic acid-levulinic acid feed were carried out under different conditions. An almost complete decomposition of FA to H<sub>2</sub> and CO<sub>2</sub> was evidenced while GVL was produced with yield as high as 60% in autogenous conditions. The appropriate time of reaction was individuated. H<sub>2</sub> yield showed a first increase with temperature, with a maximum around 200°C, while decreasing at higher temperatures where GVL production increased, indicating that the hydrogen produced by formic acid decomposition was participating in the hydrogenation (figure 1). Carbon balances higher than 80% and good product recoveries were obtained throughout all the tests. A solid precipitate was indicated as responsible for the carbon loss.

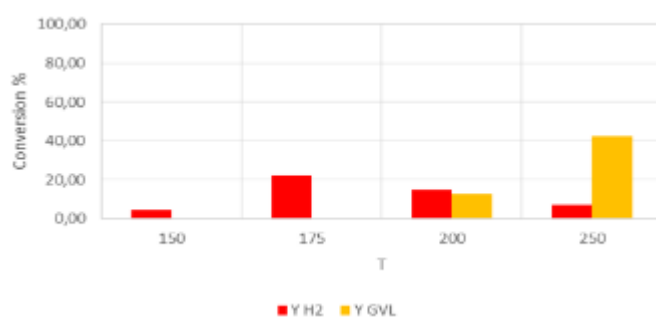


Figure 1: Hydrogen yield (Y H<sub>2</sub>) and GVL yield (Y GVL) for the Ni-Mg-Al tested for 3 h.

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## Fungal laccase with increased redox potential, redox mediator activity and stability: biochemical and electrochemical studies

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Fungal high-redox-potential laccases (HRPLs) are multicopper oxidases with a wide substrate specificity and different redox potentials of the T1Cu site ( $E_{T1}$ ). In these studies, computational design was combined with directed evolution to tailor an HRPL variant, GreeDo, with increased  $E_{T1}$  and activity toward high-redox-potential mediators as well as enhanced stability. Through this strategy, the  $E_{T1}$  of the evolved HRPL increased from 740 mV to 790 mV, with a concomitant improvement in thermal and acidic pH stability. The kinetic constants for high-redox-potential mediators were markedly enhanced [1]. Detailed electrochemical investigations of the GreeDo variant in comparison to its parental variety (the OB-1 mutant) were also performed. Both laccases, when immobilised on graphite electrodes either by direct physical adsorption or covalently attached *via* gold nanoparticles, were capable of both non-mediated and mediator-based bioelectroreduction of molecular oxygen at low overpotentials. GreeDo exhibited higher open circuit potential values and onset potentials for oxygen bioelectroreduction compared to OB-1. However, even though in homogeneous catalysis GreeDo outperforms OB-1 in terms of turnover numbers and catalytic efficiency, when exposed to high redox potential substrates, direct electron transfer based bioelectrocatalytic currents of GreeDo and OB-1 modified electrodes were similar. High operational stability of freely diffusing GreeDo and also the immobilized enzyme in the acidic electrolyte was registered, in agreement with high storage stability of GreeDo in acidic solutions [2]. Enhanced operational, thermal and pH stabilities together with increased  $E_{T1}$  of GreeDo are good prerequisites for designing stable bio-cathodes for bioelectronic devices with high open circuit voltage.

### References

1. Mateljak, I., Monza, E., Lucas, M. F., Guallar, V., Aleksejeva, O., Ludwig, R., Leech, D., Shleev, S., Alcalde, M. *ACS Catal.*, **2019**, 9 (5), 4561-4572.
2. Aleksejeva, O., Mateljak, I., Ludwig, R., Alcalde, M., Shleev, S. *Electrochem. Commun.*, **2019**, 106, 106511.

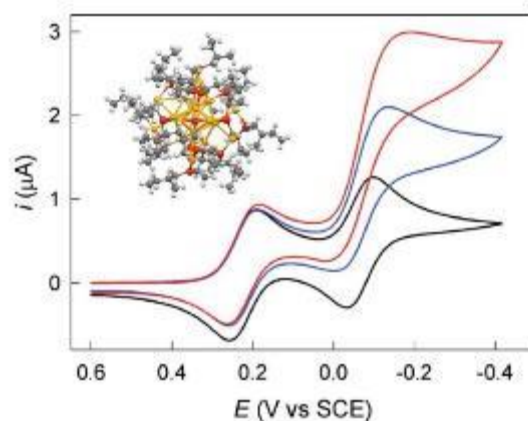
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## Tuning the Electro- and Photochemical Properties of Gold Nanoclusters

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Monolayer-protected gold nanoclusters are materials of ever-growing importance in fundamental and applied research due to their distinct optical, magnetic [1], electrochemical [2], and catalytic properties [3]. In nanoclusters with a gold core diameter of <1.6 nm quantum confinement effects make these gold clusters display features very much alike those of molecules. This borderline behavior between actual molecules and larger nanoparticles makes the study of their fundamental properties particularly important. If properties are understood well, the capability of devising novel applications is greatly enhanced. In the past, we showed how the Au<sub>25</sub>(SR)<sub>18</sub> nanocluster behaves as a molecular redox catalyst testing its performance with a series of dissociative type electron acceptors as peroxides [4], disulfides and alkylhalides [5]. More recently our know-how on nanocluster synthesis widen including series of monodoped Au<sub>24</sub>M<sub>1</sub>(RS)<sub>18</sub> nanoclusters where M was Pt, Pd, Cd, Hg [6]. This allowed us to explore new ways to tune the Au<sub>25</sub>(SR)<sub>18</sub> clusters properties in order to improve their catalytic performance. The effect of Au<sub>25</sub> doping was, for example, explored in the process of generation and detection of oxygen at the singlet state. Reactions directly or indirectly involving singlet oxygen play indeed a fundamental role in the photodynamic therapy and photocatalysis. Metal nanocluster have long-lived triplet excited states, which make them react with triplet ground-state oxygen to form singlet excited-state oxygen. Electrochemical characterization allowed us to select the best R/M combinations to test a sufficiently large oxidation-potential range.



### References

1. Antonello, S.; Maran, F. *Curr. Opin. Electrochem.* **2017**, *2*, 18.
2. Agrachev, M.; Ruzzi, M.; Venzo, A.; Maran, F. *Acc. Chem. Res.* **2019**, *52*, 44.
3. Xiangsha D.; Rongchao J. *ACS Nano* **2019**, *13*, 7383.
4. Antonello, S.; Hesari, M.; Polo, F. Maran, F. *Nanoscale*, **2012**, *4*, 5333.
5. Antonello, S.; Instuli, E.; Maran, F. *J. Am. Chem. Soc.* **2007**, *129*, 9836.
6. Fei, W.; Antonello, S.; Dainese, T.; Dolmella, A.; Lahtinen, M.; Rissanen, K.; Venzo, A.; Maran, F. *J. Am. Chem. Soc.* **2019**, *141*, 16033.

## MD and QM/MM investigation of Bacteriorhodopsin/TiO<sub>2</sub> system

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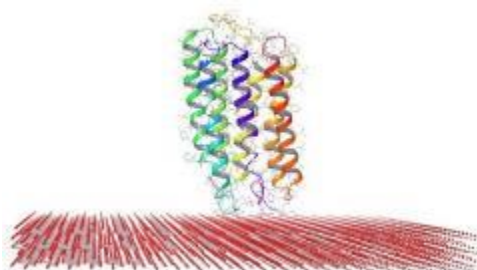
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Bacteriorhodopsin (bR) from *Halobacterium salinarum* is a light-harvesting integral membrane protein which has been used in both photocatalytic and photoelectrochemical systems to sensitize TiO<sub>2</sub><sup>1-6</sup>. Indeed, several applications are based on the ability of bR to convert solar energy into electricity or chemical fuels, such as H<sub>2</sub>. Among other environmentally sustainable biomaterials for solar energy conversion, bR holds high promise since it has a thermal robustness and keeps the functional activity for long-term while absorbing the solar radiation to produce photo-induced charge generation.

In this work, we applied molecular dynamics (MD) and hybrid quantum mechanics/ molecular mechanics (QM/MM) methods to model bR on the anatase TiO<sub>2</sub> surface. The latter has been modeled with a total of 12276 atoms corresponding of three layers on the *c* axis and an area of 115x115 Å<sup>2</sup>. We analyzed different orientations of bR on the TiO<sub>2</sub> and applied a hybrid approach<sup>7</sup> combining steered molecular dynamics (SMD) and MD simulations in order to get an understanding of the most probable orientations and interactions of the protein on the surface. The following QM/MM simulations showed that the resulting bR/TiO<sub>2</sub> models correctly reproduce the blue shift observed when the protein is physisorbed on the TiO<sub>2</sub> compared to the protein in solution. This robust model will be applied to map the long-range ET pathway that allows electrons to be injected into TiO<sub>2</sub>. This will be relevant in order to design novel and more efficient mutants of bR to employ as bio-sensitizers.



### References

1. Das, S. et al., *ACS Appl. Mater. Interfaces* **2019**, 11, 30728–30734
2. Johnson, K. et al. *Langmuir*, **2018**, 34, 7488-7496;
3. Johnson, K. et al. *ACS Appl. Mater. Interfaces* **2017**, 9, 35664–35672
4. Allam, N. et al. *Energy Environ. Sci.*, **2011**, 4, 2909-2914.
5. Reisner, E. et al. *J. Am. Chem. Soc.*, **2009**, 131, 18457–18466.
6. Thavasi, et al. *Nanosci. Nanotechnol.*, **2009**, 9, 1679-1687.
7. Utesch, T. et al. *Langmuir*, **2011**, 27, 13144-13153.

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## Nano-emulsions of Phase Change Materials for Heat Transfer/Storage and Solar Applications

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Phase change material emulsions (PCMEs) or phase change slurries have been widely investigated as heat transfer and heat storage fluids [1]. They consist on a base fluid as water or thermal oil, which is a suitable heat transfer fluid, and a phase change material (PCM) emulsified by a proper surfactant. The idea is to exploit the latent heat of melting and crystallization of PCM to increase the thermal energy storage capacity of the base fluid. The large interface between base fluid and nano PCM drops in the emulsion favors the heat transfer between the two phases. Main barriers to their application are the difficulty in maintaining emulsion stability and the sub-cooling effect (i.e. the cooling of the PCM nano-drops below their melting point before recrystallization) [2].

We investigated various PCMs, as commercial or pure paraffins with different melting temperatures (21, 55, 70°C) or sugar alcohols (melting at 120°C). Water- or oil-based emulsions with fine droplets were produced [3]. Concentrations from 2 to 10 wt% were obtained. The droplet dimensions and the emulsions stability were analyzed also along time, after freeze-thaw cycles and under mechanical shear. A sub-cooling effect was verified and reduced in some cases by adding some nucleating agents. Although the emulsions exhibited diminutions in thermal conductivity with respect to carrier fluids, enhancements in energy storage capacity with respect to base fluid reached up to 40% for temperatures close to PCM melting temperatures. The optical absorption of some emulsions containing single wall carbon nanohorns was measured to assess the possibility of using PCMEs as heat transfer media in solar applications.



An emulsion of 4wt% of a commercial paraffin melting at 55°C in water, with 0.01wt% of single wall carbon nanohorns as nucleating agent.

### References

1. J. Shao, J. Darkwa, G. Kokogiannakis, *Energy Build.*, **2015**, *94*, 200–217.
2. L. Huang, E. Günther, C. Doetsch, H. Mehling, *Thermochim. Acta*, **2010**, *509*, 93–99.
3. F. Agresti, L. Fedele, S. Rossi, D. Cabaleiro, S. Bobbo, G. Ischia, S. Barison, *Sol. Energy Mater Sol. Cells*, **2019**, *194*, 268–275.



## Strelitzia-like titanium oxide nanopetals grown onto single wall carbon nanostructures for photocatalytic applications

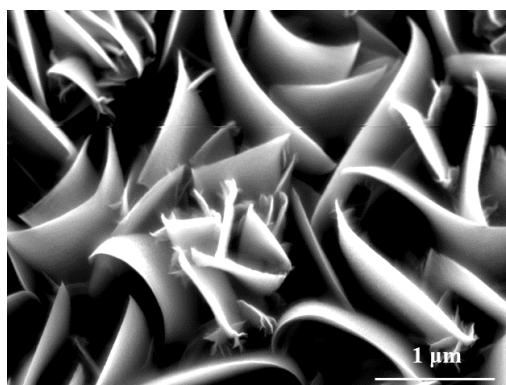
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The broad blooming of strelitzia-like titanium oxide nanopetals was obtained onto single wall carbon nanostructures by the synergistic employment of two vapor techniques: metal-organic chemical vapor deposition (MOCVD) and magnetron sputtering <sup>1</sup>. The nanocomposite photocatalyst exhibited a significant increase of phenol degradation efficiency under UV light irradiation with respect to the bare titanium oxide thin films deposited via RF magnetron sputtering and the titanium oxide coated carbon nanostructures via MOCVD <sup>2,3</sup>. The hybrid nanostructured material was characterized by scanning electron microscopy and X-ray diffraction and its peculiar synthesis conditions were discussed.



### References

1. Battiston, S.; Minella, M.; Gerbasi, R.; Visentin, F.; Guerriero, P.; Leto, A.; Pezzotti, G.; Miorin, E.; Fabrizio, M.; Pagura, C. *Carbon* **2010**, 48 (9), 2470–2477.
2. Battiston, S.; Leto, A.; Minella, M.; Gerbasi, R.; Miorin, E.; Fabrizio, M.; Daolio, S.; Tondello, E.; Pezzotti, G. *J. Phys. Chem. A* **2010**, 114 (16), 5295–5298.
3. Battiston, S.; Bolzan, M.; Fiameni, S.; Gerbasi, R.; Meneghetti, M.; Miorin, E.; Mortalò, C.; Pagura, C. *Carbon* **2009**, 47 (5), 1321–1326.

## Charge-discharge performance of 1D- metal-organic frameworks based on nickel complexes

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An increasing demand for different energy accumulation devices with high capacity and power inspires the development of new cathode materials with improved properties compared with the contemporary lithium-ion batteries. Metal-organic frameworks (MOFs) based on ligands capable of reversible redox processes are envisioned to be promising candidates in this connection as they combine the redox capacitance with the double-layer capacitance arising from the high porosity of the arranged structures of MOF systems.

We examined a new cathode material, in which the connection of monomer units into metal-organic framework was realized by means of a planar square Ni(II) complex with a couple of chelating N,O-ligands possessing extended  $\pi$ -systems, which ensure conjugation between two adjacent metal centers. The samples were tested in coin-half type cells (2032) with 1 M LiPF<sub>6</sub> in a 1:1:1 mixture of EC:DEC:DMC electrolyte.

Depending on preparation method, at the first discharge cycle capacity of polymer complexes varied from 220 to 150 mAh·g<sup>-1</sup>, exceeding the capacity of typical inorganic materials. The discharge capacity of polymers at the end of cycling (the 60<sup>th</sup> cycle) decreased to 60 mAh·g<sup>-1</sup> (see figure 1). This value, albeit appear moderate, is still higher than the capacity of the structural analog poly[Ni(salen)], which has the capacity lower than 30 mAh·g<sup>-1</sup>[1].

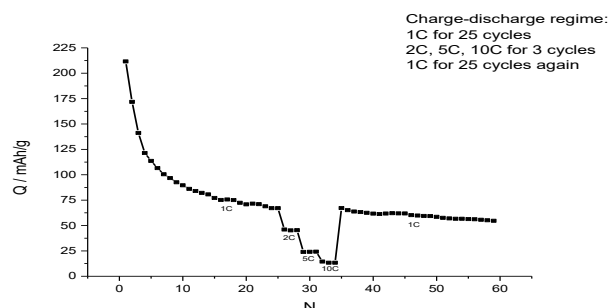


Figure 1. Discharge capacity of sample

### References

1. Eliseeva, S.N.; Alekseeva, E. V; Vereshchagin, A.A.; Volkov, A.I.; Vlasov, P.S.; Konev, A.S.; Levin, O. V. *Macromol. Chem. Phys.* **2017**, *1700361*, 1–5.

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## How to kill two birds with a stone: *urban mining* and CO<sub>2</sub> partners in the production of lanthanide molecular precursors for surface functionalization

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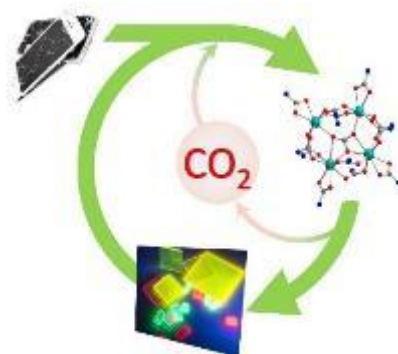
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Lanthanide elements, due to their peculiar properties, are extensively used in our society for many technological applications such as superconductors, permanent magnets, luminescent sensors and phosphors. Considering the current growth rate in their demand and their limited availability (natural reserves will be exhausted by about the middle of this century) lanthanides are considered one of the most critical raw materials. For this reason, their *urban mining*, *i.e.* the recycling process from consumer products that reached the end of their service life, will become increasingly important in the coming years. Since the formation of an aqueous solution is a recurrent step in lanthanide recycle, carbon dioxide (CO<sub>2</sub>) can be smartly used as *lanthanide scavenger* in an extraction procedure. Reacting with CO<sub>2</sub>, the metal ions are quantitatively recovered from the aqueous media as N,N-dialkylcarbamato (cbm) complexes,<sup>1</sup> that are powerful and versatile precursors for the synthesis of functional materials.

Indeed, surface acid species like M-OH can easily react with metal cbm complexes that undergo to protolytic ligand substitution with formation of strong M-O bonds. Usually only a fraction of the carbamato ligands reacts with the surface and the residual cbm moieties can be easily substituted with Brønsted's acid allowing a great synthetic flexibility.<sup>2,3</sup> As examples we report here two cases of silica surface functionalization with: *i*) Eu<sup>3+</sup> complex bearing dibenzoylmethide and the chiral molecule 2,6-bis(isopropyl-2-oxazolin-2-yl)pyridine to achieve circularly polarized emission and *ii*) the divergent ligand 1,4-benzendicarboxylic to create an ordered heterobimetallic sequence SiO<sub>2</sub>-M<sub>1</sub>-L-M<sub>2</sub>-L<sup>...</sup> with luminescent properties that depend on the order of the M<sub>1</sub>, L and M<sub>2</sub> (M<sub>i</sub> = Eu<sup>3+</sup> or Tb<sup>3+</sup>).



### References

1. Armelao, L.; Belli Dell'Amico, D.; Biagini, P.; Bottaro, G.; Chiaberge, S.; Falvo, P.; Labella, L.; Marchetti, F.; Samaritani, S. *Inorg. Chem.*, **2014**, 53, 4861-4871.
2. Armelao, L.; Belli Dell'Amico, D.; Bellucci, L.; Bottaro, G.; Di Bari, L.; Labella, L.; Marchetti, F.; Samaritani, S.; Zinna, F. *Inorg. Chem.* **2017**, 56, 7010-7018.
3. Bellucci, L.; Bottaro, G.; Labella, L.; Marchetti, F.; Samaritani, S.; Belli Dell'Amico, D.; Armelao, L. *J. Mater. Chem. C*, **2019**, 7, 4415-4423.

## Binderless graphene / three-dimensional microfibrous carbon paper composites electrode for electrochemical applications

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Recent advances in nanoscale science and technology provides new opportunities in achieving highly efficient electrodes for electrochemical applications such as: energy storage devices, sensors, catalysts. Synergizing with material chemistry, various nanostructures have great potential in stabilizing and activating the electroactive materials with performances well beyond the scope of traditional fabrication technologies. One of the most promising materials is graphene.

Graphene, a 2D planar sheet of hexagonally configured sp<sup>2</sup> hybridized carbon atoms, has attracted immense interest since its discovery in 2004. This new material shows excellent tensile strength, ballistic electrical conductivity (in the range of 200,000 cm<sup>2</sup> v<sup>-1</sup> s<sup>-1</sup>), high thermal stability (around 5000 Wm<sup>-1</sup> K<sup>-1</sup>), very highly theoretical surface area estimated to 2630 m<sup>2</sup> g<sup>-1</sup> and outstanding Young's modulus (1100 GPa). These exceptional physical and chemical characteristics make graphene an excellent candidate as a compound in nanocomposites materials for many applications.

For electrochemical applications, the use of graphene needs an electrode preparation process. Conventional methods of preparation of these electrodes comprise three steps: (i) the dispersion of graphene in solution (ii) the formation of composite film with an appropriate binder, and (iii) the assembly of the composite film on a current collector. This conventional process is complicated, inefficient, and expensive.

In this work, we report on the development of highly attractive nanostructured samples derived from three-dimensional microfibrous carbon paper uniformly covered with graphene without binder. The synthesized materials were characterized by using scanning electronic microscopy, X-ray diffraction, Raman spectroscopy, cyclic voltammetry, galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy techniques.

Results of structural characterization confirm the effectiveness of the graphene deposition on the three-dimensional microfibrous carbon paper method. Results of electrochemical tests showed high-resolution responses in different chemical media, which indicate good electrical contact between the graphene and the three-dimensional microfibrous carbon paper substrate. These architectures hold great promise for incorporation into energy storage devices, sensors, catalysts. As first application, the developed process was used to fabricate an efficient electrode for electrochemical capacitor.

## Optimization of silicon anode composition for all-solid-state lithium battery

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As demonstrated by the Nobel Prize in Chemistry, awarded for rechargeable lithium-ion batteries, the scientific community and market are focusing on lithium ion batteries thanks to the increasing interest towards the ambitious electric mobility and more energetic storage devices [1]. Unfortunately, in large-sized batteries thermal runaway, with the liquid electrolyte decomposing or, worst, burning, becomes a very serious issue [2].

In the last years, all-solid-state batteries are gaining more and more attention since they offer several advantages with respect to the liquid systems. The absence of organic solvents permits to avoid the drawbacks related to the thermal stability and reduce the side reaction at the electrodes, since Li is the only mobile species.

In this work, the composition of silicon anodes, for solid-state lithium batteries, has been studied and optimized according to a design of experiment (DoE) approach, named mixture design. As solid electrolyte, a LiI-added sulfide-based electrolyte, namely LiI-Li<sub>3</sub>PS<sub>4</sub>, has been adopted for its high ionic conductivity at room temperature (about 10<sup>-3</sup> Scm<sup>-1</sup>) and its stability window [3].

The mixture design allowed us to investigate the best composition of the anodic solid mixture, formed by: silicon nanoparticle, graphite as electronic conductor and the solid electrolyte itself. The role of each single component and their synergistic, destructive effects have been investigated with a relative few number of experiments suggested by the statistical model study, leading to the optimization of the electrochemical response in terms of capacity retention and rate capability. Specific capacity values, at the 50<sup>th</sup> cycle, higher than 1000 mAh/g with coulombic efficiency  $\geq 99\%$  have been obtained.

### References

1. A. Barré, B. Deguilhem, S. Grolleau, M. Gérard, F. Suard, D. Riu, *Journal of Power Sources* **2013**, 241, 680–689.
2. J. Janek, W. G. Zeier, *Nature Energy* **2016**, 1, 1–4.
3. Y. Aihara, S. Ito, R. Omoda, T. Yamada, S. Fujiki, T. Watanabe, Y. Park, S. Doo, *Frontiers in Energy Research* **2016**, 4, 1–8.

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## High-Energy Olivine Doped Cathode Materials for Secondary Lithium Batteries

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As of today, rechargeable Li-ion batteries dominate the world market of portable electronics and electric vehicles [1]. The research is continuously striving to develop new and more efficient battery components such as the cathode material.

In this work we describe the syntheses and the studies of a new family of high-energy olivine cathodes for lithium secondary batteries. Starting from a high-voltage and high-performing cathode of the type  $\text{LiMPO}_4$  (with M a mixture of Fe, Ni, and Co) [2,3], the olivine material is doped with

high-valence transition metal (HVTM) ions (*i.e.* V(V), Nb(IV), or Ta(IV)). In a first step, the synthesis protocol to produce a V-doped olivine is optimized modulating the reducing power of the synthesis process. Then, Nb- and Ta-doped olivine materials are prepared following the best synthesis protocol. Five different materials are so obtained: i) LFNCVP is a vanadium-doped olivine obtained under oxidizing conditions; ii) LFNCVP/C is a vanadium-doped olivine obtained under partially reducing conditions (graphite is added during the pyrolysis); iii) LFNCVP/H is a vanadium-doped olivine obtained under reducing conditions (the pyrolysis is conducted under an hydrogen atmosphere); iv) LFNCNP is a niobium-doped olivine obtained under oxidizing conditions; and v) LFNCTP is a tantalum-doped olivine obtained under oxidizing conditions.

An extensive campaign of characterization studies is conducted in order to determine the effects of the different applied synthetical protocols and ion insertion on the structural (ATR FT-MIR, FT-FIR, WAXRD), morphological (SEM, TEM), and electrochemical (CV, EIS) properties of the materials. The synthesized olivine cathodes are also implemented into Li metal anode prototypes and cycled under operating conditions.

As expected, the proposed materials show a high performance in terms of working potential (4.0÷5.0 V vs.  $\text{Li/Li}^+$ ), specific capacity ( $149 \text{ mAh}\cdot\text{g}^{-1}$ ), and specific energy ( $656 \text{ mWh}\cdot\text{g}^{-1}$ ). Moreover, the insertion of high valence transition metals is able to boost the rate capability of the cathodes, allowing for fast charge and discharge processes without depleting the cathodes.

### References

1. Dunn, B., Kamath, H., Tarascon, J. M. *Science* **2011**, 334, 928-935.
2. Pagot, G., Bertasi, F., Nawn, G., Negro, E., Carraro, G., Barreca, D., Maccato, C., Polizzi, S., Di Noto, V. *Adv. Funct. Mater.* **2015**, 25, 4032-4037.
3. Pagot, G., Bertasi, F., Nawn, G., Negro, E., Bach Delpuech, A., Vezzù, K., Cristofori, D., Di Noto, V. *Electrochim. Acta* **2017**, 225, 533-542.

## Innovative preparation and loading of Ni/CeO<sub>2</sub> nanocomposite for CO<sub>2</sub> methanation

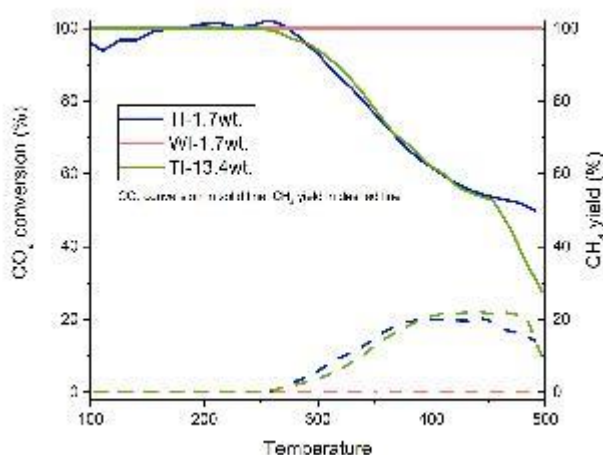
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One of the actual challenges for the scientific community is to decrease the atmospheric CO<sub>2</sub> concentration. In this framework the Sabatier methanation reaction ( $\text{CO}_2 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ ) is employed, in order to obtain fuel with a sustainable approach. One main advantage of the production of methane is its already existing distribution infrastructure and the high energy content. The reaction must be carried out between 200°C and 500°C to avoid the reverse water gas shift reaction ( $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$ ), which takes place at higher temperatures. Moreover, critical raw materials should be avoided to keep the methodology sustainable. In the present contribution a nanocomposite composed by metallic Ni dispersed on an oxide is investigated to understand the role played by Ni and by the support. The choice of Ni is motivated by high activity, high selectivity and low cost and the interaction with the support is supposed to contribute to the selectivity. Ni-deposition is carried out by comparing the traditional wet impregnation (WI) with an innovative procedure here presented, to the best of our knowledge, for the first time. Following this procedure the metal is deposited through a citrate-templated impregnation (TI) approach. Also the amount of Ni was increased from 1.7% to 13.4 % as comparison. [1] The catalysts were characterized and their catalytic performance evaluated after a reductive pretreatment. A blank support-only test demonstrated the activity of Ni. Both the deposition procedure and the amount of Ni greatly affect particle size and surface composition (XPS, EDX, SEM): higher TI dispersions enhance the catalytic activity (see image). The influence of the size is also demonstrated by reducibility analysis (TPR). Ni loading, in contrast, does not seem to be crucial for the performances. Particle size instead influences the number of active sites for CO<sub>2</sub> coordination. Secondly decreased particle size provides better chances to an effective hydrogen spillover. Noteworthy, no CO was revealed so shedding an interesting light on the reaction mechanism. [2], [3]



### References

1. Marconi E., Tuti S., Luisetto I.; *Catalysts*, **2019**, 9, 375
2. Su X. Xu J., Liang B., Duan H., Hou B., Huang Y.; *J. Energy Chem.* **2016**, 25, 4, 553-565
3. Schneider J., Matthischke S., Schlüter M., Götz M., Lefebvre J., Prabhakaran P., Bajohr S., Rönsch S.; *Fuel* **2016**, 166, 276-296

## Engineered Ferroelectric PVDF Composites Containing BaTiO<sub>3</sub>@AO<sub>2</sub> (A = Ti, Si) Inclusions: Effective Dielectric Properties and 3D FEM Modelling of Field Distribution

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The demand for high dielectric constant materials and high energy density capacitors has rapidly increased in recent years due to the continuous and rapid development of the electronic industry and the need to store electrostatic energy more efficiently. The introduction of ferroelectric inclusions in a polymeric matrix enables the effective dielectric constant of the composite to be significantly increased while preserving the high breakdown field typical of polymers, thus improving the stored energy density.

By varying the size, shape and volume fraction of the inclusions, the dielectric properties of the composite can be tailored, as a consequence of the alteration of the electric field distribution inside the material. A further approach for the modification of the electric field in the composite is coating the particles used as inclusions with an oxide layer with a different dielectric constant. In this work we have fabricated polyvinylidene fluoride (PVDF) composites containing 30 vol.% BaTiO<sub>3</sub>@AO<sub>2</sub> (A = Si, Ti) particles. Barium titanate particles with a diameter of  $\approx 100$  nm were synthesized using a hydrothermal-like method and coated with a thin shell (10 nm) of SiO<sub>2</sub> or TiO<sub>2</sub> by means of colloidal chemistry methods. The composites were prepared by solution casting and subsequent compression moulding. Reference composites were prepared by the same process using uncoated BaTiO<sub>3</sub> particles. In order to understand the effect of interfacial modification by coating of the filler, the dielectric properties of the composites (dielectric constant and loss tangent) were measured at different frequencies (1 – 10<sup>6</sup> Hz) in the temperature range 25-150 °C.

The coating results in a significant modification on the effective permittivity, which is mainly determined by the value of its dielectric constant. To gain insight into the role of the coating layer, the electric field distribution and the effective dielectric constant were calculated for the different composites using a 3D finite element modelling and compared to experimental results. This study provides some guidelines for tuning the dielectric properties of ferroelectric PVDF-ceramic composites.

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## Guidelines to design and understand Eu(III)-based luminescent thermometers and a model to predict their behaviour

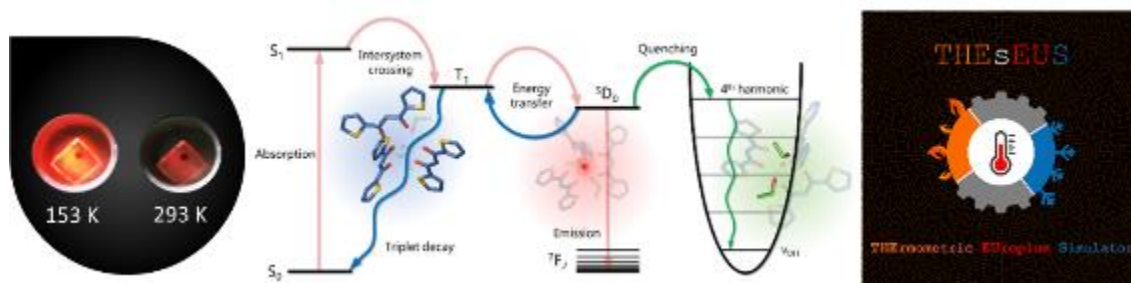
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In the last ten years, molecular thermometers (MTs) have attracted an increasing interest for the developing systems and device with improved energy efficiency. In fact, MTs, working at the nanoscale with high spatial resolution, are becoming essential for research field ranging from microfluidics to nanomedicine, where the conventional methods are ineffective. Lanthanide (Ln) based luminescent thermometers exploit the peculiar luminescence properties of these elements to detect the temperature through a semi/non-invasive approach reaching spatial, temporal and temperature resolutions unconceivable for contact measurements.<sup>1</sup>



A new model<sup>2</sup> to describe and predict the temperature dependence of Eu(III)-based molecular thermometers is here presented and exploited to delineate some general guidelines to design Eu(III) MTs. In the model, non-radiative deactivation pathways are described by the thermally activated back-energy transfer (BET) processes and, when high energy oscillators are present, also considering the vibronic coupling between Ln and the oscillators (e.g. OH). This model takes into account the energy differences between the various excited states, modulated by fixed, one-size-fits-all parameters and one single variable parameter to weight the contributions of the two main deactivation channels. The model has been developed on a series of Eu(III)-based complexes of general formula  $\text{EuL}_3\text{A}_2$ , where L is a  $\beta$ -diketone with different substitute groups in order to fine tune its triplet energy, and A is an ancillary ligand that in turn can be a quencher molecule (EtOH) or a not-quenching system (TPPO). The model resulted to be very effective in depicting the interplay between BET and vibronic deactivation channels and, by reproducing both trends and ranges of applicability, it allows to predicts the thermometric response of the MTs. Finally, we developed a MATLAB based standalone application named THEsEUS (THErmometric EUropium Simulator) that implements the discussed model.<sup>2</sup>

### References

1. Brites, C. D. S.; Millán, A.; Carlos, L.D. *Handb. Phys. Chem. Rare Earths*, **2016**, *49*, 339-427.
2. Carlotto, A.; Babetto, L. *et al.*, *submitted*

## Visible light photoactive Rare Earth oxides - ZnO interfaces investigated by EPR spectroscopy

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The still increasing industrialization, the connected environmental pollution and the energy shortage are among the most arduous challenges to which humanity has to cope in the 21<sup>st</sup> century. For this reason, the scientific community has been undertaking a great effort toward exploring sustainable and clean energy sources and developing new eco-friendly technologies. In this sense photocatalysis holds great promises; indeed, a photocatalytic process aims to exploit light energy, coming from the sun, to promote chemical transformations. The most used materials for this purpose are semiconductors, since the gap between the valence band (VB) and the conduction band (CB) allows the absorption of photons present in the solar radiation; this phenomenon causes the excitation of the electrons from the VB to the CB, with the connecting formation of holes in the VB, then generating charge carrier separation. Once the photoinduced charge carriers reach the surface, they can entail redox reactions, depending on the band potentials of the material: in particular, the electrons in the conduction band can give rise to reductive reactions as the photoreduction of CO<sub>2</sub> or to production of H<sub>2</sub> from the water photosplitting, while the holes in the valence band can be used for the oxidation of organic molecules, whose classical and emerging pollutants are constituted.

Unfortunately, often, the band gap width of the most used semiconductors can only absorb UV photons, that are just the 5% of the total solar radiation impinging our planet, then limiting their applications. Different strategies have been developed to overcome this shortcomings, as the doping or the establishment of heterojunction between two or more semiconductors. In this work, the last approach has been investigated, for two different systems, based on the ZnO matrix, interfaced with two rare-earth oxides as CeO<sub>2</sub> and Yb<sub>2</sub>O<sub>3</sub>.

The aim of the work has been the understanding of the different working mechanism of the two promising photocatalytic heterojunction system upon irradiation for the degradation of organic pollutant<sup>1,2</sup>.

In both CeO<sub>2</sub>-ZnO and Yb<sub>2</sub>O<sub>3</sub>-ZnO preparations, 1 molar percentage of the rare earth precursor has been added during the hydrothermal synthesis procedure. The structural analysis performed by means X-rays diffraction has been not able to identify a rare earth oxide phases, but Transmission Electrons Microscopy has evidenced the creation of biphasic solids in both the systems.

The Electron Paramagnetic Resonance Spectroscopies performed in vacuum condition and at the liquid nitrogen temperature, coupled with in situ irradiation, has allowed us determining how the materials work, upon irradiation. In details, For the CeO<sub>2</sub>-ZnO heterojunction, the presence of the empty 4f states of Ce<sup>4+</sup> would guarantee an electronic transition from ZnO conduction band to the 4f states, than improving charge carrier separation upon irradiation, as confirmed also by the DFT calculation performed by the Professor Pacchioni's group (Milano Bicocca University)<sup>3</sup>. For the Yb<sub>2</sub>O<sub>3</sub>-ZnO system, we suggest a hole transition from ZnO valence band to Yb<sub>2</sub>O<sub>3</sub> VB, also if this mechanism has still been verified by theoretical calculations<sup>4</sup>.

### References

1. Calza, P.; Gionco, C.; Giletta, M.; Kalaboka, M.; Sakkas, V. A.; Albanis, T.; Paganini, M. C., *J. Hazard. Mater.* **2016**, *323*, 471-477.
2. Sordello, F.; Berruti, I.; Gionco, C.; Paganini, M. C.; Calza, P.; Minero, C., *Appl. Catal., B* **2019**, *245*, 159-166.
3. Cerrato, E.; Gionco, C.; Paganini, M. C.; Giamello, E.; Albanese, E.; Pacchioni, G., *ACS Appl. Energy Mat.* **2018**, *1* (8), 4247-4260.
4. Cerrato, E.; Zickler, G. A.; Paganini, M. C., *J. Alloys Compd.* **2019**, in press.

## Photocatalytic production of regenerated fuels under unconventional conditions

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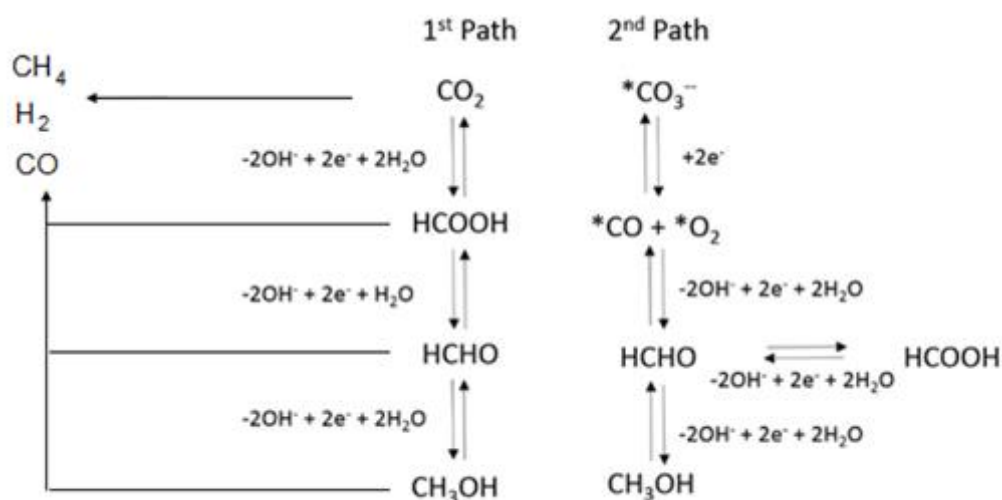
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The photocatalytic reduction of CO<sub>2</sub> is a virtuous process to regenerate valuable chemicals and fuels through spent combustion products. It is therefore an intriguing strategy to convert a greenhouse gas while storing solar energy into a chemical form. Different products can be obtained, as sketched in the following scheme, but the productivity of the reaction is very low when operated at ambient pressure. The key to improve the reactivity of the system is to operate at high pressure, which is, however, a hard task in photocatalysis, due to the need of transparent windows made of fragile materials. To this purpose, a high pressure photoreactor operating up to 20 bar allowed overperforming most literature results in terms of energy stored and productivity. Furthermore, H<sub>2</sub> production through photoreforming of wastewaters containing organic pollutants to be removed represents a challenging way to produce an energy vector while cleaning wastewater. Also in this case, unconventional reaction conditions, especially increasing the operating temperature, allowed to boost the productivity of hydrogen in the case of photoreforming of carbohydrate containing wastewater.

This work discusses different photoreactor configurations and the effect of operating parameters for both the reactions



### References

1. Wang C., Sun Z., Zheng Y. and Hu Y.H., *J. Mater. Chem. A* **2019**, 7, 865–887.
2. Bahadori E., Tripodi A., Villa A., Pirola C., Prati L., Ramis G., Dimitratos N., Wang D., Rossetti I., *Catal. Sci. & Technol.* **2019**, 9, 2253 – 2265.

## Understanding interfacial charge transfer between the lead halide perovskite and novel phenothiazine-based organic hole transport materials

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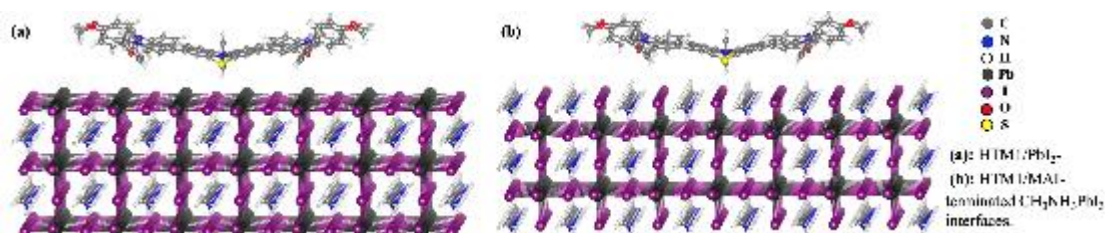
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In the past few years, perovskite solar cells (PSCs) have attracted the attention of researchers for their interesting features and promising photoconversion efficiencies, up to 25%.<sup>1</sup> Nevertheless, one of the main issues that prevent the commercialization is the lack of stability.<sup>2</sup> In order to address this problem, one of the key materials to optimize is the hole transport material (HTM), but it is also important to understand the charge transfer mechanism at the interface between the HTM and the perovskite.<sup>3</sup> In this work, we report a theoretical investigation on the behavior of a recently designed phenothiazine and triphenylamine-based HTM (named HTM1)<sup>4</sup> when interacting with the two possible surface terminations of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (001): the PbI<sub>2</sub>-terminated, exposing lead and iodide atoms, and the MAI-terminated, exposing methylammonium cations and iodide atoms (see Fig. 1). The results on HTM1 are discussed in comparison with the Spiro-OMeTAD, and other phenothiazine and triphenylamine-based HTMs, such as PTZ2.<sup>5</sup> The study has been carried with Density Functional Theory, including the dispersion correction DFT-D3 as implemented in SIESTA. The results of this study will add knowledge about the molecular processes occurring in PSCs and could be transferable to other triphenylamine-based molecules present in literature, in order to design more efficient HTMs for a wide deployment of the PSC technology.



### References

1. NREL Efficiency Chart, [www.nrel.gov](http://www.nrel.gov)
2. Wang, D., Wright, M., Elumalai, N. K., Uddin, A. *Sol. Energy Mater. Sol. Cells.* **2016**, *147*, 255–275.
3. Li, Y., Zhang Y., Zhang J., Li J., Wu W., Wang L., *Organic Electronics*, **2018**, *62*, 591-597.
4. Coppola C., Dessì A., Zani L., Parisi M.L., Basosi R., Reginato G., Sinicropi A., *in preparation*.
5. Grisorio, R., Roose B., Colella S., Listorti A., Suranna G., Abate A., *ACS Energy Lett*, **2017**, *2*, 1029–1034.

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## Hybrid Inorganic-Organic Membranes based on [Nafion/(WO<sub>3</sub>)<sub>x</sub>] as Efficient Barrier Toward Vanadium Crossover in RFB

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One of the most challenging issues affecting Vanadium Redox Flow Batteries (VRFB), an emerging electrochemical energy conversion and storage technology that is particularly suitable for applications in the power grid <sup>1</sup>, is concerned with self-discharge due to the high permeability of the ion-exchange membrane (IEMs) used as the separator between the anode and the cathode compartments <sup>2</sup>. In order to curtail the permeability of vanadium species and concurrently maintain high conductivity and mechanical properties, WO<sub>3</sub> is blended with Nafion® in different w/w ratios and used to obtain membranes that were prepared by the solvent-casting method. This new family of hybrid IEMs is indicated as [Nafion/(WO<sub>3</sub>)<sub>x</sub>]. The resulting membranes are characterized by means of Scanning Electron Microscopy (SEM) and micro-Raman spectroscopy, and exhibit two distinct layers bonded together. One layer of the hybrid IEM shows a high concentration of the WO<sub>3</sub> filler, which is neatly separated from the other Nafion-rich layer. Micro-Raman spectroscopy shows that in the Nafion-rich layer the dispersion of WO<sub>3</sub> is homogeneous. “*Ex-situ*” permeability tests towards VO<sup>2+</sup> ions show the lowest value of permeability for the [Nafion/(WO<sub>3</sub>)<sub>0.587</sub>] IEM (13.2·10<sup>-7</sup> cm<sup>2</sup>·min<sup>-1</sup> compared to 55.8·10<sup>-7</sup> cm<sup>2</sup>·min<sup>-1</sup> for Nafion 212 reference). The performance of the hybrid IEMs is tested in a single-cell VRFB at the current density of 50 mA·cm<sup>-2</sup>. The hybrid IEM demonstrates higher coulombic and energy efficiency (93% vs. 88% and 75% vs. 65% respectively) and higher capacity retention (62% vs. 42%) than Nafion 212. This result is ascribed to the lower permeability, allowing a step further towards the development of IEMs exhibiting a high conductivity and selectivity.

### References

1. Lu, W. et al. *Phys. Chem. Chem. Phys.* **2018**, 20, 23-35
2. Sun, C. et al. *Solid State Ionics* **2018**, 319, 110-116

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## Thermal properties and cyclic stability of nickel metal-complex conductive polymer with Schiff base

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The discovery of the physicochemical mechanisms of thermal transformations in conducting polymer macromolecules plays an important role in further improving the characteristics of existing batteries, as well as in developing new devices. The temperature behavior of a polymer based on a complex nickel compound with a Schiff base was investigated. The synthesis was carried out according to the standard method [1].

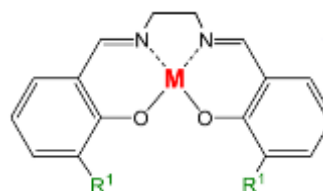


Figure 1. The structural formula of poly [M(RSalEn)]; R = MeO, EtO, HeO; M = Ni.

The structural formula of the polymer is shown in Figure 1.

The effect of temperature was studied by the nature of the change in conductivity and the electrochemical response of the sample by cyclic voltammetry before and after temperature tests. The tests were carried out both in the air atmosphere and in argon. The atmosphere has a significant effect on the temperature characteristic, and therefore the mechanism. The data obtained when heated to 250 degrees Celsius show that a change in the conductivity current is associated with an electrochemically reversible rearrangement of the electrolyte-polymer system.

Figure 2 shows the temperature dependence of the conductivity of the studied polymer:

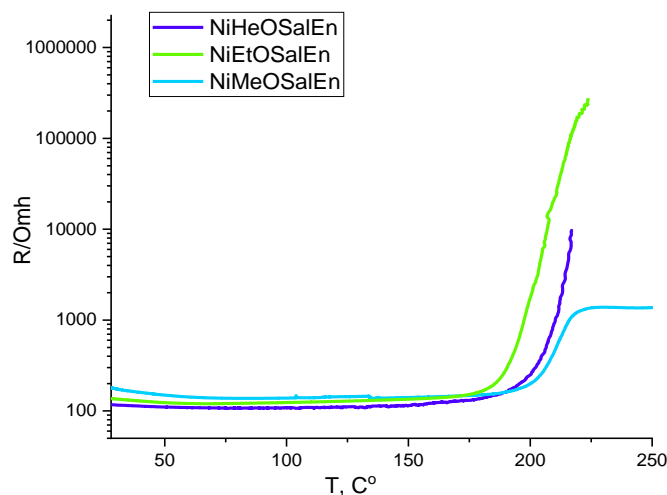


Figure 2. Temperature dependence of the conductivity of poly [Ni (Salen)].

### References

1. Eliseeva, S.N.; Alekseeva, E. V; Vereshchagin, A.A.; Volkov, A.I.; Vlasov, P.S.; Konev, A.S.; Levin, O. V. *Macromol. Chem. Phys.* **2017**, *1700361*, 1–5.

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## New organic sensitizers with improved spectral properties for application in greenhouse-integrated Dye-Sensitized Solar Cells

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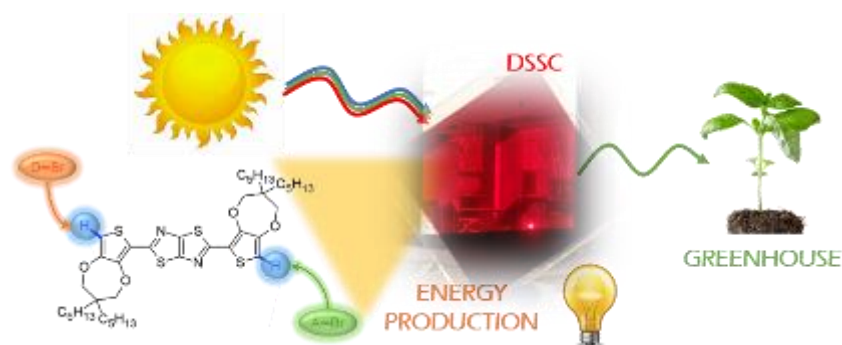
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Nowadays, the development of photovoltaic greenhouses represents a smart tool for increasing sustainability in agricultural production. However, the first target of a greenhouse is the growth of plants, so their proper illumination is crucial. For this reason, the choice of the proper solar technology should be led by the transparency and the color versatility of the devices and both these properties are actually satisfied by DSSCs (Dye-Sensitized Solar Cells).<sup>[1]</sup> In the last years, we have been interested in the synthesis of new D- $\pi$ -A organic dyes showing an intense light absorption and especially suitable to build transparent thin-layer DSSCs.<sup>[2]</sup> Starting from these compounds, which are based on a thiazolo[5,4-*d*]thiazole scaffold, we decided to synthesize a new series of photosensitizers specifically designed for greenhouses application. The aim was to minimize the light absorption in that part of the spectrum used for photosynthesis<sup>[1]</sup> and, consequently, to warrant the proper growth of the plants. A robust Pd-catalyzed direct arylation protocol was developed, in order to introduce selective modification on the dye structure and to prepare dyes on grams-scale.



### References

1. Roslan, N.; Ya'acob, M. E.; Radzi, M.A.M.; Hashimoto, Y.; Jamaludin, D.; Chen, G. *Renew. Sust. Energ. Rev.* **2018**, *92*, 171-186.
2. 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*, 13952-13955.

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## Electrochemical recycling of platinum from spent catalytic structures

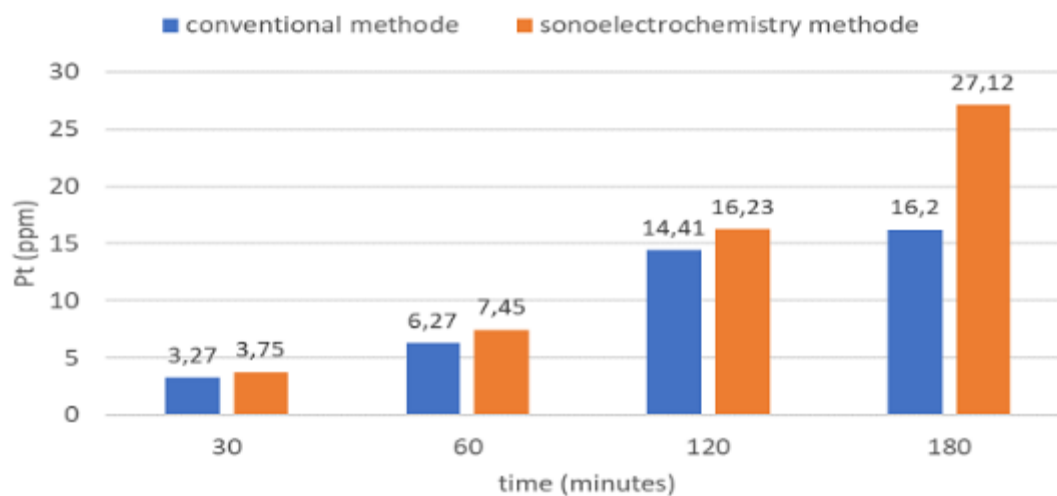
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Platinum is widely used in industries like jewellery, automotive, medicine and electronics, and has very limited availability. The recycling of platinum has become a top priority in the last few years [1,2]. Traditional methods used for recycling require use of energy intensive equipment (temperatures higher than 2000 °C) and involve the use of high concentrations acids. The methods mentioned above have a negative impact on the environment [3]. There is an urge to find alternative methods in light of circular economy principles. Electrochemical methods may be the answer to these problems, because they aren't harmful for the environment and it can use excess renewable energy. Electrochemical dissolution of platinum in different electrolytes is studied in this work. Besides conventional methods like cyclic voltammetry and chronoamperometry, a new modern method named sonoelectrochemistry was used for dissolution of platinum. With the help of a sonotrode from an ultrasound device, we were able to implement this new method. While doing the elemental analysis of the electrolytes it was found that the largest dissolution rates were achieved with sonoelectrochemistry, followed by chronoamperometry with potential step.



### References

1. Matthey J., Precious Metals Management Summary of Platinum Supply & Demand In 2017, Pgm Market Report February 2018
2. Black W., The platinum group metals industry, Woodhead Publishing limited, 2000
3. Peng Z., Li Z., Lin X., Pyrometallurgical Recovery of Platinum Group Metals from Spent Catalysts, The Minerals, Metals & Materials Society, 2017

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## Polymer-based water-processable blend nanoparticles as a tool to improve OPV sustainability

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Organic photovoltaic (OPV) technology has been intensively investigated over the last decades as it represents an intriguing alternative for electrical power generation. Nevertheless, its market penetration is limited not so much by the lower power conversion efficiencies compared to inorganic devices, but rather by the use of halogenated organic solvents, which are toxic and harmful (1-2).

Polymer-based water-processable nanoparticles (WPNPs) represent a way to overcome the problem. Amphiphilic rod-coil block copolymers (ABCPs) (3), bearing a rigid block and a hydrophilic flexible segment, are able to self-assemble *via* miniemulsion method without using any surfactant, generating organized nanostructures. The hydrophilic flexible block works as surfactant and interacting with aqueous medium assures the colloidal suspension stability (4). Also, it interacts with the electron-acceptor material (n-type), leading to the formation of pre-aggregated domains, suitable to achieve the charge percolation into the final device.

Particularly, we synthesized the low band-gap polymer PTB7, in order to connect it to a tailored segment of P4VP producing a new ABCP, the PTB7-*b*-P4VP. This polymer allows the fabrication of efficient PV cells and furthermore it is semi-crystalline (5). We carried out an in-depth characterization to confirm the molecular structure of PTB7-*b*-P4VP, and we tested its capability to self-assemble in aqueous medium to produce nanoparticles, both neat and in blend with fullerene derivatives. The obtained WPNPs were characterized by DLS and spectroscopy, deposited in films characterized by AFM and will be employed as active layer in OPV devices.

### References

1. Holmes P., Marks M., Kumar P., Kroon R., Barr M. G., Andersson R., Dastoor P. C., Belcher W. J. *Nano Energy* **2016**, *19*, 495-510
2. Zhang S., Ye L., Zhang H., Hou J. *Materials Today* **2016**, *19*, 533-543
3. Zappia S., Mendichi R., Battiato S., Scavia G., Mastria R., Samperi F., Destri S. *Polymer* **2015**, *80*, 245-258
4. Ferretti A. M., Zappia S., Scavia G., Giovanella U., Villafiorita F., Destri S., *Polymer* **2019**, *174*, 61-69
5. Zappia S., Scavia G., Ferretti A. M., Giovanella U., Vohra V., Destri S. *Adv Sustainable Syst.* **2018**, *2*, 1700155

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## Features of the crystal structure of LiFePO<sub>4</sub> cathodes of lithium-ion batteries under the influence of cyclic charge exchange on the surface layers

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LiFePO<sub>4</sub> cells are considered as the safest and the most resistant to overcharge among Li-ion batteries. The stability of LFP itself results from the olivine structure and the stable P-O bonds [1]. This allows positioning LFP as the safest and most resistant to overcharge electrode material [2]. However, if LiFePO<sub>4</sub> based electrodes are exposed to high potentials, surface and structural changes may occur in the electrode material. The small size of LiFePO<sub>4</sub> nanoparticles increases the surface area of the material. As a result of adverse reactions during charge and discharge it can lead to the formation of solid electrolyte interface layer, SEI, a layer with a complex composition and morphology, at the contact boundary of electrode materials and electrolyte [3]. It leads to increase of the internal resistance, decrease of lithium diffusion rate, and significant LIB performance degradation [4].

In this study Li/LiFePO<sub>4</sub> half-cells were overcharged under different modes with variable cut-off voltages and charge currents. The change of voltage profile, discharge capacity, surface layers composition and crystalline structure were characterized after overcharge cycles. X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) study of overcharged cathodes LiFePO<sub>4</sub> allowed detecting surface and structural changes of the material, caused by the overcharge potential. The results showed that this material is resistant to short-term overcharging up to 5 V, but undergoes irreversible changes with increasing overcharge time or potential.

### References

1. Chen, G.; Richardson, T.J. Thermal instability of Olivine-type LiMnPO<sub>4</sub> cathodes. *J. Power Sources* **2010**, *195*, 1221–1224.
2. Julien, M.C.; Mauger, A.; Zaghbi, K.; Groult, H. Comparative Issues of Cathode Materials for Li-Ion Batteries. *Inorganics* 2014, *2*.
3. Schulz, N.; Hausbrand, R.; Wittich, C.; Dimesso, L.; Jaegermann, W. XPS-Surface Analysis of SEI Layers on Li-Ion Cathodes: Part II. SEI-Composition and Formation inside Composite Electrodes. *J. Electrochem. Soc.* **2018**, *165*, A833–A846.
4. Peled, E.; Menkin, S. Review - SEI: Past, present and future. *J. Electrochem. Soc.* 2017, *164*, A1703–A1719.

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## The physicochemical properties of lithiated Nafion swollen with binary low-molecular-weight plasticizer

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The lithiated Nafion membrane (Li-Nafion) seems to be a suitable choice for the development of a polymeric lithium-ion battery (LIB). The transport properties of a polymer electrolyte largely determine the performance and operating temperature range of an electrochemical device. Phase transitions in the electrolyte dictate a low-temperature operating limit of LIB since they cause a sharp drop in conductivity and a decrease in the efficiency of the device. Therefore, the urgent task is to develop polymer electrolytes with high ionic conductivity in a wide temperature range.

The lithiated form of the perfluorinated sulphonic ion-exchange membrane Nafion (115 and 211, the thickness of 125  $\mu\text{m}$  and 50  $\mu\text{m}$  (DuPont, USA)) was obtained by replacing mobile protons with  $\text{Li}^+$ . A binary mixture of ethylene carbonate (EC)/sulfolane (SL) was used as the plasticizer. To obtain polyelectrolyte films saturated with a plasticizer, the dried Li-Nafion samples were impregnated into EC/SL mixtures for 24 h at 40 °C in a dry argon atmosphere. The sulfolane content in the EC/SL mixture varied from 0 to 100% (mass.) in increments of 5-10%. The degree of swelling (W) of the membrane in the solvent mixture was determined by the ratio of the difference between the mass of the swollen and dry membrane to the mass of the dry membrane.

It was found that the binary EC/SL system selected as a plasticizer is a simple eutectic (eutectic point -16°C, 70.5% (mass.) SL). On the phase diagram were recorded additional lines of liquidus and solidus characterizing metastable equilibria, which is typical for binary systems with SL. The use of the EC/SL mixture for plasticization of Li-Nafion has significantly reduced the freezing point of the plasticizer in the membrane to -16 °C thereby expanding the working temperature range of the electrolyte. The lithium-ion conductivity of the films was studied in the heating mode within the range of 25-80 °C. At the room temperature, the conductivity decrease with SL content up to eutectic composition (EC:SL=30:70 by weight) from  $2.3 \times 10^{-4}$  to  $0.4 \times 10^{-4}$  Sm/cm and then stop to change. Activation energy rises nearly linear from 20 to 33 kJ mol<sup>-1</sup> as SL content increases.

Membrane Nafion-211 plasticized by PC and EC/SL mixture was comparatively tested as the separator and electrolyte in anode half-cells  $\text{Li}/\text{Li}_4\text{Ti}_5\text{O}_{12}$  by galvanostatic cycling within the potential range of 1.2-2V.

*Acknowledgements:* This work was funded by the Russian Science Foundation (project No. 18-19-00014).

## Aqueous solar cells: strategies for electrodes and electrolytes design

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Photovoltaic (PV) technology has evolved rapidly in the past few decades and now encompasses a large variety of materials and device structures. A key aspect to be considered in any PV technology is the operational durability under real outdoor conditions, as well as the sustainability of materials/components and the facile integration with energy storage systems. In the last five years, dye-sensitized solar cells (DSSCs) with water-based electrolytes have been considered as one of the possible breakthroughs towards DSSC large-scale diffusion. If opportunely developed and optimized, aqueous solar cells can be truly considered a zero-impact photovoltaic device with non-toxic components [1,2,3,4].

We show the possibility of gellyfing the electrolyte into a solid matrix and the replacement of Pt cathodes with conductive polymers or biomass-derived carbon substrates could increase the long-term stability and lower fabrication costs. Also, we report morphological modifications of TiO<sub>2</sub> photoanodes, introduced by adding various kinds of additives, both molecular and polymeric, to the commercial Dyesol TiO<sub>2</sub> paste, typically used for screen printing DSSC electrodes onto conductive glass. It was found out that the addition of polyethylene glycol (PEG) modified both the morphology and the thickness of photoanodes. As a result, PEG-based cells showed an increased short-circuit current density (+18%) and power conversion efficiency (48%) with respect to the pristine counterpart.

Looking at the real application of DSSCs, the electricity production and the change of consumption for lighting and air conditioning of offices/flats depending on the different orientations of the building can be estimated. The integration of aqueous DSSCs with windows causes an increase of about 14% of the electricity consumption for lighting due to the lower light transmittance, slightly increases the energy needs for heating (less than 10%), but greatly reduces the demand for energy for cooling, shielding part of the solar thermal contributions. When the building is oriented towards the West and South, the application of the DSSC is advantageous.

### References

1. Bella, F.; Gerbaldi, C.; Barolo, C.; Grätzel, M.; *Chem. Soc. Rev.* **2015**, *44*, 3431-3473.
2. Galliano, S.; Bella, F.; Piana, G.; Giacona, G.; Viscardi, G.; Gerbaldi, C.; Grätzel, M.; Barolo, C.; *Sol. Energy* **2018**, *163*, 251-255.
3. Bella, F.; Galliano, S.; Falco, M.; Viscardi, G.; Barolo, C.; Grätzel, M.; Gerbaldi, C.; *Green Chem.* **2017**, *19*, 1043-1051.
4. Bella, F.; Galliano, S.; Falco, M.; Viscardi, G.; Barolo, C.; Grätzel, M.; Gerbaldi, C.; *Chem. Sci.* **2016**, *7*, 4880-4890.

## H<sub>2</sub> production and levulinic acid hydrogenation to GVL using the co-produced formic acid as H<sub>2</sub> source

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Levulinic acid (LA) is a useful platform molecule to produce green chemicals and it is produced from cellulose by acidic-hydrolysis together with formic acid (FA). Moreover,  $\gamma$ -valerolactone (GVL) can be produced by consecutive hydrogenation and dehydration of LA. The H<sub>2</sub> reagent for the LA hydrogenation needed in GVL synthesis can be obtained by decomposition of FA. The goal was to study the catalytic upgrading of a levulinic acid-formic acid mixture. Ni based and NiCu-based catalysts were synthesized. Best results were obtained with an ex-hydrotalcite Ni<sub>24</sub>Mg<sub>56</sub>Al<sub>20</sub> mixed oxide. The hydrotalcite precursor allowed a high dispersion of Ni and the high Mg/Al ratio provided a basic support with high surface area. Calcination of the hydrotalcite at 650°C gave a mixed oxide. This was then reduced to produce the final catalyst which was characterized by means of XRD and Temperature Programmed Reduction.

The tests were performed in an autoclave under autogenous conditions and products were analysed by GC (gas phase), HPLC (liquid phase) and GC-MS (product identification). FA decomposition was first tested and confronted with blank tests, that showed the Ni-based catalyst gave H<sub>2</sub> and CO<sub>2</sub> by FA decomposition at low temperatures, while the blank test did not provide significant FA conversions in the same conditions. Having identified the appropriate conditions for the FA decomposition, tests with a formic acid-levulinic acid feed were carried out under different conditions. An almost complete decomposition of FA to H<sub>2</sub> and CO<sub>2</sub> was evidenced while GVL was produced with yield as high as 60% in autogenous conditions. The appropriate time of reaction was individuated. H<sub>2</sub> yield showed a first increase with temperature, with a maximum around 200°C, while decreasing at higher temperatures where GVL production increased, indicating that the hydrogen produced by formic acid decomposition was participating in the hydrogenation (figure 1). Carbon balances higher than 80% and good product recoveries were obtained throughout all the tests. A solid precipitate was indicated as responsible for the carbon loss.

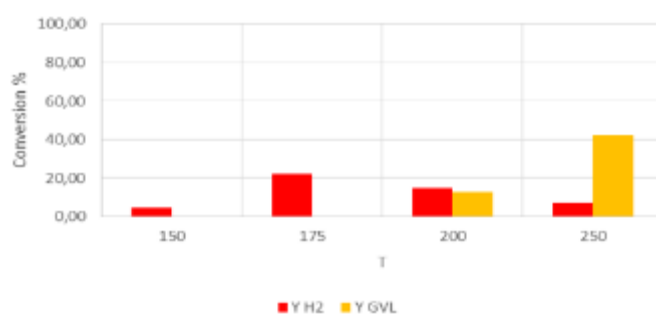


Figure 1: Hydrogen yield (Y H<sub>2</sub>) and GVL yield (Y GVL) for the Ni-Mg-Al tested for 3 h.

*Acknowledgements:* the MIUR is acknowledged for the economic support within the PRIN project Hercules

## Efficient electrochemical production of carbon monoxide and formic acid from CO<sub>2</sub> in a gas-liquid buffer layer flow cell employing carbon cloth electrodes functionalized with a fac-Mn(apbpy)(CO)<sub>3</sub>Br complex as gas diffusion cathodes

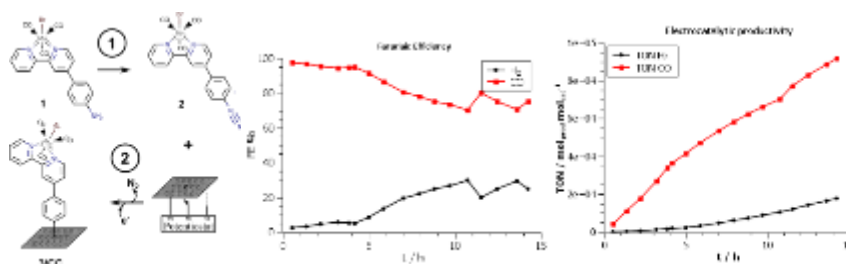
**Jonathan Filippi<sup>a</sup>, Laura Rotundo<sup>b</sup>, Hamish A. Miller<sup>a</sup>, Riccardo Rocca<sup>b</sup>, Roberto Gobetto<sup>b</sup>, Carlo Nervi<sup>b</sup>, Francesco Vizza<sup>a</sup>**

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The electroreduction reaction of CO<sub>2</sub> is one of the most challenging strategies for excess renewable energy storage into carbon-neutral fuels. Particular interest is aroused by the production of CO, as it is a fundamental building block for many industrial processes including Fisher-Thropsch. An innovative approach is to use organometallic complexes as electrocatalyst allowing, in principle, a higher metal utilization efficiency compared to metal-nanoparticle-based electrocatalyst. Furthermore, anchoring the complex on electro-conductive supports helps to overcome the mass transport limitations of the electroactive species from the bulk to the electrode surface allowing also much higher electrocatalyst stability. Among many types of electro-conductive supports, carbon cloth has excellent properties for the fabrication of gas diffusion layer cathodes for gas-electrolyte buffer layer interface. Herein we describe the use of a manganese Lehn-analogue complex (fac-Mn(apbpy)(CO)<sub>3</sub>Br) grafted on carbon cloth support by diazonium salt reduction, as electrocatalyst in aqueous media for the reduction of CO<sub>2</sub> to CO. The electrocatalyst, supported in carbon cloth working as a gas diffusion cathode, was tested in a gas-flow cell fed with pure CO<sub>2</sub> operating at atmospheric pressure. In this condition, the supported Mn complex was able to convert CO<sub>2</sub> into CO and formic acid at -0.67V vs RHE with a faradaic efficiency higher than 75% (>90% initial) and 11% for CO and HCOOH respectively. In addition a productivity rate higher than 350NICO min<sup>-1</sup> gMn<sup>-1</sup>, and turnover numbers up to 82000 and 12000 for CO and HCOOH in 14h of were observed.



**Figure:** left) fac-Mn(apbpy)(CO)<sub>3</sub>Br grafting process on carbon cloth; middle) CO-faradaic efficiency and; right) electrocatalyst turnover number (TON) time profiles.

### References

1. Nervi, C. et al. *Chem. Eur. J.* **2017**, *23*, 4782-4793.
2. Vizza, F et al. *Chem. Comm.* **2019**, *55*, 775-777.

*Acknowledgements:* This work was funded by the the PRIN 2017 project, n. 2017YH9MRK of the Italian Ministry of Instruction and Research (MIUR)

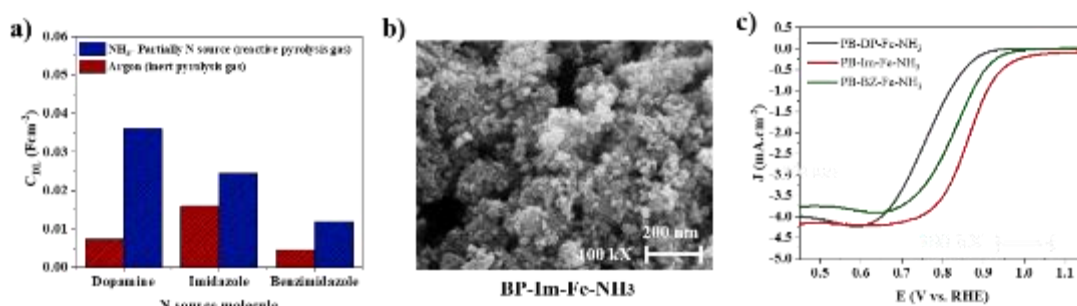
## PGM-free catalysts for anion exchange membrane fuel cells

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One of the major challenges for a widespread commercialization of fuel cells is the high cost of platinum used as electrocatalysts for the oxygen reduction reaction (ORR) at the cathode side. Although platinum-group-metal (PGM)-catalysts have shown promising features [1,2], high costs for synthesis and stability and activity issues under operating conditions still limit their applicability in fuel cells.

We propose in this work a facile synthetic strategy to obtain iron-based ORR catalysts by nitrogen and iron wet impregnation of carbon black followed by pyrolysis steps. Three different nitrogen sources (dopamine, imidazole, and benzimidazole) and two different pyrolysis atmospheres (inert Ar and reactive NH<sub>3</sub>) were used. The obtained materials were characterized in terms of structure, morphology, thermal and electrochemical properties. We found that tailoring the synthesis parameters allows obtaining electrodes with high porosity and efficient catalytic active sites to boost catalytic towards ORR in alkaline environment, as indicated by cyclic and linear sweep voltammetry with rotating disk electrode. In particular, we found that the pyrolysis step under ammonia flow led to high double layer capacitance (CDL) electrodes with high porosity (Figures 1a and 1b), and the use of imidazole as nitrogen-rich organic precursor improved ORR activity of the electrode (Figure 1c). The onset and half-wave potentials values ( $E_{\text{onset}} = 0.95$  V,  $E_{1/2} = 0.86$  V vs. RHE) recorded with the electrocatalyst prepared using imidazole and pyrolyzed under ammonia indicate that its activity towards ORR is competitive with that previously reported for platinum-based and PGM-Free electrocatalysts [3].



**Figure 1.** (a) CDL values and (b) SEM image of the sample obtained with imidazole and NH<sub>3</sub> as synthesis parameters, (c) linear sweep voltammetry of the samples obtained with different nitrogen-precursors.

### References

1. Kodali, M., Santoro, C., Herrera, S., Serov, A., Atanassov, P. *J. Power Sources*, **2017**, 366, 18–26.
2. Mecheri, B., Ficca, V. C. A., Costa de Oliveira, M. A., D'Epifanio, A., Placidi, E., Arciprete, F., Licoccia, S. *Applied Catalysis B: Environmental*, **2018**, 237, 699–707.
3. Chen, M., He, Y., Spindelov, J. S., Wu, G. *ACS Energy Letters*, **2019**, 4, 7, 1619–1633.

## Diketopyrrolo-pyrrole based molecules for Organic Field Effect Transistors (OFETs)

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Nowadays the Electronics world is dominated by Silicon. Nevertheless, there are some limits to the Silicon based technologies. For instance, it is unthinkable to produce easy large area or low cost devices by using Silicon. Furthermore, looking at the current requirements of flexibility, lightness, recycling, the organic compounds seem to be the adequate candidate to complement Silicon in semiconductor applications. Given this, we fabricated organic field effect transistors based on novel organic diketopyrrolo-pyrrole (DPP) derivatives. In Fig. 1a) we report the chemical structures of the prepared molecules where it can be seen that the dyes share a common molecular fragment and differ only for the terminal electron acceptor groups. This structural modification has a significative influence on the optical properties of the absorption and determines the reduction of the optical bandgap as the strength of the electron acceptor end group increases.

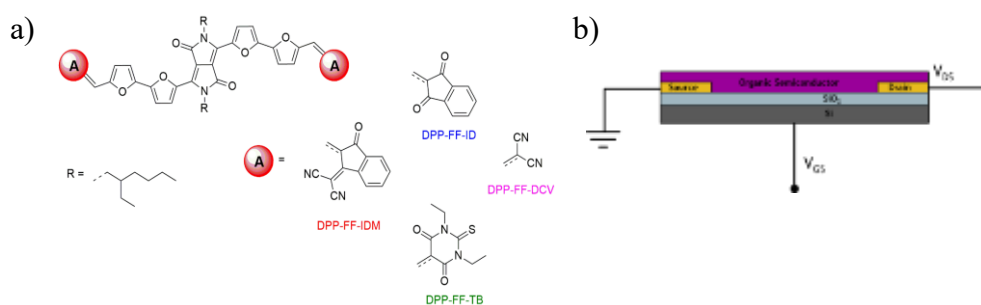


Fig. 1 – a) Chemical structures of DPP organic molecules; b) Organic FET scheme

The synthesized molecules were thoroughly characterized concerning their structural, thermal and optical features. Then they were used as active layer in organic transistors, according to the scheme of Fig. 1b).

Tab. 1 – Electrical characterization of the transistors

Compounds	Conduction type	$M_{el}$ ( $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ )	$M_h$ ( $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ )
DPP-FF-DCV	n	$1.3 * 10^{-3}$	-
DPP-FF-TB	ambipolar	$3 * 10^{-2}$	$4 * 10^{-3}$
DPP-FF-ID	ambipolar	$8 * 10^{-3}$	$8 * 10^{-4}$
DPP-FF-IDM	n	$1 * 10^{-5}$	-

The electrical characterization of the fabricated devices revealed an interesting ambipolar behavior for three of the four investigated systems with the best performance shown by DPP-FF-TB which features an electron and hole mobility ( $M_{el}$  and  $M_h$  respectively) in the order of  $10^{-2}$  and  $10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  when measured in vacuum and still clearly measurable in air, indicating a promising stability of the investigated systems in ambient conditions.



## Dye-sensitized photoanodes for photoelectrochemical water oxidation with a novel class of quinoid photosensitizers

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Nowadays, it is very important to develop green ways to produce and store energy, considering the continuous increasing of pollution from fossil fuels. For this purpose, one of the most attracting process is artificial photosynthesis, in which water and carbon dioxide are the starting raw materials for the light assisted production of fuels such as H<sub>2</sub>, methane, CO. Therefore, it is extremely interesting, and at the same time very challenging, to develop systems capable of exploiting solar light to activate the associated, photoinduced redox reactions. Dye-sensitized photoelectrochemical cell (DS-PEC) have been largely investigated, in particular for the water splitting process. In this field, great attention has been dedicated to the use of molecular chromophores capable of light harvesting in the visible region.<sup>1</sup>

Our research focuses on dye-sensitized photoanodes for photoelectrochemical water oxidation. The electrodes are constituted by a fluorine doped tin oxide (FTO) with a superficial layer of SnO<sub>2</sub> semiconductor, and are sensitized with a diquinoid dye and catalysts for water oxidation reaction.<sup>2</sup> In particular, we focused on the novel class of dyes, characterized by a pentacyclic structure with two quinones functional groups, showing excellent optical and redox proprieties. In fact, these absorb visible light in a very wide range (up to 600 nm), and promote efficient electrons injection into the SnO<sub>2</sub> semiconductor surface, matching with its energy level. The dye-sensitized electrodes are combined with several water oxidation catalysts to achieve photoelectrochemical water oxidation.<sup>3</sup>

### References

1. Kirner, J.T. et al. *J. Mater. Chem. A* **2017**, *5*, 19560-19592.
2. Galloni, P. et al. *New J. Chem.* **2017**, *41*, 2769–2779.
3. Sartorel, A. et al. *Chem. Soc. Rev.*, **2013**, *42*, 2262-2280.

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## Fructose dehydration to 5-hydroxymethylfurfural in the presence of Nb<sub>2</sub>O<sub>5</sub> based (photo)catalysts

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Biomass is a green renewable source easily available and considered a precious local resource. The valorization of biomasses to obtain fuels or chemicals represents a specific relevant issue. In this context the catalytic dehydration of hexoses in acidic medium to obtain furanic species is an important reaction giving rise to platform molecules useful in the chemical industry<sup>1</sup>. In this research the selective fructose dehydration to obtain 5-hydroxymethylfurfural (HMF) has been studied in the presence of Nb<sub>2</sub>O<sub>5</sub> based catalysts. Despite the advantage of using water as an environmentally benign solvent, the hexoses dehydration has been mainly carried out in organic solvents because the use of aqueous suspensions gave rise to low HMF yields due to subsequent reactions of the furane to levulinic acid and insoluble polymeric substances (humins). In this research, a set of acidic catalysts were prepared based on Nb<sub>2</sub>O<sub>5</sub> by using metal chlorides as precursors and an hydrothermal preparation methodology. Pristine Nb<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>, along with the composites Nb<sub>2</sub>O<sub>5</sub>-ZrO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>-CeO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> were fully physico-chemically characterized. The fructose dehydration was carried out in a 100 mL autoclave reactor. The tuning of the experimental catalytic conditions such as nature and amount of catalyst, initial hexose concentration, volume of reaction mixture, reaction time and reaction temperature allows to improve fructose conversion and HMF yield, minimizing undesirable reaction products.

The selectivity to HMF reached ca. 80% in the presence of Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> or Nb<sub>2</sub>O<sub>5</sub>-CeO<sub>2</sub>, in both cases with a fructose conversion higher than 50%. In these experiments the yield to HMF achieved 45 and 50 %, respectively. The use of pristine Nb<sub>2</sub>O<sub>5</sub> gave rise to HMF yields equal to 55 and 57% with a fructose conversion of 71 and 76% by using an amount of catalyst of 0.5 or 1 g·L<sup>-1</sup>, respectively.

The best catalytic conditions required 3 h of reaction working at a temperature of 165°C in autoclave by using 6 ml of 1 M of fructose suspension with a catalyst amount equal to 1 g·L<sup>-1</sup>. Notably, analogous catalytic experiments (130°C, 56 mM initial fructose concentration, amount of Nb<sub>2</sub>O<sub>5</sub> 1.3 g L<sup>-1</sup>), reported in literature by using Nb<sub>2</sub>O<sub>5</sub> based materials, reached a selectivity of 28 % for a conversion of around 60 %, indicating a yield of 17%<sup>2</sup>.

### References

1. Menegazzo, F.; Ghedini, E.; Signoretto, M., *Molecules* **2018**, *23*, 2201-2219.
2. Stošić, D.; Bennici, S.; Pavlović, V.; Rakić, V.; Auroux, A., *Materials Chemistry and Physics* **2014**, *146*, 337-345

## Hydrothermal synthesis of copper vanadates NanoBelts on FTO and their photoelectrochemical properties

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Transition Metal Vanadates are a well-known class of compounds that has lately gathered a lot of attention especially for the possibility to use them as photoanodes (Oxygen Evolution Reaction OER), in visible light, to obtain water-splitting (H<sub>2</sub> evolution at the counter electrode). Although active in visible light, these materials are only moderately stable in water because of the leaching of vanadium and they are also characterized by a rather low charge separation efficiency caused by the fact that the lowest-energy transitions generate excitons with high binding energy [1].

In this contribution we describe how the preparation, by hydrothermal synthesis, of NanoBelt shaped copper vanadate (phase CuV<sub>2</sub>O<sub>6</sub>) nanostructures, grown directly on FTO slides, can improve the mechanical stability and the electrical contact with the substrate. This nanostructure, characterized by a highly crystalline structure, with preferential growth along the [110] direction (ICSD-28151), enhances the diffusion length of the photogenerated electrons and holes also increasing the surface area.

We deposited cobalt oxide (Co<sub>3</sub>O<sub>4</sub>, a p-type semiconductor) on these samples by drop-casting Co<sub>3</sub>O<sub>4</sub> nanoparticles, obtained by hydrothermal synthesis or by RF sputtering, in order to have the formation of a p-n junction that can act also as protective layer.

These nanostructures were characterized by standard Photo Electrochemical (PEC) measurements and by Intensity Modulated Photocurrent Spectroscopy (IMPS) with the aim of obtaining a deeper understanding of the mechanism of holes and electrons recombination and charge transfer in the presence of p-n junction and on the as grown material (CuV<sub>2</sub>O<sub>6</sub>/FTO).

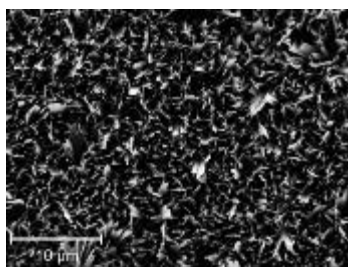


Figure 4. SEM images of Copper Vanadates

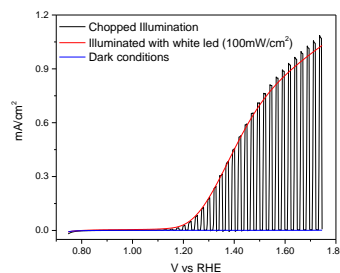


Figure 2. Linear Sweep Voltammetry of Copper Vanadates NanoBelt in Borate buffer (pH)

### References

1. J. Wiktor, I. Reshetnyak, M. Strach, M. Scarongella, R. Buonsanti, and A. Pasquarello *J. Phys. Chem. Lett.* **2018**, 9, 5698–5703

*Acknowledgements:* we thankfully acknowledge the support from the Italian Ministry of Foreign Affairs and International Cooperation (MAECI) for funding through cooperation project “GINSENG” (PGR00953) between Italy and China and MIUR (for PRIN projects: Multi-e and SMARTNESS)

## Hybrid Silicon Nanocrystals for Color-Neutral and Transparent Luminescent Solar Concentrators

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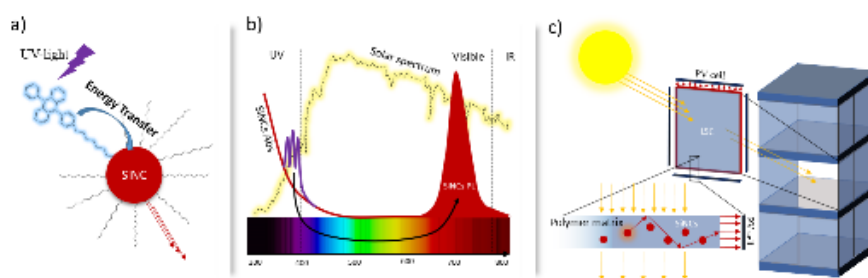
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Luminescent Solar Concentrators (LSCs) were proposed for the first time in 1973<sup>1</sup> as a viable alternative route to traditional Si-based solar panels, aiming at reducing the electricity costs and offering a solution suitable for Building Integrated Photovoltaics (BIPV).<sup>2</sup>

LSCs architecture consists in a plastic plate embedded with luminescent species that extensively absorb sunlight and emit in a spectral window where conventional Si-cells or GaAs cells have high power conversion efficiency. A substantial portion of the light emitted by the luminescent species can be concentrated to the edge of the plate (up to ~75% according to Snell’s law<sup>1</sup> for a polyacrylate waveguide) by total internal reflection. The advantages provided by this simple setup are related mostly to the possibility of preparing large area polymer plates with relatively simple procedures and low cost, coupling it to small area, band-gap matched and highly efficient conventional PV cell. One of the most detrimental loss mechanisms in Luminescent Solar Concentrators (LSCs) is re-absorption of emitted light from the luminophore.

Silicon nanocrystals (SiNCs)<sup>3</sup> in the quantum size range (diameter = 2-12 nm) have been used as a luminescent species, able to absorb in the near UV and emit in the NIR, remaining transparent in the visible spectral region. Compared to more traditional quantum dots, such as CdSe, SiNCs offer several advantages such as the lack of toxicity, the abundance of the main component, the high sustainability and the high Stokes-shift due to the indirect band gap nature, but the poor absorption properties limit their performance as LSCs luminophore.

Coupling an organic dye to SiNCs represents a smart approach to obtain sensitization of SiNCs luminescence by the organic dyes, thus resulting in tunable and improved optical properties of LSCs.<sup>4</sup> In particular, 9,10-diphenylanthracene was employed as UV sensitizer for SiNCs in order to produce LSCs with aesthetic appearance suitable to smart window application and optical efficiency as high as 4.25%. In addition, the role of the energy transfer process on LSC performance was elucidated by a thorough optical and photovoltaic characterization.



**Fig. 1** a) Schematic representation of DPA-functionalized SiNCs; b) representative absorption (empty) and PL spectrum (filled) of DPA-SiNCs. c) schematic representation of LSCs as solar windows for building integrated photovoltaics.

### References

1. M. G. Debije, P. P. C. Verbunt, *Adv. Energy Mater.* **2012**, 2, 12.
2. R. Mazzaro, A. Vomiero, *Adv. Energy Mater.* **2018**, 8, 33.
3. R. Mazzaro, F. Romano, P. Ceroni, *PhysChemChemPhys* **2017**, 19, 26507 – 26526
4. R. Mazzaro, A. Gradone, S. Angeloni, G. Morselli, P. G. Cozzi, F. Romano, A. Vomiero, and P. Ceroni, *ACS Photonics* **2019** 6 (9), 2303-2311.

## Ionic liquids as suitable electrolytes for non-aqueous vanadium redox flow batteries: a first insight

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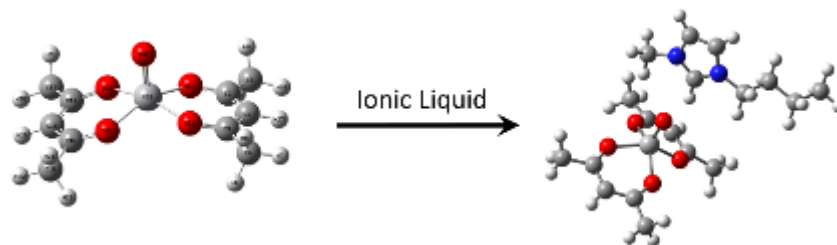
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In recent years the interest for flow batteries has constantly grown due to the increasing demand of safe, reliable and performing stationary energy storage systems to sustain the utilization of renewable energy sources.<sup>1</sup> Vanadium redox flow batteries (VRFBs), are commonly regarded as a safe, reliable and promising technology.<sup>1</sup> If aqueous VRFBs have been until now the most diffused and studied, non-aqueous electrolytes would allow, in perspective, to higher cell potential performances.<sup>2-4</sup> On the other hand, the poor solubility of vanadium species in organic solvents, as well as the low conductivity, are still a severe issue for obtaining well performing non-aqueous VRFBs.<sup>2,3</sup> Ionic liquids (ILs), due to their uncommon solvating properties and to their high conductivity, could represent promising solvents or additives for the realization of better performing non-aqueous electrolytes. The lack of literature data about the interactions occurring between ILs and vanadium complexes is however requiring to perform a preliminary study on the electrochemical influences of ILs on vanadium species, in order to obtain a wider comprehension of these novel systems and to allow a more rational and conscious future approach to ILs based VRFB electrolytes.



### References

1. Ponce de Leon, C.; Frias-Ferrer, A.; Gonzalez-Garcia, J.; Szanto, D.A.; Walsh, F.C. *Journal of Power Sources*, **2006**, *160*, 716-732.
2. Zhang, D.; Liu, Q.; Shi, X.; Li, Y. *Journal of Power Sources*, **2012**, *203*, 201-205.
3. Herr, T.; Fisher, P.; Tuebke, J.; Pinkwart, K.; Elsner, P. *Journal of Power Sources*, **2014**, *265*, 317-324.
4. Chakrabarti, M. H.; Mjalli, F. S.; Al Nashef, I. M.; Hashim, M. A.; Bahadori, L.; Low, C. T. J. *Renewable and sustainable Energy Reviews*, **2014**, *30*, 254-270.

## Optimization of Cu-based catalyst for the electrocatalytic reduction of CO<sub>2</sub> to fuels

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In the last century, with the intensification of human industrial activities, carbon dioxide levels in the environment increased, making global warming and greenhouse effect pressing issues. In this sense, the electroreduction of CO<sub>2</sub> is an interesting strategy, also if coupled with renewable energy sources to store the intermittent electric energy in form of chemical bonds [1]. Catalysts composed of a mixture of commercial copper nanoparticles (NPs) were studied. NPs with particles sizes of 25nm, 40-60nm and ZnO: 20-25 nm, named CZ 25\_B and CZ\_40-60\_B. The molar ratio between copper and ZnO is equal to 65/35. Another commercial catalyst that was analysed because it is active for the CO<sub>2</sub> hydrogenation is composed of CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> and traces of MgO (named CZA CC\_B). These catalytic mixtures were prepared in a planetarian ball mill. Another sample was prepared by pre-oxidation of the Cu NPs and then by manual mixing with the ZnO (called CZ calc 2h). Carbon Nanotubes (CNT) was used as carbon substrate to increase the conductivity and allow a better catalytic ink dispersion. All the samples were characterized by BET analysis, FESEM microscopy, X-ray diffraction, X-ray photoelectron spectroscopy and electrochemical analysis. The electrocatalytic activity was tested by using a rotating disk electrode (RDE) at ambient conditions. The best conditions were appreciated at a potential equal to -2 V vs Ag/AgCl, with the lowest FE for H<sub>2</sub> and the highest current density (mA/cm<sup>2</sup>) in absolute value. In Figure 1, the FE % of gaseous and liquid products are reported for the different prepared catalysts. From all test, the best catalytic activity with the lowest FE<sub>H<sub>2</sub></sub> was obtained with the Cu/ZnO peroxidised material (CZ calc 2h) at -2 V vs Ag/AgCl. In conclusion, it can be said that Cu-based catalysts were confirmed to be active towards CO<sub>2</sub>RR via the electrochemical method, with the advantage of performing the reactions at ambient conditions.

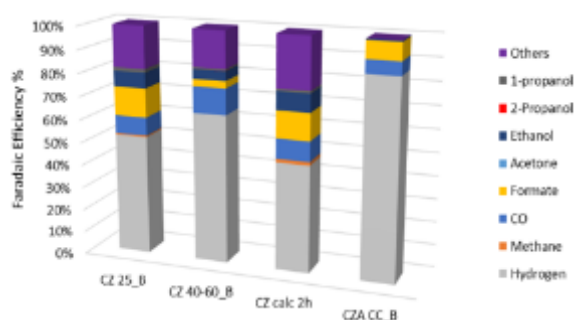


Figure 1: FE % of gaseous and liquid products for the different Cu -based catalysts

### References

- Hernandez, S., Farkhondehfar, M.A., Sastre, F., Makkee, M., Saracco, G., Russo, N. *Green Chemistry*. **2017**, 19, 2326 - 2346.

## Development of Cu-based hybrid catalysts for the electrocatalytic CO<sub>2</sub> reduction to added value products

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The simultaneous need to reduce greenhouse gas emissions and increase our energy supply makes the electrochemical reduction of CO<sub>2</sub> a very attractive alternative [1]. In this context, science seeks effective methods to transform CO<sub>2</sub> into chemicals of economic value. Among the possible products to obtain, we are especially interested in species with one or more carbon-carbon bonds, these types of compounds are favoured using copper as catalyst. Six catalysts were synthesized with different ratios of Cu, Zn Al and subsequently exposed to a thermal treatment to obtain the correspondent oxidized compounds. These kinds of catalyst are traditionally used in thermocatalysis for the efficient production of methanol at high temperature and pressure conditions [2]. Noting the good performance of this catalyst in thermocatalysis, it was chosen to carry out the experiment in the electrochemical reduction of CO<sub>2</sub> at ambient conditions. Electrochemical tests were carried out in the rotating disk electrode (RDE) in order to reduce the mass transfer limitations that may exist due to the low solubility of CO<sub>2</sub> in an aqueous medium. The chemical-physical properties of the catalyst were studied by several characterization techniques (e.g. XRD, XPS, BET, among others) to understand the role of the modification of the catalyst components during operation in the final selectivity and activity. Among the liquid products obtained are acetone, ethanol, isopropanol, formic acid and in some cases, methanol was also found. Moreover, gaseous products obtained were hydrogen, carbon monoxide and methane, being these last - gaseous products - those that present the highest faradaic efficiencies. These results were compared with the performance of the catalysts in a Gas Diffusion Electrode (GDE) cell, to obtain commercially-relevant current densities.

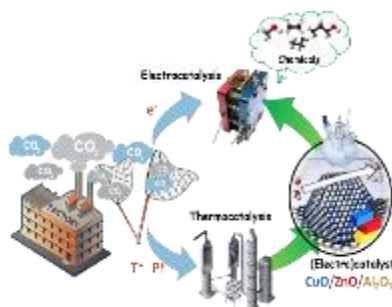


Figure 1: Synergies between thermo- and electro- catalysis for CO<sub>2</sub> conversion to added-value products

### References

- Hernandez, S., Farkhondehfar, M.A., Sastre, F., Makkee, M., Saracco, G., Russo, N. *Green Chemistry*. **2017**, 19, 2326 - 2346.
- Ganesh, I. *Renewable and Sustainable Energy Reviews*. **2016**, 59, 1269-1297.



## Design, synthesis and application of new phenothiazine-based Hole Transporting Materials (HTMs) for Perovskite Solar Cells (PSCs)

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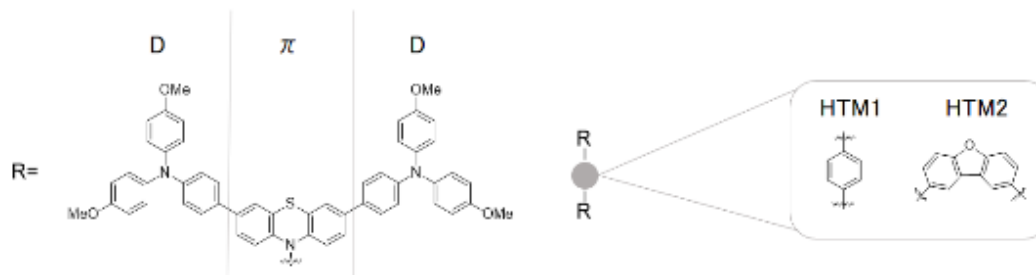
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A new solution in the field of photovoltaic technologies is represented by perovskite solar cells (indicated with the initials PSC) showing a rapid growth in power conversion efficiencies (PCE).<sup>1</sup> Hole Transporting Materials play essential roles in improving the device performances; their main task is to capture the hole formed in the perovskite layer and transport it to the cathode. Currently, Spiro-OMeTAD is the organic HTM that showed the best power conversion efficiencies (> 22 %),<sup>2</sup> but still faces some problems for its commercialization, due to its high costs and chemical instability.<sup>3</sup> Therefore, the goal of this study was to design and synthesize new, cheaper and more stable organic HTMs. Through Suzuki-Miyaura and Buchwald-Hartwig cross-coupling reactions two new HTMs have been synthesized (Fig.1); these have as their common feature a phenothiazine-based structure as a spacer between two diarylamine donor groups, to produce the typical D- $\pi$ -D sequence. Two of such building-blocks were linked through a phenyl (HTM1) or a dibenzofuran (HTM2) central core. These allowed to study how small structural modifications may affect the performance of the resulting PSCs.



### References

1. Correa-Baena, J. P.; Abate, A. Saliba, M.; Tress, W.; Jacobsson, T. J.; Grätzel, M.; Hagfeldt, A. *Energy Environ. Sci.* **2017**, *10*, 710-727.
2. Yang, W. S.; Park, B. W.; Jung, E. H.; Jeon, N. J.; Kim, Y. C.; Lee, S. S.; Seo, J.; Kim, E. K.; Noh, J. H. *Science*, **2017**, *356*, 1376-1379.
3. Saliba, M.; Orlandi, S.; Matsui, T.; Aghazada, S.; Cavazzini, M.; Correa-Baena, J. P.; Gao, P.; Scopelliti, R.; Mosconi, E.; Dahmen, K. H. De Angelis, F.; Abate, A.; Hagfeldt, A.; Pozzi, G.; Grätzel, M.; Nazeeruddin, M. K. *Nat. Energy*, **2016**, *1*, 15017.

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## Optimization of the visible light driven HOPG/CdSe/PDAC composite architecture through photochemical studies and surface analysis.

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Semiconductors are the primary components in photocells that are responsible for the conversion of solar energy to electricity. The formation of electron-hole pairs during light absorption by semiconductors generates a more useable and controlled form of energy. The goal of this research was to identify the optimal composition and architecture of a stable visible light driven photocatalytic composite consisting of a highly organized pyrolytic graphite (HOPG) substrate, cadmium selenide (CdSe) semiconductor<sup>1</sup> and conducting polymer poly (1,8-diaminocarbazole) (PDAC). The role of the polymer is to provide a protective layer for the CdSe that will decrease photocorrosion of the semiconductor. Polymerization of PDAC was conducted in three different ways; chemically in organic solution and electrochemically, in either acidic or neutral solutions<sup>2</sup>. For each of these forms of PDAC deposits, several composites were prepared that altered in the order of deposition of the semiconductor and polymer. These composites include: CdSe deposited before PDAC (HOPG/CdSe/PDAC), PDAC deposited before CdSe (HOPG/PDAC/CdSe), and CdSe and PDAC co-deposited (HOPG/CdSe+PDAC) on HOPG. Simultaneously, testing various thicknesses of the polymer layer helped optimizing the PDAC polymerization methods for each of these composites. Since the chemical method could not be controlled through the number of cycles applied during cyclic voltammetry, the thickness of the polymer was increased through multiple layers formation via successive dipping in monomer solution followed by UV light exposure. Polymerization in the neutral medium was tested for 7, 10, 15, and 20 cycles, and polymerization in the acidic medium was tested for 6, 10, 15, 20, and 25 cycles.

The stability and efficiency of all of these composites were tested through photoelectrochemical studies, such as: cyclic voltammetry, open circuit potentiometry and chronoamperometry in 0.1M Na<sub>2</sub>SO<sub>3</sub> solution. Surface analysis of the composites was conducted both before and after photo studies using techniques, such as: X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and atomic force microscopy (AFM). These studies led to conclusion that the most optimal composite HOPG/CdSe/PDAC was formed via 20 cycles polymerization in acidic solution. This sample displayed the maximum photocurrent density of 524  $\mu\text{A}/\text{cm}^2$ , whereas these values for neutral medium at 10 polymer deposition cycles and the organic medium at 2 layers of PDAC are only 281  $\mu\text{A}/\text{cm}^2$  and 146  $\mu\text{A}/\text{cm}^2$ , respectively.

### References:

1. Bienkowski, K., Strawski M., Maranowski B., Szklarczyk M., *Electrochimica Acta* **2010**, 55, 8908–8915
2. Skompska, M., Chmielewski M.J., Tarajko A., *Electrochemistry Communications* **2007**, 9, 540–544

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## Electrochemical dispersion rout for preparation of Pt-, Pd-, Rh-based electrocatalytic materials

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Nanoparticles of platinum group metals (PGM) in particular Pt, Pd, Rh, are still the most effective catalysts for processes that occur in low-temperature fuel cells [1]. As a rule, chemical and electrochemical methods for producing nanostructures containing nanoparticles of PGM are based on a “bottom-up” approach, when simple elements (atoms, ions or molecules of precursor compounds) form systems with a complex structure. In this work, we propose a “top-down” method for producing electrocatalysts based on Pt, Pd and Rh nanoparticles, which is based on the electrochemical dispersion of metal electrodes (Pt, Pd or Rh) under the action of an alternating pulse current.

It should be noted that an understanding of the fundamental principles of the process of electrochemical dispersion of PGMs would make it possible to directly influence the microstructural and crystallographic characteristics of PGMs nanoparticles and to obtain highly efficient catalytic systems with controlled functional properties.

In this work, we determined the optimal conditions for the electrochemical dispersion of platinum, palladium, and rhodium electrodes (composition and concentration of electrolyte, current density, values of cathode and anode pulses). The mechanisms of the formation of Pt, Pd, Rh nanoparticles in the conditions of electrochemical dispersion were established [2-4].

Based on the data obtained on the processes of electrochemical dispersion of Pt, Pd and Rh electrodes and the formation of metal nanoparticles under the conditions of electrochemical dispersion of metals, we developed methods for the synthesis of Pt/C, Pd-PdO/C and Rh/C materials and investigated their electrocatalytic activity in anode processes [2-4].

### References

1. Durst, J., Simon, C., Hasché, F., Gasteiger H. *J. Electrochem. Soc.* **2015**, *162*, F190-F203
2. Leontyev, I., Kuriganova, A., Kudryavtsev, Y., Dkhil, B., Smirnova, N. *Appl. Cat. A.* **2012**, *431-432*, 120-125
3. Faddeev, N., Kuriganova, A., Leont'ev, I., Smirnova, N. *Russ. J. Electrochem.* **2019**, *55*, 346-350
4. Kuriganova, A., Faddeev, N., Leontyev, I., Allix, M., Rakhmatullin, A., Smirnova, N. *ChemistrySelect*, **2019**, *4*, 8390-8393

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## Lattice Boltzmann Simulation of Water Transport in Compressed Gas Diffusion Layer of PEMFC

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Polymer electrolyte membrane fuel cell (PEMFC) is regarded as one of promising power sources for propulsion of future electric vehicles. The performance of PEMFC is highly dependent on gas diffusion layer (GDL) properties because the GDL provides the essential pathways for electron conduction, reactant transport, and water removal in the electrode [1]. The GDL is made of carbon fibers, usually in the form of paper, felt, or cloth. When assembled with other components in PEMFC, the GDL can significantly be deformed and compressed. The compression of GDL results in considerable reduction in the porosity as well as change in the pore structure (including anisotropy), which in turn alters the mass transport properties of the GDL [2]. Therefore, the understanding of liquid water transport in the compressed GDL is important to improve the performance of PEMFC.

In this study, the dynamic transport behavior of liquid water inside the compressed and uncompressed GDLs is comparatively investigated using the lattice Boltzmann method (LBM). The model GDL pore structures are generated by randomly distributing circular solid particles in the two-dimensional calculation domain under the channel/rib geometry. Then, two different scenarios of the homogeneous and inhomogeneous GDL compression (Fig. 1) are considered along with the uncompressed GDL. The LBM simulation shows that the compressed GDL results in a higher water saturation level compared with the uncompressed GDL. In addition, the compressed GDL requires a higher capillary pressure for liquid water breakthrough although the transport pathways formed in the compressed GDL are similar to those in the uncompressed counterpart.

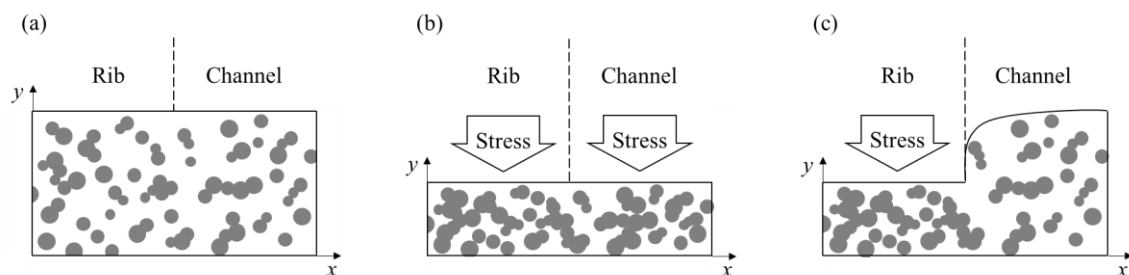


Figure 1: Two-dimensional GDL domains for LBM calculation: (a) uncompressed, (b) homogeneously compressed, and (c) inhomogeneously compressed cases.

### References

1. Wang, Y., Chen, K. S., Mishler, J., Cho, S. C., and Adroher, X. C., *Applied energy*, **2011**, 88, 981-1007.
2. Mahmoudi, A., Ramiar, A., and Esmaili, Q., *Energy Convers. Manag.*, **2016**, 110, 78-89.

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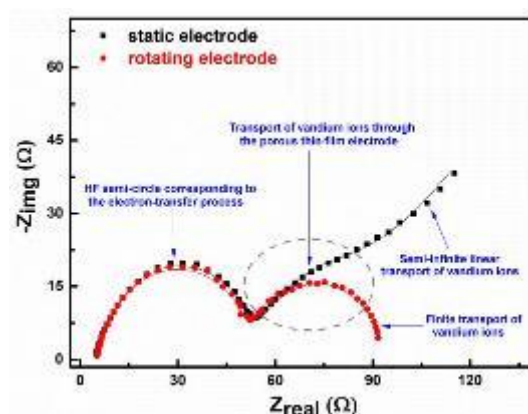
## Electrochemical Impedance Spectroscopy of $V^{2+}/V^{3+}$ and $VO^{2+}/VO_2^+$ Redox Couples on Carbon-based Electrodes for Vanadium Redox Flow Battery

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Transport kinetics of  $V^{2+}/V^{3+}$  and  $VO^{2+}/VO_2^+$  redox couples are investigated in a thin-film rotating disk electrode configuration using electrochemical impedance spectroscopy. The impedance features depend on the electrode potential, concentration of the redox species, concentration of the supporting electrolyte and constituents of the electrode [1]. Optimum concentration of the vanadium redox species and supporting electrolyte is required to resolve the HF and LF semi-circles in the EIS features corresponding to the electron-transfer process and transport of vanadium ions, respectively. Nafion and Polytetrafluoroethylene (PTFE) binders are used to bind the carbon-black catalyst on the glassy carbon disk electrode surface. The binder-free electrode shows finite and semi-infinite linear transport of redox species under the dynamic and static conditions of the electrode, respectively. Addition of binder in the electrode offers extra resistance to the transport of vanadium redox species, which helps resolve EIS features of the transport of redox species through the porous thin-film electrode and that through the bulk of the electrolyte (as shown in **Figure 1**).



**Figure 1.** EIS patterns recorded on carbon-modified glassy carbon disk electrode prepared with PTFE binder under the static and rotating condition of the electrode in 1:1 mixture of  $VO^{2+}/VO_2^+$  electrolyte.

### References

1. Gasteiger, H. A.; Kocha, S. S.; Sompalii, B.; Wagner, F. T. *Appl. Catalysis B: Environ.* **2005**, 56, 9–35.

## Phosphorescent iridium(III) complexes with Nature-inspired $\beta$ -diketone ligands as emitting layer for OLED devices

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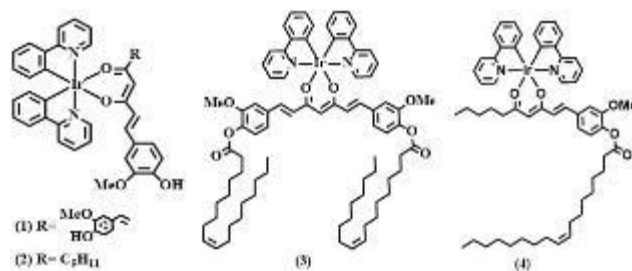
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The rise of solid state lighting represents an important breakthrough for our society due to the very high efficiency, low energy consumption and low CO<sub>2</sub> emission, making organic light emitting diodes (OLEDs) a more sustainable solution in many fields of applications ranging from civil lighting to automotive industry, from electronics to biomedical sector, from interior design to light art and fashion industry.<sup>1</sup> The research on OLEDs is very active and mainly aimed at the development of more efficient electroactive materials and at the design of more sustainable and low cost devices. In this regard the research activity of our group is aimed at testing the potentiality of natural and/or Nature inspired materials as semiconducting or emitting layer in OLED devices. Very encouraging results have been obtained by using: a) fluorescent triazatruxenes obtained from 5,6-dihydroxyindole,<sup>2</sup> the monomer precursor of the mammalian pigments eumelanins, as blue emitting layer; b) phosphorescent iridium(III) complexes featuring dopamine related ligands as red emitting layer;<sup>3</sup> c) a blend of PEDOT:PSS-Eumelanin as water resistant polymeric anode and hole injection layer.<sup>4</sup>

Starting from this background, here is reported the synthesis, characterization, study of the photo-physical properties and application in OLED devices of a new set of phosphorescent iridium(III) complexes (**1-4**) featuring, as ancillary O<sup>^</sup>O ligands, curcumin and 6-dehydrogingerdione, two natural  $\beta$ -diketones extracted from plants of the *Zingiberaceae* family. All the complexes have also been tested as emitting layer in OLED devices. This activity has been carried out in association with the ENEA Research Center in Portici.



### References:

1. Hui Xu, *Chem. Soc. Rev.*, **2014**, *43*, 3207-3812.
2. Manini, P., *ChemPlusChem*, **2015**, *80*, 919– 927.
3. Criscuolo, V., *ACS Omega* **2019**, *4*, 1, 2009-2018.
4. Migliaccio, L., *Adv. Electron. Mater.* **2017**; *3*, 1600342.

## HER catalysts based on MX<sub>2</sub>/Graphene hybrid microspheres (M = Mo, W; X = S, Se)

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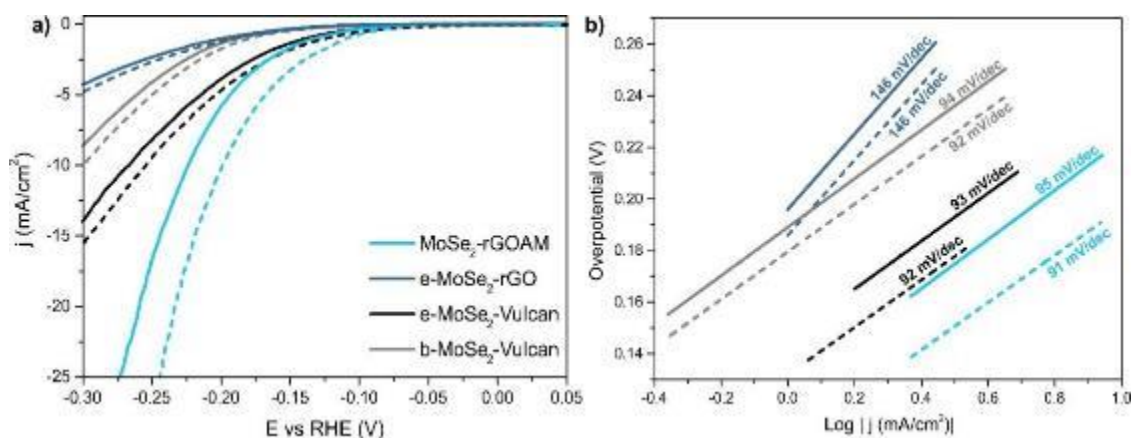
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*Graphene Oxide* (GO) is the most prominent among the chemically modified graphene materials and is often used as starting material to synthesize 3D graphene structures with high surface areas to apply in different fields, spanning from wastewater cleaning to catalysis. In this work, we explored a peculiar 3D architecture, i.e. *reduced-Graphene Oxide Aerogel Microspheres* (rGOAM), having a dandelion-like microchannels central divergence.<sup>1</sup> We used rGOAM as scaffold to incorporate exfoliated *Transition Metals Dichalcogenides* (TMDCs) nanosheets addressing an increase of their activity toward the *Hydrogen Evolution Reaction* (HER). The goal was to maximize the exposed active area of the TMDCs and have an intimate contact between the two materials (r-GO and TMDC). The procedure of incorporation has been optimized using exfoliated MoSe<sub>2</sub>, and subsequently the protocol was successfully transferred also to MoS<sub>2</sub>, WS<sub>2</sub> and WSe<sub>2</sub>.

Comparing the larger HER activity of the hybridized TMDC-rGOAM systems with respect to that of a simple mixture of TMDC and rGO and TMDC and Vulcan we were able to ascertain the role of the 3D structure and of the hybridization of the two materials. Interestingly, also the increase on the HER activity after the exposition to light reaches a maximum in the TMDC-rGOAM system, demonstrating that the photon induced electron transfer from the TMDC to the rGO sheets is more efficient when the TMDC is inside the microchannels of the 3D scaffold.



**Figure.** a) Comparison of the (photo)electrocatalytic activities for HER of MoSe<sub>2</sub>-rGOAM and the reference systems. The dashed curves were obtained by illuminating the working electrode with white light. b) Related Tafel plot for kinetics analysis.

### References

1. Liao S., Zhai T. and Xia H. Highly adsorptive graphene aerogel microspheres with center-diverging microchannel structures. *Journal of Materials Chemistry A*, **2016**; 4(3): 1068-1077

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## A Sub-stoichiometric Calcium Titanate Perovskite $\text{CaTiO}_{3-\delta}$ as Electrode Additive in Direct Methanol Fuel Cells (DMFCs)

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Oxygen reduction reaction (ORR) is one of the most important process for metal-air batteries and fuel cells, both in acid and alkaline environment.<sup>[1]</sup> Although Pt/C catalysts are widely used in low temperature fuel cells as oxygen electrode, there is still the need to find new, efficient, stable and less expensive materials to be used as cathodes.<sup>[2]</sup> Considerable efforts, in the last decade, were addressed to improve the electrochemical oxygen reduction reaction and to reduce Pt loading in order to achieve low-cost targets.

To this purpose, we here propose a study based on the use of a sub-stoichiometric perovskite calcium titanate ( $\text{CaTiO}_{3-\delta}$ , CTO), as co-catalyst for the oxygen reduction reaction (ORR).

Several physical chemical investigations for the understanding of functional features of the proposed materials will be presented.

Composite Pt/C electrodes, with different amounts of  $\text{CaTiO}_{3-\delta}$ , were prepared and their catalytic performances were investigated by rotating-disk electrode (RDE) techniques.<sup>[3]</sup> A commercial Pt/C catalyst was used as reference. The obtained results proved a higher catalytic activity for the composite electrode, with respect to pure Pt/C, in terms of electrochemically active surface area, oxygen reduction current density and onset potential.

A membrane-electrode assembly (MEA) equipped with the best formulation obtained (Pt/C:CTO = 1:1), has been investigated in DMFC and compared with an MEA equipped with a benchmark Pt/C cathode catalyst. The power density obtained at high temperature with the CTO-based electrode is one of the highest value reported in the literature under similar operating conditions.<sup>[4]</sup>

### References

1. Chen, M., Wang, L., Yang, H., Zhao, S., Xu, H., Wu, G. *J. Power Sources* **2018**, 375, 277-290
2. Lo Vecchio, C., Aricò, A.S., Monforte, G., Baglio, V., *Renew. Energy*, **2018**, 120, 342-349
3. Mazzapioda, L., Lo Vecchio, C., Paolone, A., Aricò, A.S., Baglio, V., Navarra, M.A., *Chem. Electro. Chem*, **2019**, doi:10.1002/celec.201901292
4. Thiagarajan, V., Karthikeyan, P., Thanarajan, K., Neelakrishnan, S., Manoharan, R., Chen, R., Fly A., Anand, R., Karuppa Raj, T.R., Kumar, N., *Int. J. Hydrogen Energy* **2019**, 44, 13415-13423

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## Micro- and Meso-porosity effect on the formation and activity of Fe-N-C active sites for Oxygen Reduction Reaction

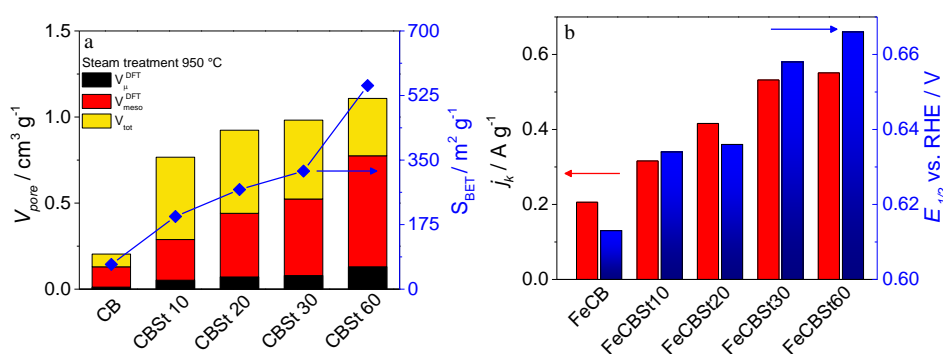
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Iron-nitrogen-doped carbon materials (Fe/N/C) have emerged as one of the best non-PGM alternative to Pt/C catalysts for the electrochemical reduction of oxygen (ORR). A lot of different iron and nitrogen precursor and porous carbonaceous support have been studied, but the type of the active sites in these catalysts and the correlation between site formation and carbon morphology are still not well understood [1]. Specific surface area and porous structure of the support (micro-, meso- and macropore ratio) are fundamental for functionalization, namely nitrogen and iron fixation and not less important for the transport of reactant and product [2]. In this work we explore the effect of steam treatment at high temperature (950 °C) on a commercial carbon black focusing on the enhancing of the porous structure [3]. Starting from this material we synthesize different Fe/N/C catalysts to achieve a better understanding of the role of micro- and mesopore on site formation and consequently on activity. In particular, different time of treatment allow to obtain an almost linear increment of surface area and microporous volume (figure 1a) which interestingly allow to obtain a better functionalization (iron-nitrogen fixing). Actually, N% (bulk composition) passes from a percentage of 0.10% to 1.06% for the 30-minute treated support.

RRDE technique showed an increment in activity of the materials in term of half wave potential and kinetic current at 0.8 V vs. RHE for the sample with the highest content of micro- and mesopore (figure 1b). In conclusion, we were able to improve kinetic current and the half-wave potential compatible with the increase of the percentage content of micro and mesopores on the total volume of pore showing the importance of these on the formation of the Fe-N-C sites and their activity.



**Figure 5:** a) Pore volume and surface area evolution in time and b) activity parameter

### References

1. Young Jin Sa et al. J. Electrochem. Sci. Technol., **2017**, 8(3), 169-182.
2. Soo Hong Lee et al. J. Am. Chem. Soc. **2019**, 141, 2035–2045
3. F. Rodríguez-Reinoso et al. Carbon N. Y. 33 (**1995**) 15–23.



## Luminescent Solar Concentrators from waterborne polymer dispersions

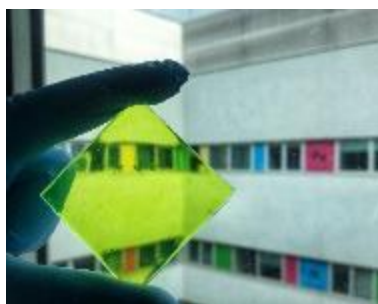
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The concept of Net Zero-Energy Buildings (NZEBs) is receiving an increasing amount of attention by the scientific community and policy organizations, such as the European Committee (1). NZEBs are technically feasible for individual houses and small buildings due to rooftop photovoltaic (PV) cells and efficient insulation. Nevertheless, being  $\sim 7 \text{ m}^2/\text{kW}$  the peak power needed for NZEBs, the use of PVs is not worthwhile for larger buildings (2). An accessible solution to this problem is represented by luminescent solar concentrators (LSCs) that are fluorophore containing semi-transparent devices able to harvest sunlight and to concentrate the fluorescence at their sides, where it is converted into electricity by photovoltaic (PV) cells. Current state of the art LSCs are based on fluorophore-doped slabs or films of polymethylmethacrylates (PMMA) obtained via thermo-formation process or by casting from organic solvent solutions (2).

In the present work a different polymer matrix is proposed and based on the utilization of polymer emulsions in water containing water soluble fluorophores (3). The use of waterborne polymer dispersions typically utilized in the industry of water-based paints results beneficial in terms of environmental impact of the coating process, high surface coverage and low cost, that is all features required for maximizing the diffusion of the LSC/PV technology in urban area. Different coatings on transparent glasses are prepared and the characteristics as LSCs are discussed in terms of the film thickness, the fluorophore content and the final size of the device and compared with the performances of those from the most recent literature.



LSC prototype based on waterborne polymer dispersion

### References

1. Kampelis, N.; Gobakis, K.; Vagias, V.; Kolokotsa, D.; Standardi, L.; Isidori, D.; Cristalli, C.; Montagnino, C.; Paredes, F.; Muratore, P. *Energy and Buildings* **2017**, *148*, 58-731.
2. Meinardi, F.; Bruni, F.; Brovelli, S. *Nature Reviews Materials* **2017**, *2*, 17072.
3. Minei, P.; Iasilli, G.; Ruggeri, G.; Pucci, A. *Italian Patent Pending* n. 102019000022068.

*Acknowledgements:* This work was funded by the University of Pisa “Bando Dimostratori Tecnologici”

## Microwave-assisted sintering of Na-β''-Al<sub>2</sub>O<sub>3</sub> electrolyte in 2450 and 5800 MHz single mode cavities

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Na-based batteries (NBBs) have attracted great attentions in the past few decades for energy storage applications. Indeed, they are considered as one of the most promising alternatives to Li-based systems because of their good performances, high abundant sodium resources and low cost. <sup>[1]</sup> Among the different Na<sup>+</sup> conductors, sodium Na-β''-Al<sub>2</sub>O<sub>3</sub> solid electrolyte has been widely utilized. <sup>[2]</sup> However, despite the huge potential applicability of this material in NBB technologies, several challenges related to the fabrication steps remain. In order to obtain dense polycrystalline solid electrolyte, time prolonged and high sintering temperatures (> 1600°C) are usually necessary, causing unwanted sodium evaporation, loss of performances and extremely high energy consumptions.

This work is focused on the microwave assisted sintering of Na-β''-Al<sub>2</sub>O<sub>3</sub> powders by the use of single mode applicators. Sintering experiments were performed both at the widespread 2450 MHz frequency as well as at the higher frequency of 5800 MHz. In order to predict the heating behaviour of the starting powders, their dielectric properties as a function of temperature were previously measured. Moreover, numerical simulation of the heating experiments were conducted with the aim to investigate the better load configuration to assure the most homogeneous heating treatment. The effect of the different frequencies, heating rate, temperature and dwell time on the density and the microstructure have been thoroughly investigated. <sup>[3]</sup>

### References

1. W. Hou, X. Guo, X. Shen, K. amine, H. Yu, J. Lu *Nano Energy* **2018**, 52, 279-291.
2. X. Lu, G. Xia, J. P. Lemmon, Z. Yang, *J. Power Sources* **2010**, 195, 2431-2442.
3. R. Rosa, C. Mortalò, *Et. al*, in preparation.

## Mechanistic studies on the enhanced carbocatalytic oxidation of alcohols by Graphene Acid

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Severe limitations due to the overstoichiometric amounts required to achieve practical conversions are reported at the employment of graphene oxide (GO) as carbocatalyst [1] Graphene Acid (GA), a well-defined graphene derivative fully covered by carboxylic groups but maintaining the electronic conductivity of pristine graphene,[2] sets new activity limits in the oxidation of alcohols working in the catalytic range (5 % wt. vs substrate) with catalytic amounts of HNO<sub>3</sub> acting as co-catalyst.[3] Indeed, GA converts benzyl alcohol to the benzaldehyde overpassing other reported carbo- and metallic catalysts for this general oxidation,[4] with an outstanding activity of 152 mmol converted per gram of catalyst and hour. Benchmark GO, however, did not show catalytic activity in the studied experimental set-up. According to experimental data and first principle calculations, the selective and high-density functionalization with carboxyl groups, combined with electronic conductivity, enhanced the surface oxidation of the co-catalyst HNO<sub>3</sub> and the conversion of the alcohol in the oxidized product. Furthermore, the controlled structure also allows to shed light regarding critical steps of the mechanism, such as the generation of the key organic nitrites intermediates, to regulate precisely the oxidation selectivity towards either possible oxidation products, and the terminating steps of the cycle, where O<sub>2</sub> acts as final oxidant (Figure 1).

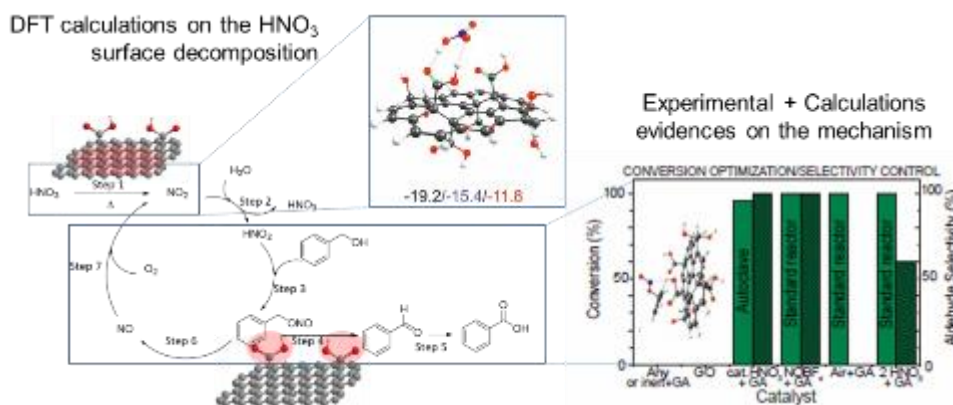


Figure 1. Systematic mechanistic investigation on the alcohol oxidation catalyzed by GA.

### References

1. Dreyer, D. R.; Jia, H.-P.; Bielawski, C.W. *Angew. Chem. Int. Ed.*, **2010**, *49*, 6813.
2. Bakandritsos, A.; Pykal, M.; Błoński, P.; Jakubec, P.; *et al.* *ACS Nano*, **2017**, *11*, 2982.
3. Blanco, M.; Mosconi, D.; Otyepka, M.; Medved, M.; *et al.* *Chem. Sci.* **2019**, *10*, 9438.
4. Wang, B.; Lin, M.; Ang, T.P.; Chang, J.; Yang, Y.; Borgna., A. *Catal. Commun.*, **2012**, *5*, 96.

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## Investigation of Hydrogen Interaction (Electrosorption and Evolution) with Si in Hydrogen Fluoride Electrolyte

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Metallization of silicon is important to make electrical contacts. Thus, copper (Cu), nickel (Ni) etc. are deposited on Si by various methods including electrochemical and photo-electrochemical methods. Nature of the electrochemical processes of Si with the electrolytes at relevant potentials decides the success of metallization. Thus, it is important to investigate the interaction of electrolyte with Si at cathodic overpotentials. Therefore, n-type and p-type Si of different doping concentrations are investigated in 1% HF electrolyte at cathodic overpotentials. Hydrogen evolution reaction (HER) is expected at very high cathodic overpotentials but very interesting processes occur at intermediate overpotentials. Therefore, the Si/electrolyte interface is investigated using voltammetry (CV), electrochemical impedance spectroscopy (EIS) and Mott-Schottky (MS) analysis. At very high concentration of the dopants, metal-like features are observed with Si. There are very good correlations between dopant concentration, overpotentials, and flat -band potential and inductive behavior of the semi-conductor.

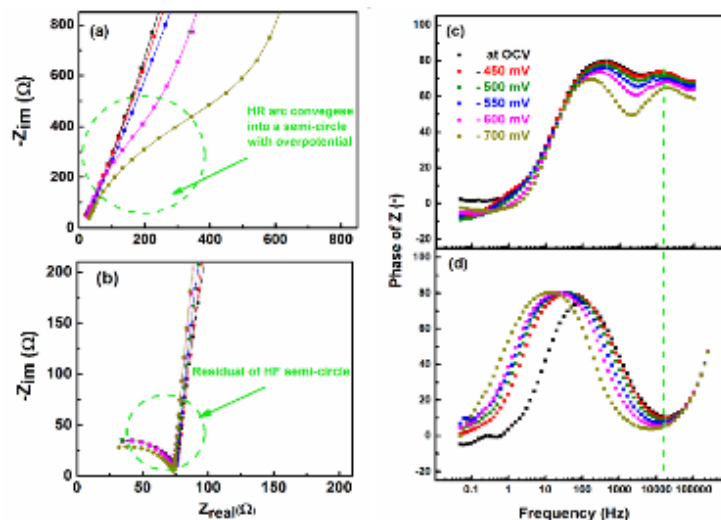


Figure. EIS recorded on n-Si at different cathodic overpotentials in 1% HF (a) 4-7  $\Omega\text{cm}$  (b) 0.00-0.005  $\Omega\text{cm}$ . The corresponding Bode plots are shown in (d) and (f), respectively.

### Reference

1. Zhang, X. G. *Electrochemistry of Silicon and Its Oxide*, Kluwer Academic/Plenum Publisher, New York **2001**.

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## Development of an efficient CFD model for monolithic steam methane reactor using effectiveness factor correlations

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In recent years, many studies have focused on the development of small-scale methane reformer systems suitable for fuel cell applications. An accurate prediction of the reforming process is essential for designing the reformer systems and determining their optimal operation policies. In this regard, computational fluid dynamics (CFD) provides a proper tool to obtain the detailed information needed for such design and optimization tasks. However, CFD simulations with realistic reformer geometries require significant computational costs because large numbers of grid points are inevitable to accurately consider the reforming process in thin reaction zones. In this study, we propose an efficient CFD model that can greatly reduce the computational costs by using the effectiveness factor correlations. The coupled heat transfer, mass transfer, fluid flow, and chemical reactions inside the reformer are calculated using ANSYS FLUENT. The accuracy and efficiency of the proposed CFD model is demonstrated by simulating a monolithic steam methane reactor composed of square channels coated with Ni washcoat layers and then comparing the results with available numerical and experimental data.

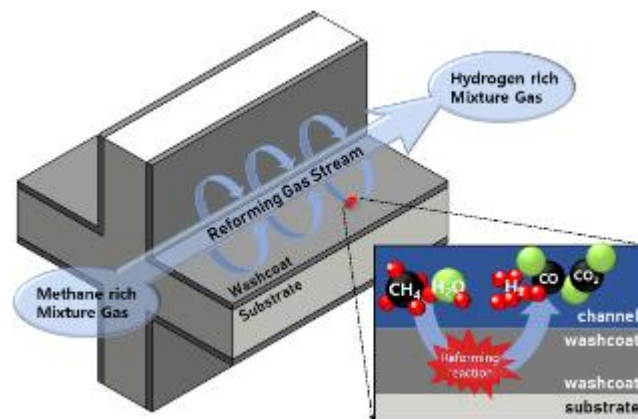


Figure 1. The steam methane reforming process inside a square channel of a monolithic reformer.

### References

1. Steam reforming of methane over Ni catalyst in microchannel reactor, X. Zhai, Y. Cheng, Z. Ahnag, Y. Jin, Y. Cheng, *Int. J. Hydrogen Energy* **2011**, 36, 7105-7113
2. Effectiveness factor correlations for spherical nickel catalyst pellets used in small scale steam methane reformers, J. H. Nam, *Int. J. Hydrogen Energy* **2015**, 40, 5644-5652
3. Effectiveness factor correlations from simulations of washcoat nickel catalyst layers for small scale steam methane reforming applications, A. Jeong, D. Shin, S. M. Baek, J. H. Nam, *Int. J. Hydrogen Energy* **2018**, 43, 15398-15411

*Acknowledgements:* This work was funded by the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT(MSIT) (NRF- 2019R1F1A1041995).

## Functionalized graphene oxide for efficient capacitive deionization

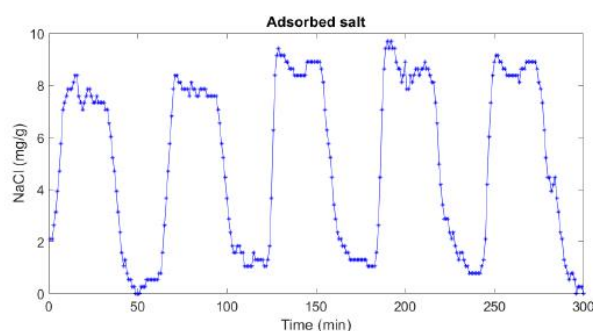
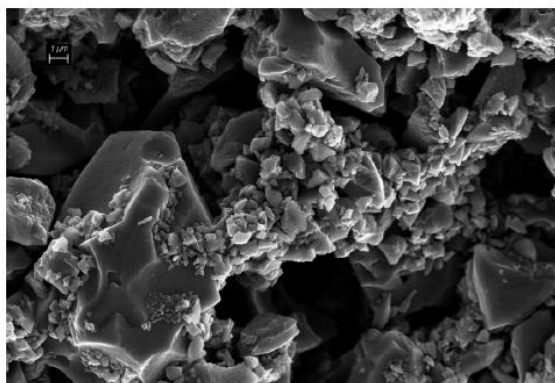
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Graphene oxide functionalized with a novel positively charged monomer is proposed for application in water desalination. The functionalized graphene oxide has been obtained by a simple and scalable method, based on a modification of the one recently proposed by Roppolo et al [1]. The material obtained this way has been mixed in organic solvent with activated carbon and hydrophobic polymeric binder to obtain a stable dispersion. The as prepared slurry has been coated on a metallic current collector with the doctor blade method and then dried at 50 °C in order to obtain one of the two final electrodes. The counterpart is obtained by replacing the functionalized graphene oxide with pristine graphene oxide in the previously described preparation. The final device, exploiting high surface asymmetric electrodes with opposite charges, is obtained juxtaposing a pair of these electrodes inside a homemade cell specifically designed for capacitive deionization application. Inlet and outlet are connected to a peristaltic pump. All the capacitive deionization tests have been performed in batch configuration, using NaCl 10 mM. A conductimeter is used for real-time measurement of the solution's conductivity. Material characterization techniques such as electron microscopy and infrared spectroscopy are employed to study the physical and chemical structure of the proposed materials. Thermogravimetric analysis is used to investigate the effectiveness of the functionalization procedure. Electrochemical methods are chosen to evaluate the efficiency of salt removal from water. The final device demonstrates a remarkable desalination performance, reaching values higher than 8 mg/g of salt removal, while showing a stunning charge efficiency above 98%.



### References

1. Roppolo, I. et al., *Carbon* **2014**, 77, 226-235.



## Water-soluble polythiophenes: a further step towards green energy production

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Recently, since the fossil fuels strongly decreased, several studies have been conducted in order to exploit solar power as an alternative source of energy. To make this possible with sustainable costs, the attention has been focused on the development of organic photovoltaic solar cells (OPVs) based on polymeric photoactive layer.

However, despite the interesting and promising results achieved in the last few decades, it should be recognized that the production of OPVs very often requires the consumption of large amounts of chlorinated and/or aromatic organic toxic solvents. Indeed, there is a clear need for the next generation of photovoltaic technologies to move towards the study of large-scale environmentally friendly techniques.<sup>1</sup>

In this context, due to the effective combination of excellent intrinsic optoelectronic properties with unique solubilities in more green solvents, water/alcohol-soluble conjugated polymers (WSCPs) have attracted increasing attention in recent years.<sup>2</sup>

Starting from a soluble homopolymeric precursor (PT6Br), a ionic water soluble material - poly[1-methyl-3-(6-(thiopen-3-yl)hexyl)-1H-imidazole-3ium bromide (PT6I) - was obtained by substitution reaction on the bromoalkyl side chain with N-methylimidazole.

To evaluate the main features of the prepared materials, both precursor and post-functionalized polymers have been characterized by common analytical techniques, such as <sup>1</sup>H-NMR, gel permeation chromatography (GPC), thermal analyses (DSC, TGA) and UV-Vis spectroscopy. Finally, the synthesized ionic polymer (PT6I) - blended with PC<sub>61</sub>BM (1:1 w/w) as acceptor material - was tested as a photoactive layer in organic solar cells.

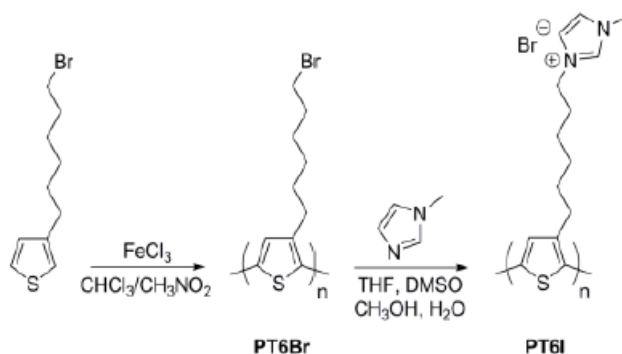


Figure 1. Synthesis of precursor and ionic homopolymers.

### References

- Burke, D. J., Lipomi, D. J. *Energy Environ. Sci.*, **2013**, 6, 2053-2066.
- Lanzi, M., Salatelli, E., Giorgini, L., Mucci, A., Pierini, F., Di Nicola, F. P. *Eur. Polym. J.* **2017**, 97, 378-388.

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## BiO<sup>+</sup>-based nanocomposite for environmental remediation: modulation of the functional properties by composition tailoring

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In the field of environmental remediation strategies, multifunctional materials able to act for pollutants adsorption and degradation at the same time are highly desirable. In this framework, post-synthesis treatments represent a powerful tool for the modulation of the chemico-physical and functional properties of nanocomposite materials. In this study, Bi<sub>12</sub>O<sub>17</sub>Cl<sub>2</sub>/(BiO)<sub>2</sub>CO<sub>3</sub> nanocomposite materials were studied as bifunctional systems for depuration of wastewater and synthesized at room temperature and ambient pressure by means of controlled hydrolysis of BiCl<sub>3</sub> followed by post-synthesis treatments. Cold treatments with UV-light, thermal annealing at different temperatures (370 – 500 °C) and atmospheres and chemical treatments (basic environment) of the pristine samples were adopted in order to modulate the Bi<sub>12</sub>O<sub>17</sub>Cl<sub>2</sub>/(BiO)<sub>2</sub>CO<sub>3</sub> couple. Such treatments allow a fine-tuning of relative amounts, morphology, crystalline phases, surface areas, ζ-potential and optical absorption in the UV-visible range. The adsorption/degradation properties have been tested with two model pollutants (Rhodamine B and Methyl Orange). The obtained results evidenced the ability of the employed strategy to modulate sample properties in a wide range thus pointing out the effectiveness of this approach in the synthesis of multifunctional inorganic materials for environmental remediation.

### Dye adsorption and photodegradation



### References

1. Mian, F.; Bottaro, G.; Rancan, M.; Pezzato, L.; Gombac, V.; Fornasiero, P.; Armelao, L. *ACS Omega* **2017**, *2*, 6298–6308.



## Electrochemical Formation of Nitrogen-Doped Reduced Graphene Oxide/Hematite Heterojunction: Characterization and properties

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This study shows the results obtained in the electrochemical formation of the heterojunction between hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and nitrogen-doped electrochemically reduced graphene oxide (N-ERGO) in order its use as a photoanode in a photoelectrochemical cell for the hydrogen production through the photoelectrochemically assisted water splitting. The heterojunction was carried out through two electrochemical steps: The electrochemical reduction of nitrogen-doped graphene-oxide (N-GO, which is synthesized through a modified Hummer's method [1]) onto a FTO substrate forming a N-ERGO layer onto this surface (FTO/N-ERGO), followed by the Fe electrodeposition onto this modified surface. In order to complete the hematite formation through the Fe oxidation, the FTO/N-ERGO/Fe samples are annealed in air at 450-350°C for two hours. Finally, the samples are characterized through different techniques: X-ray diffraction, Raman spectroscopy, and SEM images, which confirm the formation of the N-ERGO/ $\alpha\text{-Fe}_2\text{O}_3$  heterojunction. Electrochemical and photoelectrochemical measurements show that the N-ERGO/ $\alpha\text{-Fe}_2\text{O}_3$  heterojunction can be used as a photoanode in a photoelectrochemical cell for water splitting.

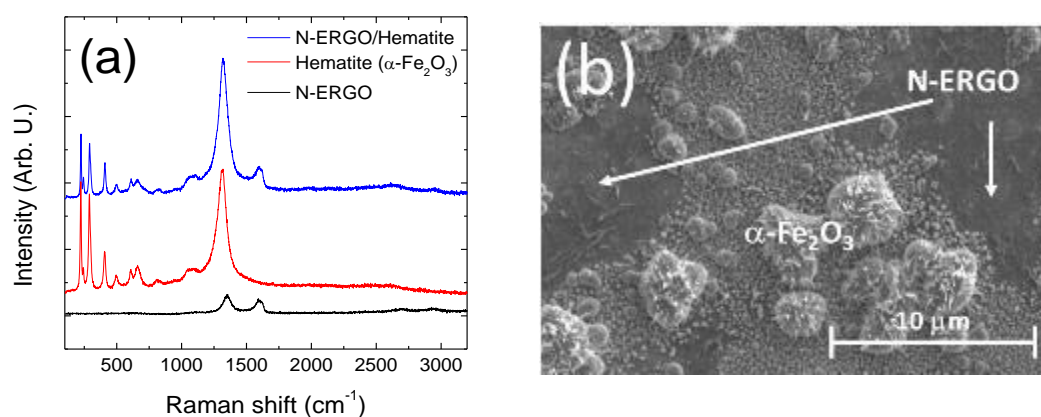


Figure 1: (a) Raman spectra of N-ERGO, hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), and the N-ERGO/ $\alpha\text{-Fe}_2\text{O}_3$  heterojunction obtained after an annealing at 350°C in air. (b) SEM image of the N-ERGO/ $\alpha\text{-Fe}_2\text{O}_3$  heterojunction, incanting the presence of both compounds.

### References

1. Du, M.; Sun, J.; Chang, J.; Yang, F.; Shi, L.; Gao, L. *RSC Adv.* **2014**, *4*, 42412-42417

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## p- and e- type Silver functionalized Dense Titanium Dioxide Semiconductor Layer for Efficient Perovskite photovoltaics (SOLAR)

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Perovskite solar cells (PSC) have an advantage over conventional silicon solar cells in its simplicity of processing and notable power conversion efficiency (PCE) of ~ 22%. However, their performance is limited by the recombination of charge carriers occurring at the TiO<sub>2</sub>/PSC interface[1]. This work controls recombination at the Electron transport layer (ETL) (c-TiO<sub>2</sub>+mp-TiO<sub>2</sub>)/Perovskite interface through elimination of pinhole defects followed by Silver-functionalization (dense-TiO<sub>2</sub>/mesoporous-Ag-TiO<sub>2</sub>) to enhance the photo-absorptivity. An innovative method was used to construct a compact Ag functionalized a-TiO<sub>2</sub> film consisting of a mixture of ethanol, titanium(IV) isopropoxide, and silver nitrate spin coated on a fluorine-doped tin-oxide substrate in the absence of ZnO as supportive photoanode[2]. The performance of PSC/Ag-TiO<sub>2</sub> and TiO<sub>2</sub> films were probed using scanning electron microscopy (HRSEM), x-ray diffraction (XRD), UV-visible spectroscopy, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). The uniformly distributed Ag-nanoparticles attached to the mesoporous TiO<sub>2</sub> matrix fashioned a TiO<sub>2</sub> compact layer with excellent blocking capability and improved electron mobility as observed in Fig.1. Particular Ag doping percentage of ~ 0.9% altered the electrical conductivity of the TiO<sub>2</sub> film, reducing the recombination process occurring at the ETL/PSC interface [3]. From IV-measurements, the PSC developed via two steps, yielded satisfactory efficiencies. The dense-TiO<sub>2</sub>/mesoporous-Ag-TiO<sub>2</sub> UV-Vis results revealed an induced red shift and band gap of 3.29 eV; indicative of enhanced luminescent properties. Hence, the synergy of dense TiO<sub>2</sub> and the surface plasmon resonance effect of metallic Ag nanoparticles successfully enhanced the optical absorption in the visible light region as well the power conversion efficiency compared to the pristine TiO<sub>2</sub> perovskite solar cell.

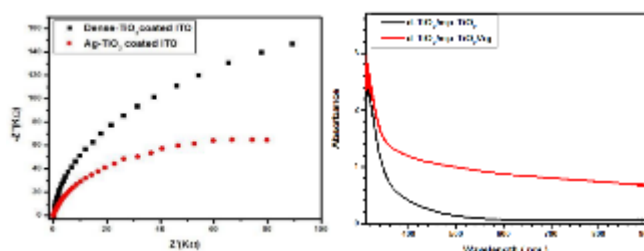


Fig.1. Electrochemical Impedance Spectroscopy and UV-Absorbance spectra of dense-TiO<sub>2</sub>/mesoporous-Ag-TiO<sub>2</sub>

### References

1. Li, X. Bi, D.Q. Yi, C.Y. Decoppet, J.D. Luo, J.S. Zakeeruddin, S.M. Hagfeldt, M. *Science*. **2016**, 353, 6294.
2. Akhavan, O. solar light irradiation, *J. Colloid Interface Sci.* 336 (2009) 117–124.
3. He, J. Ichinose, I. Fujikawa, S. Kunitake, T. Nakao, A. *Chem.Commun.* **2002**, 8, 1910.

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## Chemical Modification of Carbon Nano Structures for Solar Energy Conversion

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The use of carbon nanostructures (CNSs) in energy related applications attracts large attention for different scopes, ranging from energy harvesting to storage and release. The combination of CNSs, such as carbon nanotubes (CNTs) and graphene based materials (e.g. reduced graphene oxide, RGO), with p-conjugated polymers is particularly interesting for a possible use of the resulting polymer nanocomposites as active materials in energy related applications such as photovoltaic devices. The development of targeted functionalization processes can be a valid strategy to contrast CNS aggregation, while limiting the loss of electronic properties, and to tune the interactions between conductive polymers and CNSs.

In an effort towards such a direction, we studied functionalization strategies to obtain CNS based functional materials that have been investigated for possible applications in the energy related fields. Among them, the preparation of photoactive heterojunction active layers based on blends of poly(3-hexylthiophene) (P3HT) and derivatized (both covalently and non-covalently) CNTs bearing thienyl moieties. In this contest, we observed how an increase of functionalization degree affects the electronic communication of CNSs with P3HT. Different P3HT nanocomposites, based on functionalized CNTs and RGO, were used as hole transporting materials in perovskite solar cells (PSC), providing higher  $\eta$  and prolonged shelf-life stabilities. In the field of dye-sensitized solar cells (DSSC), grafting of photoactive molecules on RGO has led to novel photosensitizing agents that showed stronger binding to the semiconductor oxide in comparison to the reference dye, paving the way to a new generation of DSSC photoanodes with improved chemical stability.

### References

1. Gatti, T.; Lamberti, F.; Topolovsek, P.; Abdu-Aguye, M.; Sorrentino, R.; Perino, L.; Salerno, M.; Girardi, L.; Marega, C.; Rizzi, G.A.; Loi, M.A.; Petrozza, A.; Menna, E. Interfacial Morphology Addresses Performance of Perovskite Solar Cells Based on Composite Hole Transporting Materials of Functionalized Reduced Graphene Oxide and P3HT. *Solar RRL* **2018**, 2, 1800013.
2. Guarracino, P.; Gatti, T.; Canever, N.; Abdu-Aguye, M.; Loi, M.A.; Menna, E.; Franco, L. Probing photoinduced electron-transfer in graphene-dye hybrid materials for DSSC. *Phys. Chem. Chem. Phys.* **2017**, 19, 27716.
3. Gatti, T.; Manfredi, N.; Boldrini, C.; Lamberti, F.; Abboto, A.; Menna, E. A D- $\pi$ -A organic dye - reduced graphene oxide covalent dyad as a new concept photosensitizer for light harvesting applications. *Carbon* **2017** 115, 746-753.
4. Sartorio, C., Figà, V., Salice, P., Gragnato, D., Cataldo, S., Scopelliti, M., Improta, R., Menna, E., Pignataro, B. Thiophene pyrenyl derivatives for the supramolecular processability of single-walled carbon nanotubes in thin film heterojunction. *Synth. Met.* **2017**, 229, 7-15.

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## SnO<sub>2</sub>-based composite anodes for high energy density LIBs

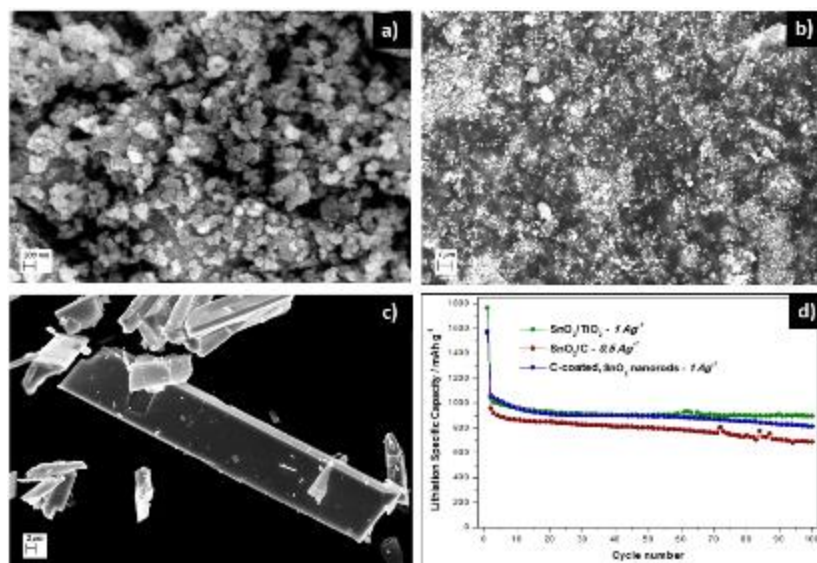
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Since their development, rechargeable Li-ion batteries (LIBs) quickly became the devices of choice for powering portable electronics and for the ever rising electric (EVs) and hybrid (HEVs) vehicles. With the advancement of technology, high energy density materials are required to satisfy the new energetic needs <sup>1</sup>. The present work proposes three SnO<sub>2</sub>-based composites (SnO<sub>2</sub>/TiO<sub>2</sub>, SnO<sub>2</sub>/C, and C-coated SnO<sub>2</sub> nanorods) with high experimental capacities (1411 mAh/g for bare SnO<sub>2</sub>) compared to standard graphite (372 mAh/g), as possible replacements for the latter <sup>2</sup>.

Structural and morphological characterizations were achieved through X-ray Diffraction spectroscopy and Scanning Electron Microscopy, respectively. Electrochemical characterization involved galvanostatic cycling, cyclic voltammetry, rate capability, GITT and PEIS, in order to study the behavior of the materials upon cycling and evaluate the internal resistances associated to the processes involved. All analyses have been performed by employing 1M LiPF<sub>6</sub> in EC:DMC 1:1 + 2% VC electrolyte.

All materials were found to display high average specific capacity values (> 750 mAh/g) over prolonged cycling at high current densities, with improved cycling stability and good coulombic efficiencies.



**Figure 1.** SEM images of a) SnO<sub>2</sub>/TiO<sub>2</sub>, b) SnO<sub>2</sub>/C and c) C-coated SnO<sub>2</sub> nanorods; d) Cycling performance of the three composites.

### References

- Hannan, M. A., Hoque, M. M., Hussain, A., Yusof, Y., & Ker, P. J. (2018). State-of-the-art and energy management system of lithium-ion batteries in electric vehicle applications: Issues and recommendations. *Ieee Access*, 6, 19362-19378.
- Tian, H., Xin, F., Wang, X., He, W., & Han, W. (2015). High capacity group-IV elements (Si, Ge, Sn) based anodes for lithium-ion batteries. *Journal of Materiomics*, 1(3), 153-169.

## The Effect of RTILs-PVDF/HFP as Gel Electrolytes for High Voltage Supercapacitor

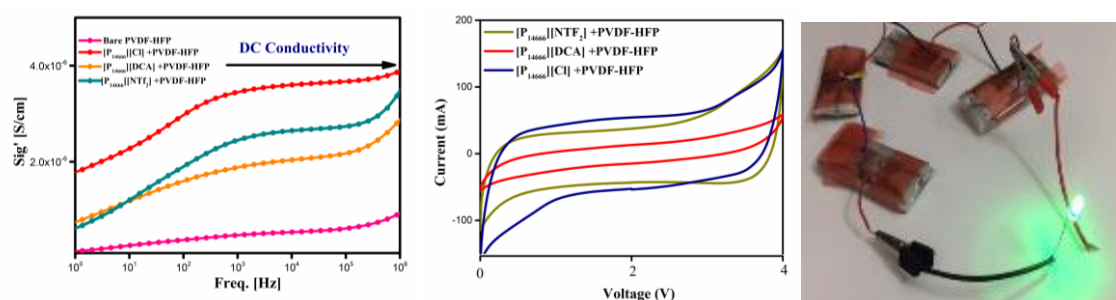
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A new gel polymer electrolyte based on three phosphonium ionic liquid with different anions ([P<sub>66614</sub>][DCA], [P<sub>66614</sub>][NTf<sub>2</sub>] and [P<sub>66614</sub>][Cl]) entrapped in poly(vinylidene fluoride-hexafluoro propylene) (PVdF-HFP) is prepared and optimized. It is used as the electrolyte material for the fabrication of flexible electric double layer supercapacitors (EDLCs) with activated carbon (AC) electrodes. To establish the conduction mechanism and molecular dynamics of electrolytes broadband dielectric spectroscopy was used. The structural, thermal and electrical properties of the prepared gel electrolytes were investigated using X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), Raman spectroscopy, broad band dielectric spectra and FTIR. The performances of flexible EDLCs are evaluated using cyclic voltammetry, galvanostatic charge–discharge and impedance measurements. The 20 PVdF-HFP:80[[P<sub>66614</sub>][Cl] gel polymer electrolyte owns a high ionic conductivity ( $4.5 \times 10^{-6} \text{ S cm}^{-1}$ ) specific capacitance (435F/g) and energy density (36.25Wh/kg) and wide electrochemical stability window (4 V) at room temperature compared to other two.



### References:-

1. Jeong, H. T., Du, F. & Ryeol, Y. Development of Flexible Energy Storage Device by Using Polymer Electrolyte Based on Ionic Liquid. 6057–6061 (2017). doi:10.1002/slct.201701073
2. Pilathottathil, S., Kannan Kottummal, T., Thayyil, M. S., Mahadevan Perumal, P. & Ambichi Purakakath, J. Inorganic salt grafted ionic liquid gel electrolytes for efficient solid state supercapacitors: Electrochemical and dielectric studies. *J. Mol. Liq.* **264**, 72–79 (2018).
3. Díaz-delgado, R. & Doherty, A. P. Carbons, Ionic Liquids, and Quinones for Electrochemical Capacitors. **3**, 1–7 (2016).
4. Kumaran, V. S. *et al.* The conductivity and dielectric studies of solid polymer electrolytes based on poly (acrylamide-co-acrylic acid) doped with sodium iodide. 1947–1953 (2018).

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## Comparative Life Cycle Assessment of Solar Home Systems

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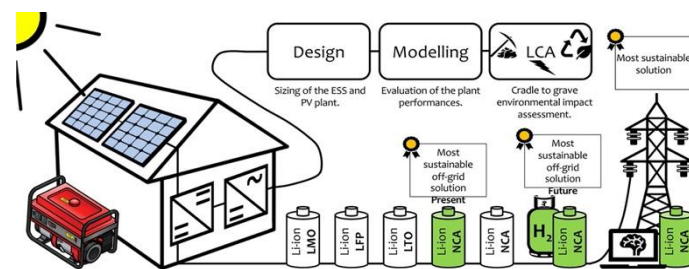
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Energy storage systems (ESSs) represent a fundamental technology to overcome the problem of intermittent nature of renewable energies and increase their contribution to the energy mix. Nevertheless, to assess power grids sustainability, it is necessary to evaluate their environmental impact with a cradle to the grave approach. For these reasons, a Life Cycle Assessment of off-grid user scale electric systems named Solar Home Systems (SHSs) is performed assuming Siena, Italy, as the installation site [1]. To this aim a simulation model has been developed to analyse the SHS operative phase. SHSs are composed of a PV plant, a battery ESS and a backup generator. The goal of this analysis is to evaluate which type of Lithium-ion batteries is more suitable for SHSs. Furthermore, off-grid SHSs are compared with the Italian electricity mix, with some Hybrid Nano-Grids (HNGs) integrating batteries and hydrogen storage and with a grid-connected SHS. Concerning the HNGs, four scenarios are presented depending on hydrogen pressure (350 or 700 bar) and technologies lifespan (12,000 h or 60,000h). The Life Cycle Inventory is based on Ecoinvent 3.2 database and other harmonized data [2]. Results show that NCA batteries are the most sustainable solution and the impact of the related SHS is assessed to 46.66 Pts/MWh. The Italian electricity mix (69.5 Pts/MWh) is more impactful whereas the HNGs could have a lower impact only in long lifespan scenarios (37.8 Pts/MWh). If, ideally, all the PV energy could be accepted by the grid, the best solution would be represented by the grid connected configuration (22.8 Pts/MWh).



### References

1. Rossi, F., Parisi, M. L., Maranghi, S., Basosi, R., Sinicropi, A. *Sci. Total Environ.* **2020**, 700, 134814.
2. Peters, J.F., Weil, M. *J. Clean. Prod.* **2018**, 171, 704–713.



## Zeta potential of activated carbon on the performance of electric double layer capacitors in salt aqueous electrolyte

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Electrochemical double layer capacitors (EDLCs), known as supercapacitors, are electrochemical devices for energy conversion and storage. For the development of the EDLC technology, the main goal is how to increase the capacitance and specific energy while maintaining the high charge rate, high specific power, and high cycleability. In such system, activated carbon (AC) is selected as the material of choice due to its high surface area, tailored porosity and low cost. Aqueous electrolytes have shown excellent promise for safe electrochemical energy storage devices, but their widespread use is limited by the very low electrochemical window. For this reason, the key thing is to explain the degradation mechanism and corrosion of carbon-based electrodes in this electrolyte. An accelerated ageing (AA) test at different voltages have been used to determine the factors influencing the life-time of EDLC [1]. In the present study, **zeta potential (ZP) of carbon electrode suspension in pure water and in various aqueous media was performed in different pH and salts concentration** after AA experiments. Combined with electrochemical impedance spectroscopy (EIS), solid-state nuclear magnetic resonance (ssNMR), temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and porous structure characterization, **the zeta potential values were used to discuss the charge transfer, self-discharge and charge/discharge mechanism at the carbon electrode/electrolyte interface.** Additionally, the **electric double layer structure** was proposed. Table 1 shows that the positive electrode is significantly susceptible to oxidation processes showed by decreasing of ZP resulting from the appearance of oxygen functional groups. The opposite situation occurs for the negative electrode, where the reduction processes are visible by increasing the ZP value.

Table 1. Zeta potentials of 0.01 g L<sup>-1</sup> suspension of AC in pure water (pH 6.1) or in 1.0 mol L<sup>-1</sup> the same salts electrolyte after 10 h of accelerated ageing at 1.5 V in 1.0 mol L<sup>-1</sup> electrolyte.

AC carbon material study in 1.0 mol L <sup>-1</sup> electrolyte:	Zeta potential, mV <i>in H<sub>2</sub>O (in the same 1.0 M electrolyte)</i>	
	(+) Positive electrode	(-) Negative electrode
Li <sub>2</sub> SO <sub>4</sub>	-35.3	-21.1
Na <sub>2</sub> SO <sub>4</sub>	-43.8 (-6.1)	-22.2 (-4.7)
NaNO <sub>3</sub>	-36.0 (-7.6)	-27.0 (-5.6)
NaClO <sub>4</sub>	-41.8	-33.3
fresh electrode	- 34.6	

### References

1. Ratajczak, P. Jurewicz, K. Skowron, P. Abbas, Q. Béguin, F. *Electrochim. Acta* **2014**, 130, 344–350.

## Energy harvesting and storage system for indoor application

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On the path towards independence from fossil fuels, solar energy is the most promising solution, but it needs a robust and reliable storage system to face its intrinsic fluctuations due to location, day cycle and weather. The integration between harvesting and storage technologies is a must toward clean energy production and it becomes even more appealing considering the possibility of producing electricity not only from direct sunlight but also from diffuse light and indoor illumination.

Dye-sensitized solar cells (DSSC) showed an impressive light-to-energy conversion efficiency when employed under low-light illumination, diffuse solar radiation and indoor light sources. Moreover, low temperature- and atmospheric-pressure-based manufacturing processes make them compatible with roll-to-roll fabrication. This make DSSC an engaging alternative in the landscape of recovering energy from indoor illumination and directly power low-consuming devices (e.g. Internet of Things devices).

For the storage section, electrochemical double layer capacitors (EDLCs) represents a promising solution since they can sustain an incredible number of cycles without appreciably change the capacitance nominal value and they are less sensitive to the voltage output of the harvesting section like a battery. These features perfectly match with the intermittent character of photovoltaic energy production.

Herein we present a DSSC module developed to harvest indoor illumination and directly store it into an EDLC. Six series-connected DSSC are fabricated on the same substrate and the module is integrated with a high-voltage EDLC. The integrated device is characterized under indoor light sources (e.g. LED, fluorescent, halogen lamp) and under mixed natural and artificial light illumination.

### References

1. Sacco, A., Rolle, L., Scaltrito, L., Tresso, E., & Pirri, C. F. (2013). Characterization of photovoltaic modules for low-power indoor application. *Applied Energy*, 102, 1295–1302.
2. Scalia, A., Varzi, A., Lamberti, A., Tresso, E., Jeong, S., Jacob, T., & Passerini, S. (2018). High energy and high voltage integrated photo-electrochemical double layer capacitor. *Sustainable Energy and Fuels*, 2(5), 968–977..



## Monitoring of Solid Oxide Fuel Cell Performance Through Deconvolution of Electrochemical Impedance Spectra

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In this study we present a method to identify the main processes behind polarization losses in Solid oxide cells (SOCs), in order to build an equivalent circuit model (ECM) suitable for real-time diagnosis based on EIS measurement.

SOCs are one of the most efficient energy conversion system, yet a performance drop may be caused by either unfavourable operating conditions or derating factors. Therefore, in-operando analysis techniques are useful to characterize material fitness and to detect early stages of degradation<sup>1</sup>.

Electrochemical impedance spectroscopy (EIS) and its distribution of relaxation times (DRT) is a powerful and non-destructive tool to address the physio-chemical processes occurring inside the cell, as well as modification in the membrane electrode assembly<sup>2</sup>. In order to find the proper ECM, we have performed a wide experimental campaign on a commercial SOC by changing several working parameters such as: temperature (640-820°C), current density (0-1500 mA cm<sup>-2</sup>), fuel flow (150 ± 50 mL min<sup>-1</sup>) and its composition (H<sub>2</sub> from 100%<sub>vol</sub> to 50%<sub>vol</sub> and 25%<sub>vol</sub> on dry basis, balanced with N<sub>2</sub>).

As relaxation time lengthens, DRT deconvolution highlights five major processes, namely: reaction and charge transfer at the triple phase boundary, anodic diffusion, charge transfer at the cathode and cathodic diffusion.

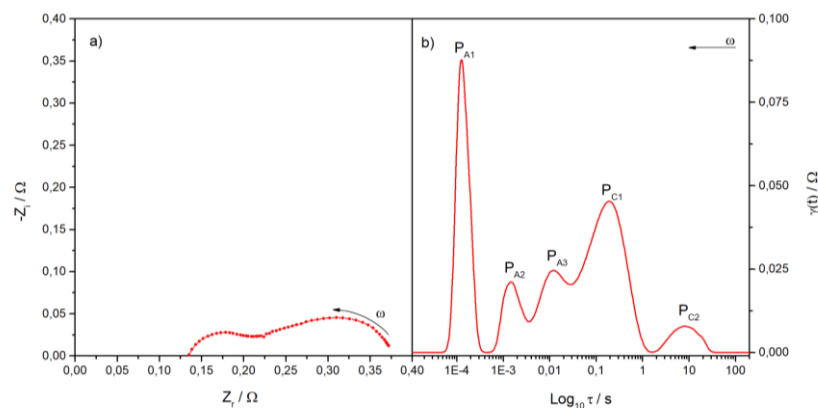


Figure 1 - a) Nyquist plot acquired at 800°C, OCV, H<sub>2</sub> 100% 200 mL min<sup>-1</sup> and air 300 mL min<sup>-1</sup>; b) deconvolution of the EIS by distribution of relaxation times

### References

1. Virkar, A. V. Mechanism of oxygen electrode delamination in solid oxide electrolyzer cells. *Int. J. Hydrogen Energy* **35**, 9527–9543 (2010).
2. Leonide, A., Sonn, V., Weber, A. & Ivers-Tiffée, E. Evaluation and Modeling of the Cell Resistance in Anode-Supported Solid Oxide Fuel Cells. *J. Electrochem. Soc.* **155**, B36 (2007).

## Electrochemical performance of doped hematite/reduced graphene oxide nanocomposites as anode materials for Na-ion batteries

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Although lithium-ion batteries (LIBs) still currently represent the dominant electrochemical energy storage systems, the limited availability and geographically uneven distribution of Li-sources in the Planet could raise their price and hinder their large-scale implementation. Sodium has a similar chemistry to lithium. Benefiting from the greater abundance and wide geographical distribution of its sources, sodium-ion batteries (SIBs) are emerging as a more sustainable alternative to LIBs, but the development of the SIB technology needs of highly performing electrode materials.

Thanks to its chemical stability, high theoretical specific capacity (1007 mAh/g), easy synthesis and environmental friendliness, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is gathering attention as SIB anode material. However, it suffers from poor electronic transport properties and large volume change during sodiation/de-sodiation cycles. It has been shown that doping the oxide with aliovalent elements [1] or combining it with a conductive additive (e.g. graphene) [2] are successful strategies to partly overcome these limits.

In this work,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>:D@rGO nanocomposites consisting of doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles anchored on reduced graphene oxide (rGO) are synthesized by one-step solvothermal method. The effect of the nominal rGO content of the nanocomposites (50 or 30 wt%) and of the type of dopant (titanium or manganese) on their physicochemical properties and electrochemical performance as active SIB anode materials is investigated. The results indicate that, for fixed rGO content, Ti-doping improves the rate capability at lower rates, whereas Mn-doping enhances the electrode stability at higher rates. Nanocomposites with higher rGO content exhibit better electrochemical performance.

### References

1. Fiore M., Longoni G., Santangelo S., Pantò F., Stelitano S., Frontera P., Antonucci P., Ruffo R. *Electrochim. Acta* **2018**, 269, 367–377
2. Modafferi V., Fiore M., Fazio E., Patanè S., Triolo C., Santangelo S., Ruffo R., Neri F., Musolino M.G. *Model. Measur. Control B* **2018**, 87, 129–134

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## Kesterite solar-cells by drop-casting of inorganic sol-gel inks

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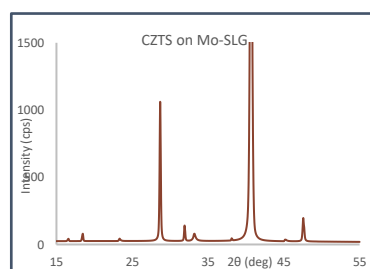
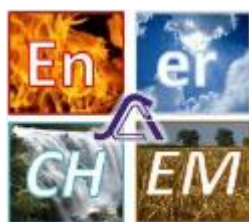
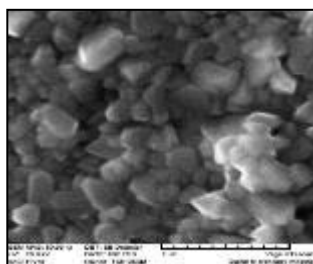
Nowadays, the research of new sustainable energy sources is a necessary requirement and the photovoltaic studies grew in interest thanks to the great potential provided by the amount of available solar energy. Among the PV technologies, silicon cells have always taken a central role in the research and this has allowed to produce commercially competitive panels in the last 30 years. In current days, the PV research is focused on finding low cost and easily processable materials.

Here we propose a new chemical procedure for the synthesis and characterization of chalcogenide-based materials containing cheap and earth-abundant elements such as copper, zinc and tin, where thiourea is the only source of sulphur, in order to obtain well-defined crystalline kesterite thin films ( $\text{Cu}_2\text{ZnSnS}_4$ ). The process of deposition is straightforward and very cheap, based on the sol-gel technique.

The thin films were fabricated thanks to a direct drop-casting of the precursor solution, followed by a gelation process and heat treatment in Ar atmosphere and for short time to generate the required crystalline phase without any further introduction of sulphur. Metal acetate precursors were proved to have a primary role in creating a network in the sol-gel transition by bridging the metals in solution, together with thiourea and dimethylsulfoxide (DMSO) coordination.

The synthesized layers have been characterized by UV-Vis,  $\mu$ -Raman, XRD, XPS and EDX spectroscopy measurements and their morphology was studied by SEM proving the high quality of the material. The first devices produced (with SLG/Mo/CZTS/CdS/ZnO/AZO as cell architecture) show promising interesting results in terms of efficiency and short current density, despite the whole process still has to be optimised.

The same process is now being used to produce easily related layers ( $\text{Cu}_2\text{Zn}_x\text{Fe}_{1-x}\text{SnS}_4$  and  $\text{Cu}_2\text{ZnGeS}_4$ ) with higher band gap aiming to produce a completely kesterite-based tandem device.



## Graphene Aerogel as a support for highly dispersed metals for catalytic reactions

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One of the most important challenges in catalytic reactions is dispersing catalytic metals on a high surface area support atomically and uniformly. This is particularly important for noble metal catalysts especially at high metal loadings to decrease the cost and to increase the number of catalytic sites for metal catalyst. Another challenge is utilization of low-cost transition metals and improve the catalytic performance of such systems as an alternative to expensive noble metals. Carbon based materials as alternatives to metal oxides have attracted considerable interest due to their abundance, processability, high surface area and bulk properties. As support materials, graphene aerogels (GAs) are very promising thanks to their high specific surface area and electrical conductivity that enhance dispersion of catalyst nanoparticles and promote electron transfer.

To meet these challenges, we used graphene aerogels with high surface area that bonds strongly to metal cations. I will demonstrate different metal/metal oxide systems dispersed uniformly on graphene oxide aerogel for different catalytic applications. With our technique, we can easily control the loading and distribution of metals/metal oxides on graphene aerogel support. For example, I will demonstrate Ru loaded graphene aerogel system, which outperforms catalytic systems for  $\text{NH}_3$  conversion in the literature. Other examples are atomically dispersed single site iridium on graphene aerogel as an efficient catalytic system of hydrogenation reactions<sup>1</sup> and controllable dispersion of NiO/Ni nanoparticles on GA for electrocatalytic reactions<sup>2</sup> (Figure 1).

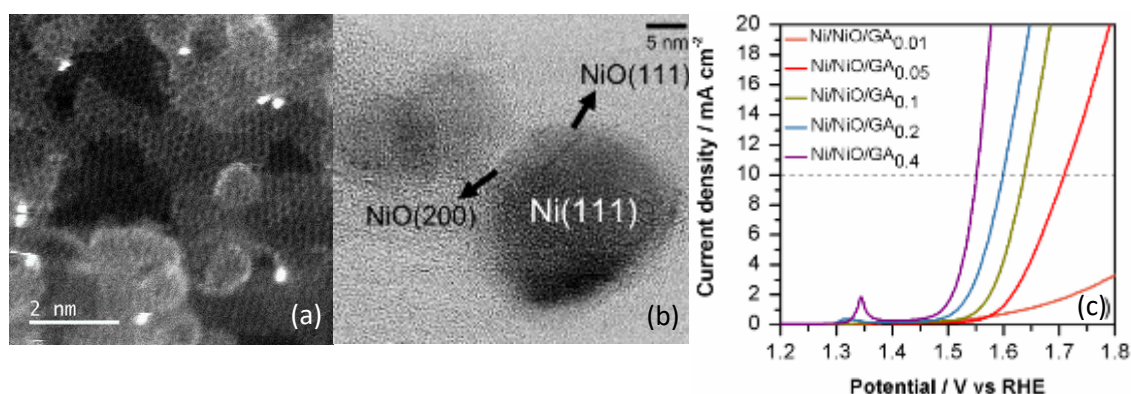


Fig.1 a) Single Ir atomic sites on graphene aerogel, b) Ni/NiO nanoparticle on graphene aerogel and c) its electrocatalytic performance

### References

1. Babucci M., Oztuna F. E., Depesve L. M., Boubnov A., Bare, S. R., Gates, B. C., Unal, U and Uzun, A. *ACS Catalysis*, **2019**, 9, 11, 9905-9913
2. Oztuna F.E., Beyazay T., Unal U., *J. Phys. Chem. C* **2019**, 123, 28131-28141.

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## Dye-sensitized photoanodes for water oxidation based on a novel KuQuinone dye

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Photoelectrochemical cells (PECs) represent a promising technology for the synthesis of solar fuels. However, photoelectrochemical water oxidation still represents a major obstacle toward efficiency. Conversely to conventional photoanodes, dye-sensitized photoanodes address this challenge by combining three different highly specialized components: a nanostructured semiconducting metal oxide for effective charge separation, a visible-light-harvesting dye to match the solar emission spectrum, and a water oxidation catalyst (WOC) to achieve fast catalysis.[1] However, fulfilling all the energetic requirements is not sufficient to ensure an optimal coupling of the three components, since more electron transfer steps are now involved, and an efficient intercommunication is thus necessary. Hence, molecular water oxidation catalysts are often preferred over the heterogenous counterpart, since this allows for a more precise tuning of the dye-catalyst interaction. [2]

In this presentation, we report dye-sensitized photoanodes combining a novel class of totally organic polycyclic quinoid dyes, KuQuinones [3], and a state-of-the-art tetraruthenium polyoxometalate water oxidation catalyst [4]. [5] KuQuinones are characterized by extended absorption in the visible region up to 650 nm with extinction coefficients as high as  $15000 \text{ M}^{-1}\text{cm}^{-1}$ , combined with compelling electrochemical properties and high stability toward oxidation: their facile synthesis and derivatization, *e.g.* with anchoring functionalities, further sustain their use as sensitizers.

### References

1. Kirner, J.T. et al. *Journal of Materials Chemistry A* **2017**, *5*, 19560-19592.
2. Bonchio, M. et al. *Nature Chemistry* **2019**, *11*, 146-153.
3. Galloni, P. et al. *Journal of Materials Chemistry C* **2016**, *4*, 622-629.
4. Sartorel, A. et al. *Journal of the American Chemical Society* **2009**, *131*, 16051-16053.
5. Submitted results.

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## Flexible and high temperature laser induced graphene supercapacitor based on ionic liquid, a de-rated voltage analysis

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Herein we present results about the fabrication and electrochemical characterizations of a supercapacitor obtained coupling laser-induced graphene (LIG) electrodes and 1-Butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([PYR14][TFSI] Ionic Liquid (IL) as the electrolyte. Several parameters have been optimized in order to increase the performance of the flexible pouch-bag devices, such as the laser-writing conditions, type of electrode layout and amount of nitrogen-doping.[1] Among them, the laser writing parameters are found to strongly influence the specific capacitance allowing to achieve about 3.7 mF/cm<sup>2</sup>, as measured from the galvanostatic charge-discharge measurement at 10 μA/cm<sup>2</sup>, with a maximum operating voltage of 3 V at 25 °C.

In order to probe the potential application of such device, the i) flexible pouch architecture, in view of wearable energy storage systems, and ii) high temperature measurements, considering harsh environment field, have been performed. This type of flexible devices demonstrates good stability even at high bending condition while the electrochemical measurements increasing temperature up to 100 °C reveal a 30% of rise in capacitance, high cycling stability as well as high coulombic efficiency. Moreover, a de-rated voltage analysis (DVA) analysis is proposed as a safe procedure to characterize devices/materials in an extended temperature range without compromising the system properties.

### References

1. Lamberti, A. *Nanotech.* **2017**, 28, 174002.

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## Highly selective on site electrochemical H<sub>2</sub>O<sub>2</sub> production from functionalized graphene derivatives

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Large-scale on-site production of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) via two-electron (2e<sup>-</sup>) oxygen reduction reaction (ORR) relies on efficient, robust, and selective electrocatalysts.[1, 2] Among them, carbon materials are a promising class of catalysts to selectively drive the 2e<sup>-</sup> ORR pathway and to realize scale-up electrochemical synthesis of H<sub>2</sub>O<sub>2</sub> (e-H<sub>2</sub>O<sub>2</sub>) due to their tunable surface functionalization and catalytic properties.[3, 4] Here, a recently discovered graphene derivative, graphene acid (GA), was employed for the electrosynthesis of H<sub>2</sub>O<sub>2</sub>. GA was drop-casted on the rotating ring-disk electrode (RRDE) and rotating disk electrode (RED) showing selective and efficient H<sub>2</sub>O<sub>2</sub> formation in acid, neutral and alkaline conditions (Figure 1). In neutral and acid electrolytes the selectivity was comprised between 80 and 100%. In this contribution, we will present H<sub>2</sub>O<sub>2</sub> generation at different pH for several graphene derivatives, drawing structure-activity relationships using materials characterizations results and a quasi in situ XPS analysis of samples conditioned at different potentials. This work opens up the exploration of chemically functionalized graphene derivatives as highly active and selective electrocatalyst for efficient e-H<sub>2</sub>O<sub>2</sub> production.

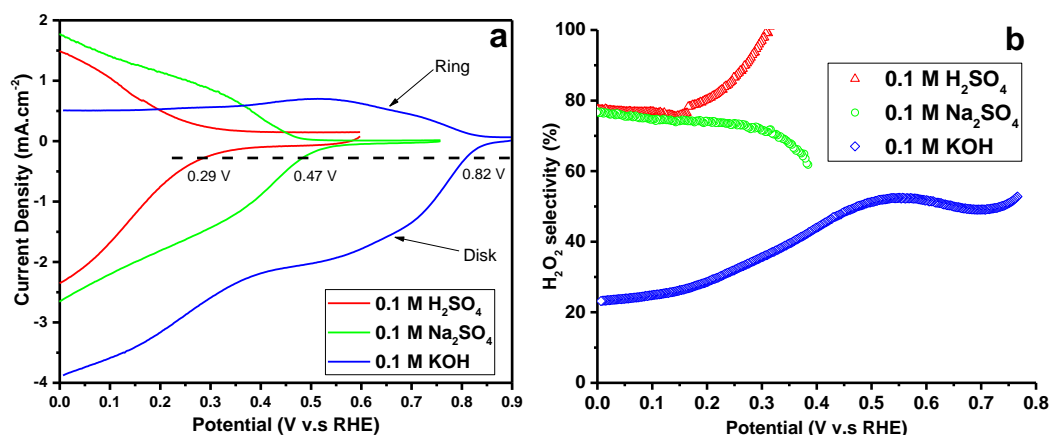


Figure 1 a) RRDE measurements of graphene acid at 1600 rpm in 0.1 M KOH 0.1 M Na<sub>2</sub>SO<sub>4</sub> and 0.1 M H<sub>2</sub>SO<sub>4</sub>. b) The H<sub>2</sub>O<sub>2</sub> selectivity of graphene acid calculated by RRDE

### References

- Jiang, Y. Ni, P. Chen, C. Lu, Y. Yang, P. Kong, B., A. Fisher, X. Wang, *Advanced Energy Materials*. **2018**, 8, 1801909.
- Melchionna, M. Fornasiero, P. Prato, M. *Advanced Materials*. **2019**, 31, 1802920.
- Iglesias, D. Giuliani, A. Melchionna, M. Marchesan, S. Criado, A. Nasi, L. Bevilacqua, M. Tavagnacco, C. Vizza, F. Prato, M. Fornasiero, P. *Chem*. **2018**, 4, 106-123.
- Lu, Z. Chen, G. Siahrostami, S. Chen, Z. Liu, K. Xie, J. Liao, L. Wu, T. Lin, D. Liu, Y. Jaramillo, T.F. Nørskov, J.K. Cui, Y. *Nature Catalysis*. **2018**, 1, 156-162.

## Synthesis of NIR Rylene Dyes and Cobalt-based Redox Couple for Colourless Dye-sensitized Solar Cells

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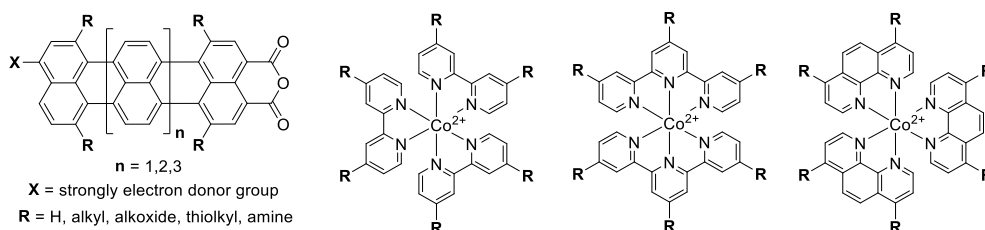
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Photovoltaic cells (PV) assembled with semiconductor technology techniques are, nowadays, the most efficient systems for solar energy conversion.<sup>1,2</sup> Dye-Sensitized Solar Cells (DSSCs) represent one of the best performing technologies developed in the last decades to overcome the limitations of the well-known silicon-based photovoltaics cells<sup>1,2</sup>. Building Integrated PhotoVoltaics (BIPV) based on DSSC are a promising application to make DSSC more attractive in the energy production field. An innovative approach resides on the implementation of a new class of colourless DSSCs based on NIR rylene dyes along with transparent cobalt complexes based redox couples.<sup>3,4</sup>



**Figure.** Schematic representation of the rylene-based dyes and Cobalt (II) redox mediators.

In this work, we will stepwise extend the rylene aromatic core to tune the electronic properties of the dyes, while introducing various substituents on the bay positions to improve the processability properties of the final materials. On the other side, di, ter-pyridine-based ligands, decorated with various substituents, will be synthesized to produce a large library of cobalt (II) complexes as redox mediator for BIPV devices. The overall properties of the dyes and complexes will be investigated and modulated to achieve the photophysical and electronic requirements to assemble innovative devices able to shorten the gap with the silicon-based photovoltaic cells.

### References

1. M. Freitag, J. Teuscher, Y. Saygili, X. Zhang, F. Giordano, P. Liska, J. Hua, S. M. Zakeeruddin, J.-E. Moser, M. Grätzel, M. et al., *Nature Photonics*, **2017**, *11*, 372-379.
2. N. Barbero, F. Sauvage, in *Materials for Sustainable Energy Applications: Conversion, Storage, Transmission and Consumption*, CRC Press, **2016**, 87-147.
3. M. Wang, C. Grätzel, S. M. Zakeeruddin, M. Grätzel, *Energy Environ. Sci.*, **2012**, *5*, 9394.
4. C. Ji, W. Cheng, Q. Yuan, K. Müllen, M. Yin, *Acc. Chem. Res.*, **2019**, *52*, 2266-2277.

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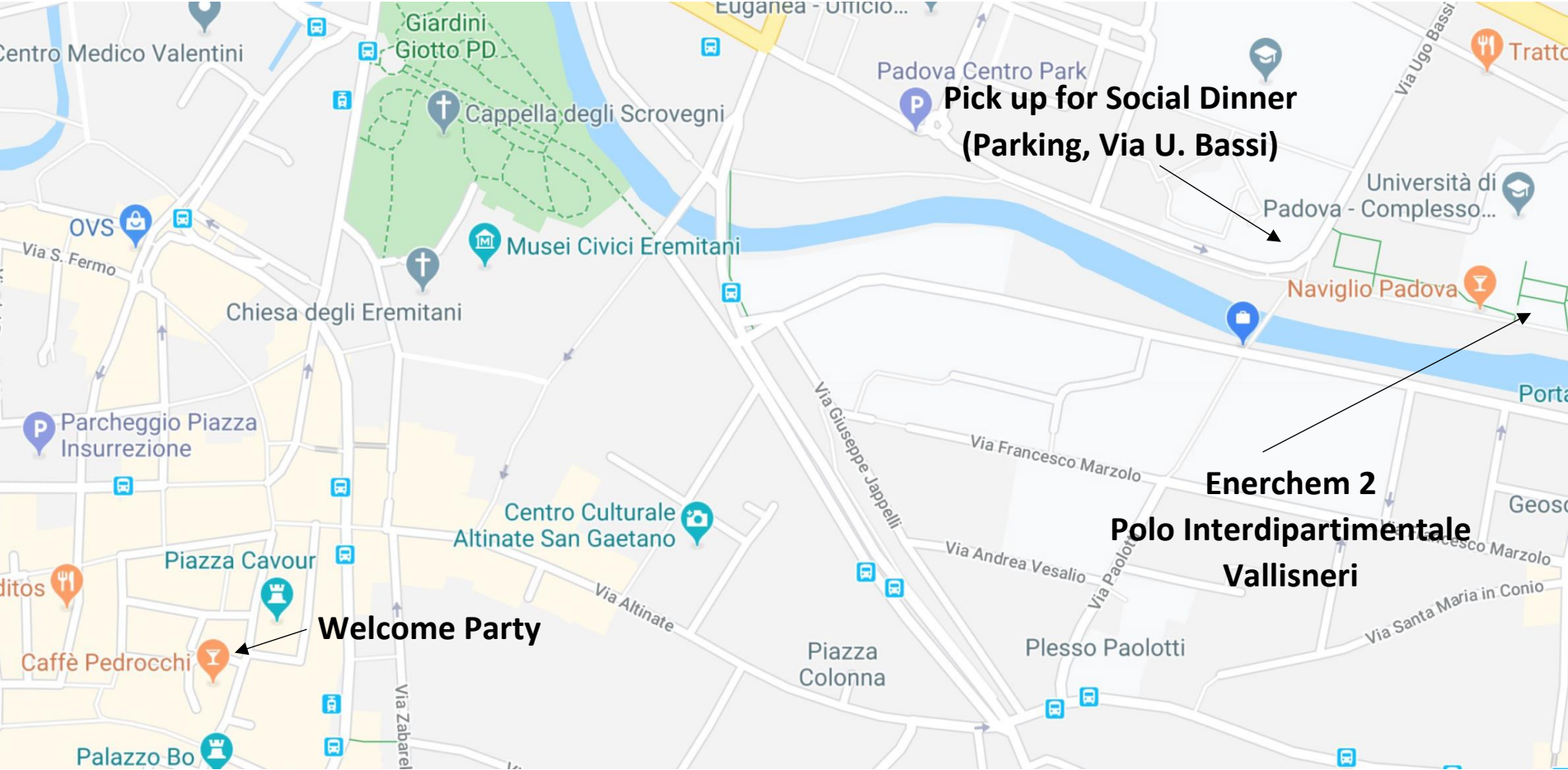
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**Pick up for Social Dinner  
(Parking, Via U. Bassi)**

**Welcome Party**

**Enerchem 2  
Polo Interdipartimentale  
Vallisneri**