ÉCOLE DOCTORALE
Sciences chimiques : molécules, matériaux, instrumentation et biosystèmes

1st FRENCH/GERMAN JOINT SYMPOSIUM ON MATERIALS FOR CATALYSIS AND ENERGY APPLICATIONS

10th – 11th October 2019
Université Paris-Sud
Orsay – France

BOOK OF ABSTRACTS

Organizers:
Prof. Pierre Millet
Université Paris-Sud

Prof. Christophe Colbeau-Justin
Université Paris-Saclay

Prof. Isabelle Leray
ENS Paris-Saclay

Steven Angel
University of Duisburg-Essen

Keynote Lectures

Venue: Conference Building 338 / Université Paris-Sud / Orsay / France (Rue du Doyen André Guinier, 91400 Orsay)

Thursday, October 10

09:15

"Electrocatalysts for water electrolysis and photo-electrolysis"
Prof. Pierre Millet
Université Paris-Sud / France

14:00

"Gas-phase synthesis of functional nanoparticles: From fundamental experiments to processes"
Prof. Christof Schulz
Institute for Combustion and Gas Dynamics (IVG)
University of Duisburg-Essen

16:30

"All-solid-state-batteries : from microelectronics to automotive applications"
Prof. Sylvain Franger
Université Paris-Sud

Friday, October 11

09:30

"Computational chemistry in spectroscopy and catalysis - from molecules to electrocatalysis"
Prof. Alexander Auer
Max-Planck-Institut für Kohlenforschung / Germany

14:20

"Conjugated polymer nanostructures for photocatalytic applications : water treatment and hydrogen generation"
Dr. Hynd Remita
Université Paris-Sud / France

Scientific Program (Talks)
1st French/German Joint Symposium on Materials for Catalysis and Energy Applications
October 10 – 11, 2019
Orsay / France

Venue for all talks: Conference Building 338 / Université Paris-Sud / Orsay / France (Rue du Doyen André Guinier, 91400 Orsay)

Keynote lectures duration: 35 min plus 5 min discussion.

Talks duration: 15 min plus 5 min discussion.

	Thursday, October 10
08:30	**Registration**
09:00	**Opening**
09:15	**Introductory Lecture: "Electrocatalysts for water electrolysis and photo-electrolysis"** ***Prof. Pierre Millet*** Université Paris-Sud / France
09:55	**Talk: "Phosphorene: a hydrogen evolution photocatalyst with a twist"** ***Uttam Gupta*** Max Planck Institute for Chemical Physics of Solids / Germany
10:15	**Talk: "Conducting polymer nanostructures for photocatalysis applications"** ***Xiaojiao Yuan*** Université Paris-Sud / France
10:35	**Coffee break and poster session**
11:15	**Talk: "Exploring the electrochemical mechanisms of InSb as negative electrode for Mg-ion batteries"** ***Lucie Blondeau*** NIMBE/LAPA, CEA, CNRS, Université Paris-Saclay / France
11:35	**Talk: "Scanning electrochemical microscopy (SECM) as a characterization technique for fuel cell catalysts"** ***Alice Boudet*** CEA Saclay / France
11:55	**Talk: "Influence of Fe content and low-temperature heating on spray-flame made $LaCo_{1-x}Fe_xO_3$ nanoparticles for water oxidation catalysis"** ***Baris Alkan*** University of Duisburg-Essen / Germany
12:15	**Talk: "Foam-like Ni-BDC MOF as efficient photosensitizer for TiO_2 Nanorods array and application to photoelectrochemical water splitting"** ***Sheng-Mu You*** Université Paris Saclay / France
12:35	**Talk: "Electrochemical study of iridium oxide materials for the OER reaction in proton exchange membrane water electrolyzers (PEMWE)"** ***Silvia Duran*** LCM, CNRS, École Polytechnique / France
12:55	**Lunch**
14:00	**Keynote lecture: "Gas-phase synthesis of functional nanoparticles: From fundamental experiments to processes"** ***Prof. Christof Schulz*** Institute for Combustion and Gas Dynamics (IVG) University of Duisburg-Essen
14:40	**Talk: "Spray-flame synthesized $Li_7La_3Zr_2O_{12}$ electrolyte for solid state batteries"** ***Yusuf Ali Md*** University of Duisburg-Essen /Germany

15:00	**Talk: "One-pot Sol-Gel Self-biotemplating Assembly of Metal Oxides: Original approach for Photocatalyst Design"** ***Cong Wang*** Université Paris-Sud / France
15:20	**Talk: "Organic membrane design towards a self-healing Li-S batteries"** ***Fanny Betermier*** LAMBE, Université d'Evry Val d'Essonne, Collège de France / France
15:40	**Coffee break and poster session**
16:10	**Talk: "High-Performance Lithium-Ion Battery Anodes based on SiN_x Nanoparticles from Gas-Phase Synthesis"** ***Stefan Kilian*** University of Duisburg-Essen / Germany
16:30	**Keynote lecture: "All-solid-state-batteries : from microelectronics to automotive applications"** ***Prof. Sylvain Franger*** Université Paris-Sud
	Friday, October 11
09:30	**Keynote lecture: "Computational chemistry in spectroscopy and catalysis - from molecules to electrocatalysis"** ***Prof. Alexander Auer*** Max-Planck-Institut für Kohlenforschung / Germany
10:10	**Talk: "Stabilization of Nitrenes beyond Cryogenic Temperatures in Nafion"** ***Nesli Özkan*** Ruhr University Bochum /Germany
10:30	**Talk: "Hydrodechlorination of chlorobenzene on Ni/γ-Al_2O_3 catalysts: influence of γ-Al_2O_3 type and modifier HSiW"** ***Daria Ryaboshapka*** Lomonosov Moscow State University / Russia
10:50	**Talk: "Synthesis and characterization of 7,7' disubstituted isoindigo and bis-isatin derivatives for organic electronic applications"** ***Ren Shiwei*** LPICM, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris / France
11:10	**Coffee break**
11:50	**Talk: "Transition metal chalcogenides as additives for Li_2S-cathodes with high capacity retention"** ***Sebastian Hirt*** Zentrum für BrennstoffzellenTechnik GmbH / Germany
12:10	**Talk: "Nanohybrids in microfluidic chips for heterogeneous catalytic reactions and recycling of carbon dioxide"** ***Joseph Farah*** Université Paris-Saclay / France
12:30	**Talk: "Probing the local pH modulation during CO_2 reduction using Ag-based gas diffusion electrodes"** ***Stefan Dieckhöfer*** Ruhr University Bochum /Germany
12:50	**Lunch**
14:00	**Talk: "Surface modification of TiO_2 nanotubes by i-Sb_2S_3 and i-MoS_2 for electrochemical reduction of CO_2"** ***P. Allazov*** Université Paris-Sud / France
14:20	**Keynote lecture: "Conjugated polymer nanostructures for photocatalytic applications : water treatment and hydrogen generation"** ***Dr. Hynd Remita*** Université Paris-Sud / France
15:00	**Closing remarks**
15:10	**Departure**

Phosphorene: a hydrogen evolution photocatalyst with a twist.

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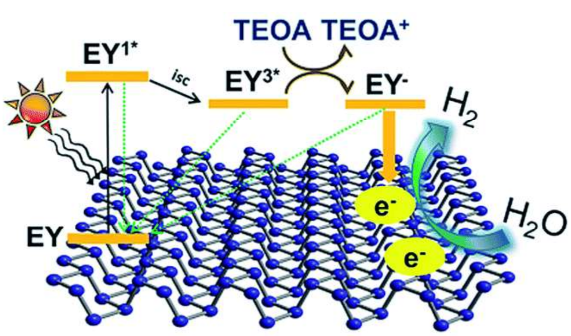
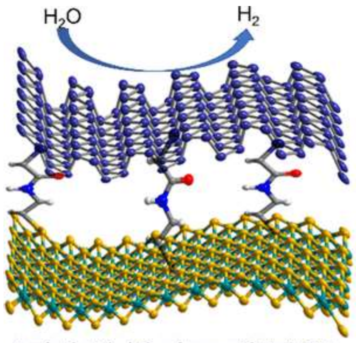
Phosphorene, a mono-elemental 2D material of phosphorus, can catalyze the hydrogen evolution reaction (HER) owing to the suitable position of its conduction band minimum but the ambient instability of phosphorene is the major challenge for its application. Functionalization of phosphorene show stability under ambient conditions as well as good dispersibility in water and exhibit good hydrogen yields superior to pristine phosphorene [1]. Further, covalently cross-linked nanocomposites of phosphorene with MoS_2 as well as $MoSe_2$. The phosphorene−MoS_2 nanocomposite shows excellent photochemical HER activity. The enhanced HER activity of the phosphorene−MoS_2 nanocomposite can be attributed to the ordered cross-linking of the 2D sheets, increasing the interfacial area as well as the charge-transfer interaction between phosphorene and $MoS(Se)_2$ layers [2]. We highlight the strategies to utilize the hydrogen evolution potential of phosphorene, which is otherwise unstable under ambient conditions.





Covalently Linked Phosphorene with MoS_2/$MoSe_2$

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Conducting polymer nanostructures for photocatalysis applications

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Conducting polymer nanostructures (CPNs) emerge as a new class of photocatalysts for organic pollutant degradation under UV and visible light[1,2,3,4]. Polyprrole (PPy), as a conjugated polymer, exhibits a wide range of applications. We present here the first illustration of employing pure PPy nanostructures as a very efficient photocatalyst for the depollution of water. PPy was synthesized in soft template by chemical polymerization (PPy-c), obtained by radiolysis (PPy-γ), and synthesized without template via chemical method (PPy-b) as bulk. Among these three samples, PPy-c shows the best photocatalytic performance under UV light, while PPy-γ exhibits the highest activity for phenol degradation under visible light. These samples have been characterized by different techniques such as SEM, TEM, NanoIR, FTIR, UV-Vis spectroscopy. We modified PPy nanostructures with co-catalysts based on mono-Pt, Ni, and bimetallic PtNi nanoparticles for H_2 production. The modified PPy nanostructures give also promising results for hydrogen generation under UV-vis light. The effect of the nature of the metal precursors and their concentrations were studied.

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Exploring the electrochemical mechanisms of InSb as negative electrode for Mg-ion batteries

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The continued acceleration of the lithium demand combined with its relatively low abundance and uneven concentration on the Earth's crust might dramatically increase its price in a near future. Magnesium batteries are promising candidates to replace Li-ion batteries thanks to Mg abundance, theoretical capacity (2.2Ah/g - 3.8Ah/cm^3), low cost and safety. [1] However, metallic Mg reacts with standard electrolytes to form a blocking layer on its surface, preventing cation exchange, and thus dramatically limiting reversible stripping/deposition. An interesting alternative is to substitute Mg metal electrode with another negative electrode material compatible with conventional electrolytes. *P*-block elements (Sn, Sb, In, Pb, Bi) are a valuable solution as they electrochemically alloy with Mg and possess adequate stability in standard electrolytes. [2]

In a recent work, we investigated the electrochemical reactivity and performance of the InSb alloy as a negative electrode for Mg-ion batteries. [3] A strong synergy between In and Sb has been evidenced with the promotion of the electrochemical activity of Sb towards magnesiation along few cycles, in contrast to what was already reported in other studies. While crystalline MgIn has always been detected in the case of pure In or InBi electrodes [4], we observed a kinetically dependent electrochemically-driven amorphization of MgIn which seems unique to the InSb. This behavior suggests a possible competition between crystallization and amorphization in the material. The characterization of the phase formations and the peculiar electrochemical behavior of InSb will be describe. To this aim, we will present preliminary results on *operando* X-Ray Diffraction and X-Ray Absorption Spectrosopy to follow phase changes and the atomic environement of In and Sb during the first magnesiation/demagnesiation of InSb.

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Scanning electrochemical microscopy (SECM) as a characterization technique for fuel cell catalysts

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The future of energy supply depends on innovative breakthroughs regarding the design of efficient systems for the conversion and storage of energy. Fuel cell is one of these technologies that could offer suitable solutions, however the cost of the platinum catalyst represents a limitation for its present development. That is why more and more platinum-free catalysts are developed. This is precisely the aim of the European project PEGASUS.

The improvement of the characterization of these new catalysts is a challenge that scanning electrochemical microscopy (SECM) could take up. SECM enables to study the intrinsic properties of platinum-free catalysts by probing a very low amount of material, which allows to get rid of the transport within the material. A benchmarking of some catalysts developed in the project PEGASUS will be achieved in order to compare the performances of the different catalysts versus the oxygen reduction reaction (ORR).

Combined with modeling, SECM will enable a better comprehension of the origin of the measured performances. In particular, the catalytic activity will be linked to the agglomeration state of the material that can be controlled and characterized thanks to a precise deposition method and thanks to the atomic force microscope (AFM) for the characterization. This will lead to the improvement of agglomerate models used for the modeling of PEM fuel cells.

Finally, the production of hydrogen peroxide which is a source of degradation in fuel cells will be also investigated by SECM.

Influence of Fe content and low-temperature heating on spray-flame made $LaCo_{1-x}Fe_xO_3$ nanoparticles for water oxidation catalysis

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The improvement of the kinetics of oxygen evolution reactions (OER) through proper tuning of the physical properties of electrocatalysts inherently depends on a synthesis method that enables the production of high surface area catalysts – primarily nanoparticles with high phase purity, minimum surface contamination, and high stability under the applied electric potential. We utilized spray-flame synthesis as a suitable method to fulfill these criteria to synthesize transition metal-based mixed-oxide perovskite nanoparticles. We produced $LaCo_{1-x}Fe_xO_3$ perovskite nanoparticles ($x = 0.2$, 0.3, and 0.4) as they are considered promising OER catalysts. Infrared spectral and qualitative phase analyses revealed that the composition of all as-prepared nanoparticles contain a high degree of combustion residuals, and mostly consist of both stoichiometric and oxygen-deficient perovskite phases. Heating as-prepared nanoparticles at low temperature (250°C) in oxygen was found beneficial to remove combustion residuals and increase the content of stoichiometric perovskite. Detailed characterization of the heat-treated nanoparticles through phase analyses and microscopic techniques indicated that increasing content of Fe in perovskites leads to more oxygen deficient phases and ordered atomic structures. Surface-sensitive techniques revealed an increasing extent of carbonation and low-coordinated oxygen species at higher concentration of Fe. OER catalytic activity tests of both as-prepared and heat-treated nanoparticles pointed out that the most active catalyst is heated-treated $LaCo_{0.6}Fe_{0.4}O_3$. This study highlights that spray-flame synthesis is a promising technique to synthesize perovskite catalyst as oxidation catalyst while low-temperature heating of as-prepared perovskites can improve the OER catalytic activities of $LaCo_{1-x}Fe_xO_3$ perovskite at high Fe concentrations ($x = 0.3$ and 0.4).

Foam-like Ni-MOF as efficient photosensitizer for TiO_2 Nanorods applied on PEC of water splitting

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Abstract

Photoelectrochemical (PEC) water splitting has been widely regarded as one of the most promising routes for hydrogen production from water. Titanium dioxide (TiO_2) and TiO_2–based) materials were mostly used for that purpose. However, performance limitations require innovative strategies to maximize the efficiency of such systems. Nano-structuration and surface modification of TiO_2 substrates are both necessary to optimize water splitting under solar light. In this work, we successfully decorated TiO_2 nanorods (TNRs) arrays with thin layers of a nickel metal organic framework (MOF) using a layer-by-layer growth process. Ni-BDC (NBF) was selected as a surface photosensitizer and co-catalyst for the oxygen evolution reaction (OER). The morphology of the final product contains vertically-oriented TNRs decorated with NBF nanoparticles, forming a foam-like nanostructure. The loading concentration of NBF was found to impact the resistance, electrons transfer and photo-response of the photo-electrode, and fine tuning was required to optimize the photoactivity. After optimization, this unique architecture of NBF@TNRs photoanodes shows an enhanced OER photo-activity, with a photocurrent of 0.46 mA cm^{-2} under 100 mW/cm^2 UV + Visible light intensity (42.4 μA cm^{-2} under 63 mW/cm^2 intensity of visible light >420 nm) which are ~20 times higher than on bare TNRs. The high PEC performance was attributed to the presence of NBF, which enhances the visible light absorption, but also to the large surface area of the interface, that provides efficient charge separation and high carrier mobility. Based on the analysis of experimental UV and visible optical response, electrochemical impedance spectroscopy, and chrono-amperometry, a microscopic mechanism was proposed to explain the observed activity of these systems.

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Electrochemical study of iridium oxide materials for the OER reaction in proton exchange membrane water electrolyzers (PEMWE)

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Proton Exchange Membrane Water Electrolyzers (PEMWE) is a promising hydrogen production technology due to its high efficiency and compact design that will make hydrogen energy more available[1]. However, the electrolyzer performance is impeded by the catalyst at the anode for the Oxygen Evolution Reaction (OER), this problematic motivates the search for new catalytic materials. The latter should possess high catalytic activity and long-term stability as state of art materials, RuO_2 and IrO_2[2]. Also, diminishing the iridium loading in PEMWE is crucial, however, for its ability to combine electrical conductivity, activity, and stability, Ir-based materials are still attractive as anode material[3].

The present work concerns the electrochemical study of IrO_2 materials prepared by Coordinating Etching Precipitating (CEP) and by spray-drying process, the latter been recently investigated for catalysts for PEMWE[3]. The mixed-metal oxide materials obtained by both methods were subjected to different thermal treatments in the range 400–800 ºC. The electrochemical characterization was determine using the three-electrode electrochemical setup. Samples heated between 400–500 ºC presented the best performance as compared to commercial IrO_2, showing at 10 mA/cm^2 an overpotential range of 140-160 mV. These results demonstrate the possible use of the synthesis techniques to fabricate porous noble-metal oxides or catalysts for PEMWEs.

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Spray-flame synthesized $Li_7La_3Zr_2O_{12}$ electrolyte for solid state batteries

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The increasing energy demand and environmental issues are the motivation for increasing research on energy storage systems. In comparison with other metal based electrochemical systems (Al, Zn, Mg, etc.), Li has the highest negative potential which renders it high discharging voltage and high energy density as an anode in a battery [1]. However, these excellent properties come with limitations such as Li metal reacts with almost all the known liquid electrolytes to form a solid electrolyte interphase and uneven deposition of metal ion endows dendrite formation. Moreover, dendrite formation results in a decrease in battery performance and compromises with safety, requiring intercalation of lithium into graphite as substitute anode material. One of the possible solutions for the direct utilization of lithium metal can be to substitute a liquid with a solid electrolyte. Solid electrolytes are much more resistant towards Li metal and do not contain F^- thus avoiding the unwanted formation of LiF and HF. Here we have investigated the optimal conditions to form cubic/tetragonal $Li_7La_3Zr_2O_{12}$ (LLZO) solid electrolyte by spray-flame synthesis as this process is inexpensive and very easy to scale up with high purity, unlike other wet synthesis procedures. We found that acetates are better than nitrates as metal precursors and Al, excess Li is indeed necessary in precursor solution to synthesize cubic LLZO. We characterized the resulting nanoparticles by state of art techniques such as P-XRD, XPS, TEM, Raman Spectroscopy etc. The as-prepared spray flame synthesized nano-particles are found to be $La_2Zr_2O_7$ (LZO) [2] with Li carbonate on the surface as confirmed by XPS and it requires a high-temperature calcination to finally form LLZO. The temperature-dependent electrical conductivity has been measured along with the temperature-dependent powder-XRD to study the phase change from LZO to LLZO to validate the temperature of the solid-state reaction stated by TGA/DSC. The nano-LLZO can be used also as an additive to support the densification of coarse-grained solid electrolyte powders made by classical solid-state reaction.

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One-pot Sol-Gel Self-biotemplating Assembly of Metal Oxides: Original approach for Photocatalyst Design

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Solar energy conversion using photocatalysis becomes a subject of great interest with important potential applications in environment, such as chemical fuel production (H_2).[1-3] Titanium dioxide (TiO_2) is the most popular semiconductor used in photocatalysis. However, TiO_2 has a large band gap that can only be excited by UV light and fast recombination of electron-hole pairs, which lower the solar energy conversion efficiency. Design of the photocatalyst in 3D structure appears as a promising strategy to increase the production of electron/hole.[4] In this aim, sol-gel chemistry and biotemplate nanomaterial (cellulose nanocrystals; CNC) was combined for one-pot generation of chiral photocatalysts, which enables to improve light harvesting.

CNC is obtained from the sulfuric acid-catalyzed hydrolysis of bulk cellulose. At the right concentration and ionic conditions, CNC is stable in suspension by repulsive interactions and form an anisotropic phase with a chiral nematic structure. Evaporation-induced self-assembly (EISA) produce iridescent freestanding films in which the characteristic helicoidally chiral nematic arrangement of CNC is preserved. The chiral nematic ordering can act as a 3D photonic structure, and selectively reflect the circular polarized light that has a wavelength nearly matching the pitch.[5][6] The final photocatalysts with a mesoporouse photonic structure was used for light harvesting in order to improve the photoefficiency, which will be used for H_2 production.

References:

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Organic membrane design towards a self-healing Li-S batteries

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Intense research efforts a currently dedicated to developing higher performances batteries. Lithium-Sulfur (Li-S) batteries have currently attracted wide attention because of their high energy density of 2600 Wh.kg^{-1} and low costs.[1] Nevertheless, many technological issues need to be addressed such as low efficiency and poor cycling stability mainly caused by the polysulfides shuttle effect.[2] During the electrochemical reduction of S, different chain-lengths polysulfides (S_8^{2-}, S_6^{2-}, S_4^{2-}, S_2^{2-}) are formed and diffuse towards the Li anode which can be passivated (Li_2S deposit) or can chemically reoxidised through species which is linked to a capacity fade.

Taking advantage of the remarkable molecular recognition of cyclodextrins (α, β, γ) which are well-known as bioavailable supramolecular hosts, [3] we introduced smart organic separators expected to efficiently suppress shuttle effect by reversible trapping/delivery of the polysulfides. Because of the presence of cyclodextrins, supramolecular inclusion complexes can be formed dynamically avoiding them to reach the Li anode and improving the cycling life of the battery.[4]

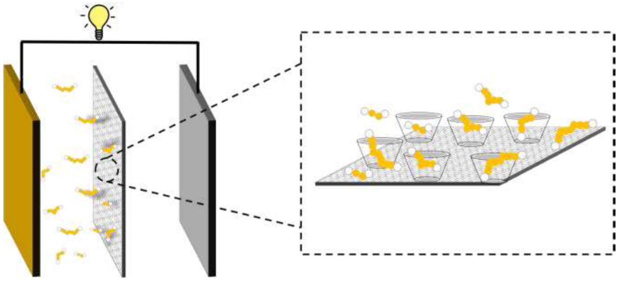

Fig. 1: Conceptual illustration of the membrane of cyclodextrins as a smart separator in a Li-S battery to reversibly trap polysulfides.

This presentation will disclose the characterization of the different inclusion complexes {cyclodextrins/polysulfides}, the interaction mechanism and the reversibilty of the complexation equilibrium at the molecular level. Different cyclodextrins and chain-lengths polysulfides were screened and investigated in order to select the most promising candidate. Our attempts to propose a good design and an efficient architecture for the separator will also be discussed regarding the electrochemical performances of Li-S batteries.

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High-Performance Lithium-Ion Battery Anodes based on SiNx Nanoparticles from Gas-Phase Synthesis

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With the current target of numerous countries to push electro mobility to the mass market, the demand for high performance batteries has increased drastically. Currently, the next goals on the roadmap are to achieve sufficient mileage and to reduce charging time of electrical vehicles. To accomplish these goals, the energy density as well as rate capability of lithium-ion batteries (LIBs) needs to be increased.

Silicon is widely recognized as the most promising component in high-capacity anode materials for next-generation lithium-ion batteries (LIBs) owing to its natural abundance, relatively low working potential, and its high theoretical storage capacity of 3579 mAh/g. However, the practical application of Si-based anodes is severely hindered by its low intrinsic electrical conductivity and its large volume change (>300%) during charging and discharging. The resulting mechanical stress causes rapid pulverization of the silicon and insulation and disconnection of the active material from the current collector. These failure events can cause rapid degeneration of the Si electrode and is especially prominent for silicon particles exceeding the size of a few hundred nanometres. Thus, recent research mainly focusses on nanostructures and nanocomposites that can tolerate the volume change.

A very promising way to stabilize silicon in LIB anodes is the incorporation of nitrogen, which has been shown to significantly improve the cycle performance. We therefore developed a gas-phase synthesis method based on the pyrolysis of monosilane in ammonia-rich atmosphere. Production rates are as high as 30 g/h and can be easily scaled. Based on this technology we are able to synthesize high-performing SiN_x nanoparticles for lithium-ion battery anode. Moreover, their electrochemical properties can be designed by adjusting the synthesis parameters, thus affecting N/Si stoichiometry, particle morphology, size, and crystallinity.

We further demonstrate that SiN_x nanoparticles with medium nitrogen content show significantly enhanced cycling performance of LIB-electrodes compared to pristine silicon. They show an initial specific discharge capacity as high as 1400 mAh/g and a highly stable cycle performance with a capacity retention of 96% after 100 cycles and over 80% after 500 cycles. Rate capability tests show that more than 60% of their capacity can be retained at a charging/discharging rate of 10 C. These results imply that silicon-rich SiN_x based LIB electrodes are promising candidates for high-performance lithium-ion batteries with very high durability.

Stability of Nitrenes beyond Cryogenic Temperatures in Nafion

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Triplet nitrenes are monovalent nitrogen based reactive intermediates. Due to their large magnetic anisotropy at the spin center, they can be used as organic building blocks for metal free high spin systems. However, it is a great challenge to investigate and improve the magnetic properties of nitrenes at ambient conditions because of their reactivity. Triplet nitrenes have one main decay pathway; radical dimerization which lead to formation of azodimers above cryogenic temperatures. In this project, we show how long nitrenes preserve their paramagnetism and triplet state once they were confined in Nafion ionomer.

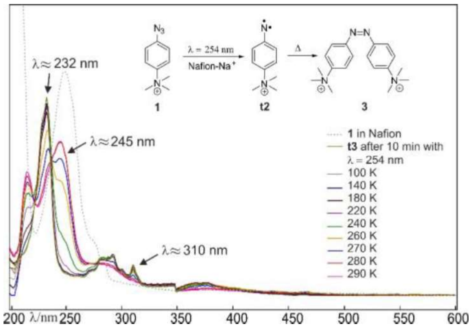

Fig. 1. UV/Vis spectra showing the generation of nitrene 1 inside Nafion matrix from 2 and decay of 1 through the annealing

The generation of cationic nitrene **2** from its precursor **1** and its thermal stability inside Nafion was studied with low temperature UV/Vis spectroscopy. The precursor **1** was embedded into Nafion by ion exchange reaction at 40°C in MeCN. Photolysis of Naf-**1** complex at 77 K with λ= 254 nm light for 5 min result in quenching of the azide transition at 250 nm and formation of a new band at 310 nm which is assigned to nitrene **2.**[1] Decay of the nitrene band throughout annealing up to 290 K was followed by UV/Vis spectroscopy. The spectra above shows that the band at 310 nm decreases upon annealing, however still observable at 280 K. Beside the band at 310 nm, another band at 245 nm rises upon temperature increase. This band was assigned to the expected thermal product, cis azo-dimer **3** by comparison to a reported experiment [2] and UV/Vis spectrum of the authentic sample of 3 in MeCN.

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Hydrodechlorination of chlorobenzene on Ni/γ-Al_2O_3 catalysts: influence of γ-Al_2O_3 type and modifier HSiW

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Ni/Al_2O_3 catalysts proved to be very effective in hydrodechlorination (HDC) of chlorinated organic compounds; thus, they can replace more expensive noble metals. Nickel in Ni/Al_2O_3 catalysts is coordinated by Lewis acid sites (LAS) on Al_2O_3 surface; their quantity strongly depends on preparation method of alumina. LAS on the surface of nickel-containing species can be important to provide catalytic activity in HDC. Modification of the support by Keggin-type heteropolyacid (HPA) may influence the reduction of surface nickel oxides and, therefore, catalytic activity. The approach mentioned above was applied in our research to elucidate the change in chemical state of Ni after such modification. We investigated LAS during each step of catalysts' preparation. Gas-phase HDC of chlorobenzene (CB) was chosen to test the catalytic performance.

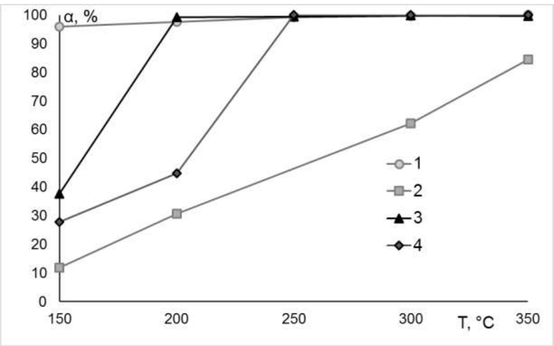

Fig. 1: CB conversion (α) vs. temperature on: (1) Ni/HPA/A, (2) Ni/HPA/E, (3) Ni/E, (4) Ni/A

Two types of γ-Al_2O_3 supports (E was supplied by Engelhard; A was synthesized by hydrolysis of Al(O-*i*-Pr)$_3$ and calcined at 600°C) were used. Both types were modified with HPA $H_8Si(W_2O_7)_6{*}nH_2O$ and then impregnated with $Ni(NO_3)_2$ solution. Four catalysts Ni/A, Ni/E, Ni/HPA/E, Ni/HPA/A containing around 6 wt.% Ni and 20 wt.% HPA were prepared.

All catalysts were active in HDC of CB to produce benzene as the main product. Ni/E catalyst worked better than Ni/A. Modification with HPA provides an improvement: Ni/HPA/A showed the best catalytic performance, at 150°C CB conversion was ~100%. However, Ni/HPA/E was less active catalyst. XPS demonstrates no changes in Ni and W oxidation states after modification with HPA, although TPR profiles significantly change.

According to IR spectroscopy with CO adsorption the surface of E contains stronger LAS than that of A due to the structure and texture differences confirmed by TEM, SEM and N_2 adsorption. HPA molecules are mainly coordinated by strong LAS. Introduction of HPA also results in increased electron accepting ability of Ni^{2+} LAS in unreduced precursors. IR-spectra of the reduced catalysts confirmed that interaction between Ni^{2+} and tungsten-containing species takes place and it eases the reduction of Ni from NiO_x. So, more active component will be available for reagents' adsorption during HDC reaction. Formation of polymeric NiOW phases was previously reported,[1] therefore, we assume that such structures may occur on the surface of our catalysts and ease the reduction of NiO_x species.

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Synthesis and characterization of 7,7’ disubstituted isoindigo and bis-isatin derivatives for organic electronic applications

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The development of novel electron-deficient acceptor building blocks plays a vital role in conjugated materials for electronic applications.[1] Incorporation of lactam moieties on conjugated backbones is one of the most important design concepts of acceptor units. Isoindigo (iI) is a lactam core fused with phenyl group, it is an excellent electron-accepting building block and recently it has become very popular in semiconductors for OPV applications.[2] Isatin (1H-indole-2,3-dione) and its derivatives are also an important class of dyes that can be used as precursors for organic semiconductors synthesis. They display broad optical absorption and large molar absorptivity in visible region and near infrared regions. Isoindigo can be functionalized on different position.[3] The electronic effects of substitution pattern (5,5’ vs. 6,6’) and substituent nature have been reported. Previous studies showed that substitution patterns played significant roles on the photo-physical properties of molecular iI compounds. The 6,6’ substituted derivatives had more extended conjugation than the 5,5’ substituted derivatives because of the large contribution of electronic transition dipole moment in the axis aligned with the 6, 6’ carbons.[4] However, little attention has been paid to the substitution at 7,7’ positions, Figure **1**.

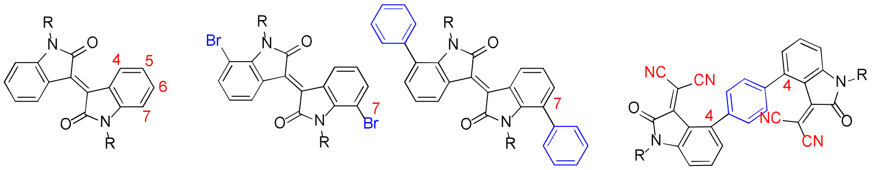

Figure **1**: Structure of Isoindigo and bis-isatin derivatives

In this work, we report on the synthesis and opto-electronic properties of various 7,7’ disubstituted iI, as well as some new derivatives of di-2-(2-oxindolin-3-ylidene) malononitrile (DIM). Hence, we have developed a new method for the synthesis of various bromo-isatin and bromo oxindole derivatives. Extending the conjugation at the 7-position via Suzuki or Stille cross-coupling reaction yields to useful functionalized-isatin, as synthon for further transformation. A knoevenagel condensation of bis-isatin derivatives with malononitrile, afforded to the introduction of malononitriles onto bis-isatin derivatives. Direct condensation of 7-bromoisatin and 7-bromo-oxindole in acetic acid gave 7,7′-dibromo-iI.The chemical structures of all these new materials were defined by *^{1}H, ^{13}C NMR* and *mass spectroscopy* analyses. The optical properties of these π-conjugated systems were investigated by UV-visible, absorption spectroscopy. The electrochemical behavior was also investigated and the HOMO/LUMO energies were determined and correlated to the molecular structure.

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Transition metal chalcogenides as additives for Li_2S-cathodes with high capacity retention

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Due to the high theoretical capacity of sulfur (1672 mAh g^{-1}) and lithium sulfide (Li_2S, 1166 mAh g^{-1}), lithium-sulfur batteries are promising candidates to meet the requirements for future energy storage devices. However, low coulomb-efficiency and poor capacity retention are still unsolved problems of the lithium-sulfur technology.[1] These challenges are mainly caused by the so called polysulfide shuttle mechanism. This shuttle mechanism implies the dissolution of polysulfides as intermediate products into the electrolyte, their diffusion from the cathode to the anode (and backwards) as well as their chemical reaction at the surfaces of the electrodes.[2]

Our work focuses on the reduction of the polysulfide shuttle. In the course of this investigation we prepared Li_2S cathodes with transition metal chalcogenides. These compounds can adsorb polysulfides (Fig. 1a). Thus, the loss of active material in the cathode is reduced,[3] leading to an enhanced capacity retention (Fig. 1b).

The Li_2S cathodes are prepared by a simple mixing procedure which is cost efficient and easily scalable.

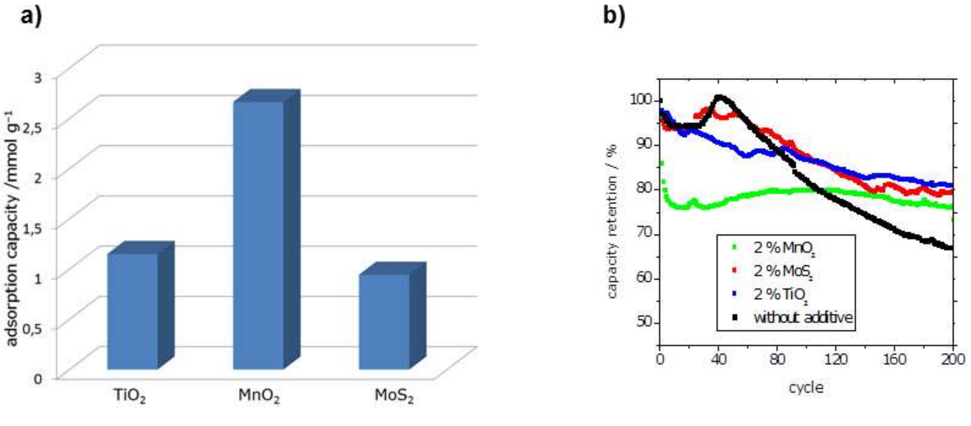

Fig. 1: a) Adsorption capacity for Li_2S_6 of three transition metal chalcogenides measured by UV-VIS spectroscopy, b) capacity retention of Li_2S with and without transition metal chalcogenides

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Nanohybrids in microfluidic chips for heterogeneous catalytic reactions and recycling of carbon dioxide

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In recent years, microfluidics led to the development of numerous research projects and industrial applications in various fields, such as health, environment, cosmetics, and energy [1]. In this study, we developed a new application of microfluidics in organic chemistry, in particular heterogeneous catalytic reactions.

The main objective of this study is to integrate heterogeneous catalysts supported on carbon nanotubes into a microfluidic device. At a micrometric scale, this combination of microfluidics and catalytic reactions improves the system's performance in terms of heat transfer efficiency, reaction kinetics, yield, effluent treatment, recycling of catalysts and safety of use. Thus, using microfluidic systems in organic chemistry can develop a sustainable chemistry by reducing the quantities of chemicals and the risks of accidents compared to conventional experiments in batch.

For this purpose, gold nanoparticles were first assembled on the surface of carbon nanotubes to form functional catalytic systems *(figure 1)* [2]. Second, dedicated microfluidic chips were designed in order to retain the nanohybrids while allowing the fluid to flow through. Finally, these nanohybrids were tested by doing a catalytic reaction (oxidation of dimethylphenylsilane). The results confirmed that the catalytic reaction was successfully done using microfluidic chips as reactors.

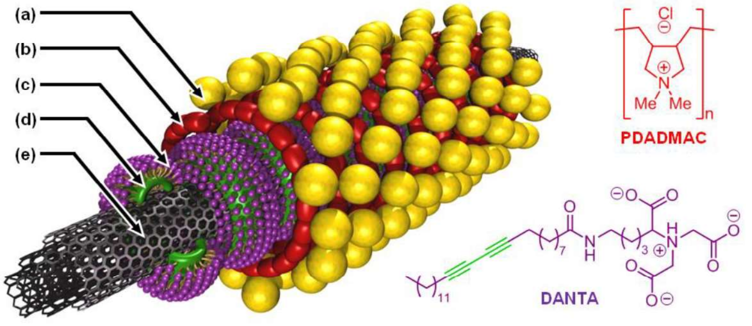

Figure 1: Schematic representation of the AuCNT nanohybrid: a) AuNP; b) PDADMAC layer; c) DANTA nanorings; (d) polymerized region (green); e) multiwalled CNT.

In the future, the work and strategies described in this study will be applied to recycle carbon dioxide. The ultimate target is to drive CO_2 photo reduction to liquid fuels while using H_2O as the primary, carbon free, renewable source of reducing equivalents.

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Probing the local pH modulation during CO_2 reduction using Ag-based gas diffusion electrodes

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Electrocatalytic CO_2 reduction represents a promising carbon recycling strategy for establishing a sustainable carbon feedstock for renewable energies.[1] Time-variant local reaction environments during electrocatalysis are known to exert a complex influence on the CO_2 reduction product selectivity.[2] This is particularly true for gas diffusion electrodes (GDE), where the electrocatalytic centers are equilibrated with both CO_2 gas phase and liquid electrolyte phase significantly shortening the CO_2 diffusion path length.[3] The resulting high current densities in the order of several kA/m² strongly alkalize the local electrode environment are severely impacting on the reaction selectivity at relevant CO_2 reduction rates.[4]

Herein, we demonstrate the quantitative assessment of the local ion activity changes at the surface of operating of CO_2 reduction gas diffusion electrodes. Pt microelectrodes positioned via shear-force feedback in close proximity to the GDE serve as an ion-sensitive probe by monitoring the potential of the pH-dependent PtO reduction peak. This concept is applied to Ag-based gas diffusion electrodes, which yield predominantly two main products, CO and H_2, at varying ratios.[5] We evaluate how the local pH environment changes during high-turnover catalysis and influences the CO_2 reduction product spectrum.

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Surface modification of TiO_2 nanotubes by i-Sb_2S_3 and i-MoS_2 for electrochemical reduction of CO_2

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Global warming, atmospheric pollution and ocean acidification are the main ecological issues that humanity is facing today. The increasing human population requires a much larger energy production infrastructure to satisfy the demand. CO_2 valorization to make solar fuels is an interesting option. The capture, storage and chemical or electro(photo)chemical transformation of CO_2 is a very promising approach. The research work reported here focuses on the elaboration and characterization of nanostructured photo-active electrodes made of arrays of TiO_2 nanotubes (nt-TiO_2) surface-covered by different functional layers such as Sb_2S_3 or MoS_2, deposited by atomic layer deposition [1]. TiO_2 is a good substrate for such applications thanks to its chemical and electrochemical stability, and its low cost, but its n-type semiconductor nature requires an additional functional layer in order to (i) allow CO_2 reduction reaction and (ii) absorb visible light (Figure). The nt-TiO_2 photo-electrodes were obtained by anodization of Ti sheets in organic or aqueous solution, assisted by addition of fluoride ions. The anodization parameters have been optimized in order to obtain highly ordered arrays of nanotubes. Atomic Layer Deposition was then used to deposit nano-layers of i-Sb_2S_3 and i-MoS_2 on these TiO_2 nanotubes, and the surface ratio between the two semiconductors has been optimized. The reduction products have been identified by gas chromatography. In terms of perspectives, a major limitation in the development of photoelectrodes for CO_2 reduction is due to the lack of selectivity that leads to mixtures of products [2]. Therefore, our next objective will be to improve the selectivity of our photoelectrodes by grafting molecular co-catalysts at the surface.

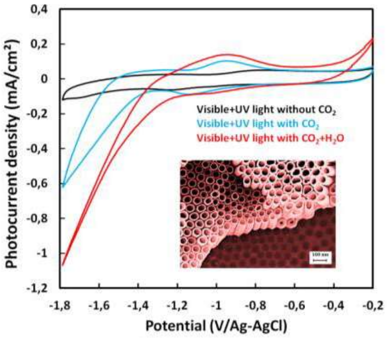

Figure : Cyclic voltammetry of direct CO_2 reduction with or without water on TiO_2 nanotubes-based electrodes under full sunlight (buffer solution Na_2SO_4 pH=7, scan rate 10 mV/s)

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