

7^{èmes} Journées Nationales des Carburants Solaires

Ecole Normale Supérieure de Lyon
Du 19 au 21 Juin 2023



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Présentation

Le GDR « Solar Fuels » regroupe les acteurs français de la recherche dans le domaine de la production de petites molécules (les « carburants » tel H₂) à partir de ressources abondantes (eau, biomasse, CO₂...) et en utilisant l'énergie solaire.

Les « journées nationales des carburants solaires » (dont la 7^{ième} édition est organisée à Lyon) correspondent aux rencontres annuelles des acteurs de ce réseau. Depuis le début, l'un des objectifs clés de ces journées est de créer une émulation nationale autour du développement des carburants solaires en faisant se rencontrer des scientifiques venant de champs disciplinaires variés qui n'auraient pas eu la possibilité de se rencontrer dans des conférences de leur domaine individuel : Chimistes de synthèse de matériaux et de molécules, électro-chimistes, photochimistes, théoriciens, chimistes de la catalyse... Par ces rencontres, de nouvelles collaborations et de nouveaux projets de recherche voient régulièrement le jour. Les « journées nationales des carburants solaires » permettent donc la coordination de la recherche fondamentale française pour répondre aux grands défis de la transition énergétique : production d'hydrogène, capture et valorisation du CO₂, valorisation de la biomasse.

Le comité d'organisation de ces 7^{èmes} journées souhaite la bienvenue à Lyon à toute la communauté des carburants solaires et espère que découleront de ces journées des collaborations permettant de relever les défis (et ils sont nombreux !) associées à la production des carburants solaires.

Le comité d'organisation

Audrey, Eric, Jean-François et Tangui

Programme

19-juin-23		20-juin-23		21-juin-23	
10:00-14:00	Accueil	9:00-9:20	O7 - Christian Cariño	9:00-9:20	O20 - Philipp Gotico
		9:20-9:40	O8 - Stéphanie Roualdes	9:20-9:40	O21 - Félix Taulou
		9:40-10:00	O9 - Muammad Akif Ramsan	9:40-10:00	O22 - Christian Seassal
		10:00-10:20	O10 - Alisha Khan	10:00-10:20	O23 - Nathalie Herlin
		10:20-10:40	Pause	10:20-10:40	Pause
		10:40-11:00	O11 - Jean-Charles Arnault	10:40-11:00	O24 - Fabrice Odobel
		11:00-11:20	O12 - Jérôme Fortage	11:00-11:20	O25 - Sébastien Roth
		11:20-11:40	O13 - Maria Drosou	11:20-11:40	O26 - Angélique Bousquet
		11:40-11:50	sponsors	11:40-12:00	O27 - Charlotte Jonis
				11:50-13:20	Déjeuner
		13:20-14:00	O14 - Olivier Vidal		
14:00-14:40	O1 - Stephan Steinmann	14:00-14:20	O15 - Javier Ivanez		
		14:20-14:40	O16 - Daniel H. Cruz Neto		
14:40-15:00	O2 - Clément Maheu	14:40-15:00	Pause		
15:00-15:20	O3 -Jiefeng Liu	15:00-15:30	O17 - Valentin Diez-Cabenas		
15:20-15:50	O4 - Matthieu Haake	15:30-15:50	O18 - Khadija Talbi		
15:50-16:10	Pause	15:50-16:10	O19 - Sébastien Blanchard		
16:10-16:50	O5 - Negar Naghavi	16:10-17:10	AG - Poster		
16:50-17h10	O6 - Jesús González-Cobos				
17:10-18:00	Poster	17:10-18:00	Poster		
19:10	Cocktail	20:00	Diner Gala		

Organisation

Lieu

Oraux : Salle D8-001 du site Buisson de l'ENS de Lyon (entrée 19 Allée Fontenay 69007 Lyon)

Posters : Salle D8-003 et D8-galerie du site Buisson de l'ENS Lyon

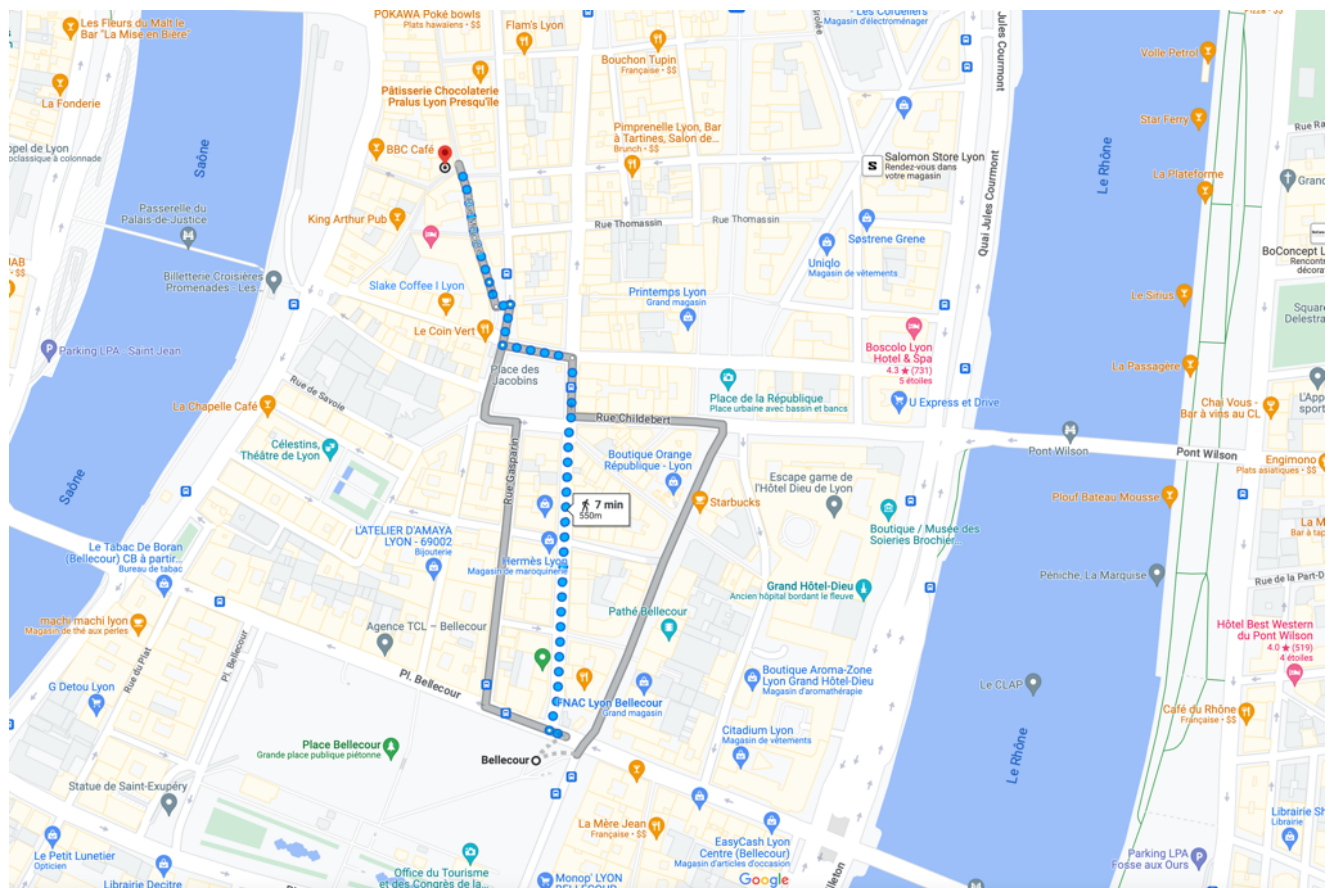
Pauses : Salle D8-004

Cocktail du lundi 19 Juin

Salle des colloques du restaurant Descartes à l'ENS de Lyon (départ groupé depuis la salle D8-001 à la fin des oraux du lundi). Cocktail dinatoire de 18h30 à 21h30.

Restaurant du mardi 20 Juin

Restaurant « le Bistrot de Lyon » (64 Rue Mercière 69002 Lyon), métro « Bellecour » (ligne D et A).



Plan pour se rendre du métro Bellecour au Bistrot de Lyon

Présentations orales

Atomistic Modelling of Reactions at the Co-Catalyst in Photo-Electrocatalysis

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Photo-electrocatalytic devices often consist of a light-harvesting (semi-conductor) unit and a “co-catalyst”: Photons are adsorbed in the semi-conductor, the exciton splits and the electron and holes are transferred on the “anode” and “cathode” co-catalyst, respectively. The holes and electrons generate an electrochemical potential at these co-catalyst interfaces and this electrochemical potential is then transformed into chemical energy via bond-formation reactions. In this contribution we will discuss the theoretical methods that are apt to describe the chemical reactions at the co-catalyst/solution interface and give insights into the origin of the overpotentials.¹ We will exemplify and compare selected methods on the example of two non-noble co-catalysts: CoOOH for water oxidation (see Fig. 1)² and MoS₂ for water reduction.^{2,3} This second example will serve as an illustration of the progress of atomistic modelling towards the quantification of not only thermodynamic, but also kinetic quantities.

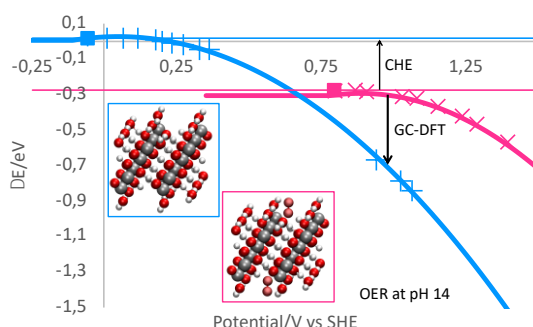


Figure 1: Example of the impact of taking the electrochemical potential explicitly into account: O₂ desorption changes from endothermic when neglecting the potential (horizontal lines), to exothermic when placing one-self in the OER relevant potential region (thicker lines and symbols).

References

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Stability of the electronic and surface properties of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ perovskite under Oxygen Evolution Reaction

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The oxygen evolution reaction (OER) limits the efficiency of water electrolysis due to high overpotential. The development of efficient, earth-abundant, and stable OER electrocatalysts is therefore crucial. LaFeO_3 a typical perovskite oxide is a promising one due to its good stability in alkaline electrolytes and adjustable electronic structure. We found that Sr-doping results in the oxidation of Fe^{3+} to Fe^{4+} and enhances OER activity.^[1] We argued that filled electronic states near the Fermi level (E_F), the so-called hole state, improve the formation of key OER reaction intermediates.

In this work, we investigated the electronic and surface stability of single crystal $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0, 0.33, 0.8$) electrocatalysts before and after OER treatment. The cyclic voltammetry (CV) cycles result in the enhanced OER performance of LaFeO_3 while the ones of $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_3$ and $\text{La}_{0.2}\text{Sr}_{0.8}\text{FeO}_3$ decrease. Atomic force microscopy, X-ray diffraction, and X-ray reflectivity reveal that the surface of the three catalysts underwent a reconstruction accompanied by recrystallization during OER treatment.

Synchrotron X-ray photoemission spectroscopy (SXPS) and near edge X-ray absorption fine structure (NEXAFS) were performed *quasi-in situ* at the solid-liquid-interface analysis system (SOLIAS) endstation, at BESSY II synchrotron in Berlin [2]. Measurements evidence a global shift of the core level (e.g. O 1s) and valence band edge indicating a gradual down-shift of the E_F of the LaFeO_3 sample with the increase of the CV cycles. NEXAFS spectroscopy at the O K-edge indicates an increase of the new hole states due to the formation of Fe^{4+} species with the increase of the CV cycles. On the contrary, the electronic properties of $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_3$ and $\text{La}_{0.2}\text{Sr}_{0.8}\text{FeO}_3$ behave differently among the OER treatments.

References

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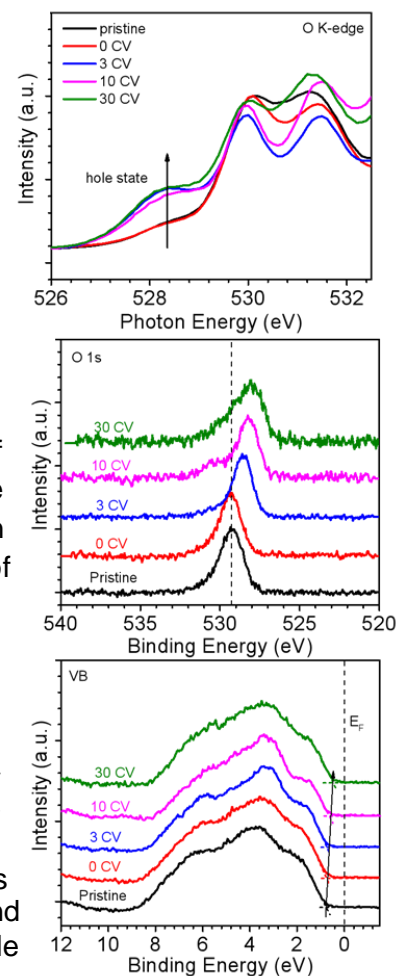


Figure 1: O K-edge NEXAFS, O 1s core level, and VB edge measured by SXPS of LaFeO_3 with different CV cycles (pristine, in contact with the electrolyte i.e. 0 CV, 3 CV, 10 CV, 30 CV)

Reduced electricity consumption using co-electrolysis of CO₂ and ethylene glycol

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The electro-reduction reaction of carbon dioxide (CO₂) is a key technology for converting fossil resources into renewable resources[1,2]. Common CO₂ reduction methods use the precious metal oxide: IrO_x for the anodic oxygen evolution reaction (OER), which results in high electricity consumption and high operating costs (OPEX). Here, we replaced IrO_x with NiFe layered double hydroxide (NiFe LDH), which has a larger electrochemically active surface area and a higher charge transfer rate. We then combined the CO₂ reduction reaction (CO₂RR) with the organic oxidation of ethylene glycol and analyzed the performance and selectivity of the catalysts at the anode and cathode. In my presentation, I will explain how this study provides a feasible alternative to reduce electricity requirements and improves the technoeconomics of the CO₂ reduction reaction.

References

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Molecular engineering and grafting of cobalt tetraazamacrocyclic catalysts: towards the development of noble metal-free cathodes for hydrogen evolution

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Production of green hydrogen requires the development of sustainable processes. To this end, water electrolysis is more and more envisioned to enable clean production of H₂. However, as of today, most electrolyser technologies still relies on the use of scarce platinum-group metals (PGMs).^[1] The study of molecular catalysts represents a strategy which can enable the replacement of PGMs with earth-abundant first-row transition metals through their integration within specifically designed coordination spheres.^[3] Among the most active reported molecular catalysts for hydrogen evolution reactions (HER) is the cobalt tetraazamacrocyclic complex [Co(N₄H)Cl₂]⁺ (**1**, Figure 1). It is an effective catalyst for the HER in organic solvents as well as in fully aqueous conditions.^[3-4] Through ligand scaffold engineering of **1**, we describe the synthesis and full characterisation of novel derivatives **2** and **3** (Figure 1) functionalised with a pyrene moiety at two different positions on the macrocycle. Following their smooth non-covalent integration to MWCNTs-based electrodes, the electrochemical and electrocatalytic properties of the two molecular hybrid electrodes towards H₂ production were tested in fully aqueous conditions. Notable differences could be observed for their catalytic activities depending on the pH of the electrolyte. Both catalysts could reach high turnover numbers with up to 100% faradaic efficiency for H₂ generation at both acidic and neutral pHs at a moderate overpotential. Interestingly, complex **2** demonstrated a higher stability over the course of the electrolysis experiments than **3**.

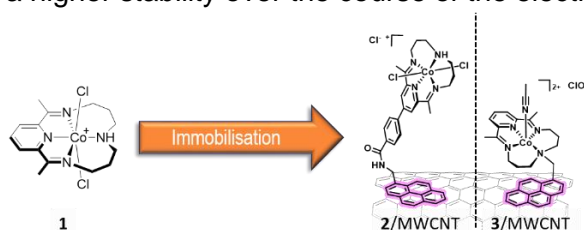


Figure 1: The tetraaza macrocyclic Co-complex **1** and the modified tetraaza macrocyclic complexes **2** and **3** for immobilisation onto MWCNT (right).

References

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From solar cells to solar fuels: can we use photovoltaic materials electrodes ?

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Achieving carbon-neutral energy cycles from renewable energy sources is one of the most exciting and vital tasks for a sustainable future. Today, one of the fastest growing renewable sectors is photovoltaics (PV). In this context, driving catalytic chemical reactions from photovoltaic materials and systems through (photo)electrochemical (PEC) approaches offers new pathways for sustainable chemical and fuel synthesis, while providing a mechanism for storing intermittent solar energy in stable chemical forms. While conventional industrial routes typically require harsh operating conditions (e.g., high temperature and pressure), photoelectrocatalytic (PEC) processes, which rely on sunlight as an energy source to drive highly selective chemical reactions, are a promising approach for fuel production. However, the conversion efficiency of these systems is still too low for industrial applications.

The use of photovoltaic materials as photoelectrodes allows the capture of a large part of the visible solar spectrum, which can potentially lead to a higher efficiency conversion of solar to fuels. Solar cells work with visible light and have a much higher quantum efficiency compared to conventional semiconductors. Most absorbers used for photovoltaics, in view of their excellent light absorption and tunable band gaps, are excellent candidate as photoelectrodes. Moreover, in photovoltaics, the charge carrier separation mechanism is often based on pn junctions, which increases the photocurrent by an order of magnitude compared to a bare photo-absorbing electrode. In PEC systems, another critical point is the kinetic requirement for multiple electron and proton transfers, resulting in high energy barriers for some products, requiring efficient catalysts for high current densities and high selectivity for the target product.

This presentation first describes the similarities and differences between solar cells and solar fuel systems. Then, through some examples, we will show how photovoltaic materials can be used for solar fuel production.

Generation of value-added chemicals from glycerol by photoelectrocatalysis

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Glycerol, as a by-product of biodiesel industry, is an attractive renewable platform molecule for making added-value bio-sourced chemicals like glyceraldehyde (GAD) or dihydroxyacetone (DHA) [1]. Our group has unravelled the outstanding properties of nanostructured WO₃-based materials for the selective conversion of glycerol via photocatalysis [2] and has reported the potential improvement achieved through via photoelectrocatalysis (PEC) [3]. Recently, we went a step forward in the development of a device able to simultaneously produce H₂ and valuable C₃ products by means of a proton-exchange membrane (PEM) photoelectrolyser.

We obtained a stable product generation at the anode of 11.1 and 5.2 mmol m⁻² h⁻¹ for GAD and DHA, respectively, along with 44.0 mmol H₂ m⁻² h⁻¹ at the cathode, under optimum conditions (60 °C and 1.2 V) (Figure 1). We confirm the synergistic effect between light irradiation and the external bias, WO₃ standing as a promising material for the sustainable generation of hydrogen and target biomolecules from organic wastes.

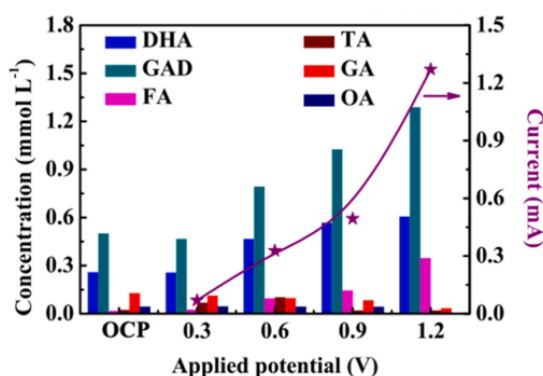


Figure 1: Influence of the cell voltage on the concentration of Dihydroxyacetone (DHA), Glyceraldehyde (GAD), Formate (FA), Tartronate (TA), Glycolate (GA), Oxalate (OA), and on the obtained current after 6 h. Anode: WO₃/C, Cathode: Pt/C, Temperature: 60°C, Initial glycerol concentration: 0.1 M. UV power density: 41 mW cm⁻².

References

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Photoactive polyoxometalate-based molecular hybrids for solar energy conversion

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To achieve successful conversion of sunlight into chemical fuels, artificial photosynthetic devices must replicate the key steps of photosynthesis in natural systems: light-harvesting, charge separation, charge accumulation, and multielectron redox catalysis. The application of a hybrid molecular system in these devices offers full control over the structure allowing the fine-tuning of the charge transfer kinetics and the charge storage properties by modular design. Polyoxometalates (POMs) are good candidates for the development of such system due to their ability to store multiple electrons while maintaining structural integrity^[1]. Here, we present photoactive hybrids composed of a bodipy photosensitizer covalently linked to a Dawson or Keggin POM that acts as an electron-storage site. POM-bodipy hybrids were previously determined to have fast photoinduced electron transfer kinetics down to dozens of picoseconds making them suitable for applications in photoelectrochemical devices^[2,3]. More recently, we have demonstrated the photoinduced charge accumulation of these hybrids in the presence of sacrificial electron donors (Figure 1).

In this communication, we will describe the synthetic strategy employed in preparing the POM-bodipy hybrids as well as the preliminary results of photophysical and electrochemical studies and grafting onto photocathodes.

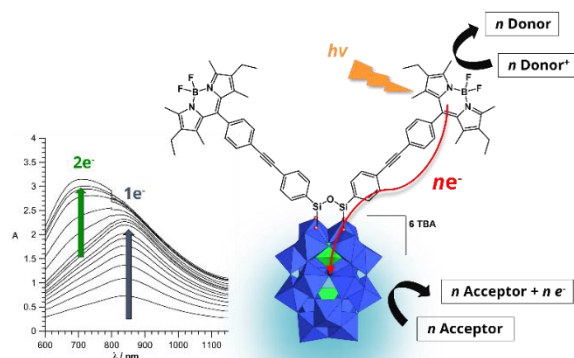


Figure 1: Light-induced electron transfer and charge accumulation in the POM unit monitored by UV-Vis spectroscopy

References

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Poly(3,4-ethylenedioxythiophene)/TiO₂ nano-tree films deposited by oCVD/CVD for water splitting

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The hydrogen production from photo-electrocatalytic water splitting attracts extensive attention as a direct way to convert solar energy into chemical fuels. In this work, innovative photo-anodes composed of PEDOT/TiO₂ bi-layers are prepared by a dry process strategy, combining oxidative and metalorganic chemical vapor deposition (CVD) [1,2]. Pure anatase, dendritic TiO₂ films of variable thickness are obtained at 500°C by varying the deposition time. Increase of TiO₂ films thickness from 474 to 2133 nm results in morphologies that evolve from dense and angular structures to isolated and nanostructured tree-like columns with a concomitant decrease of the charge transfer resistance. The PEDOT/TiO₂ sample with a 1350 nm thick TiO₂ film and a 50 nm thick upper-PEDOT layer shows the highest photocurrent response (0.26 mA.cm⁻² at 1.8 V/RHE), and the fastest photocurrent response under illumination with e⁻/h⁺ stability up to 64 ms average time before recombination. This best photocurrent value is approximately 1.8 times higher than that of the bare TiO₂ film with equivalent thickness, indicating a significant enhancement of the photo-generated electrons and holes due to PEDOT layer. This synergistic effect between PEDOT and TiO₂ enhances the hydrogen yield up to 4.1 μmole.cm⁻².h⁻¹ (twice that of TiO₂ alone). Such innovative PEDOT/TiO₂ p-n junction prepared by MOCVD and oCVD opens new prospects for photo-electrochemical cells.

H₂ evolution coupled with water remediation (i.e. water splitting using a polluted water as inlet resource) is in progress.

References

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Elucidating the reactivity of MoS₂ edges for photocatalytic reduction of CO₂ to HCOOH using grand-canonical DFT

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MoS₂ is a cheap electro- and photo-catalytic material which holds promise for realizing a neutral carbon balance by converting CO₂ into value-added chemicals at ambient conditions. Here, we have investigated how different edge sites of 2H-MoS₂ catalyze the reduction of CO₂ into formic acid (HCOOH) which is an economically desirable transformation.¹ For that purpose, we apply grand-canonical density functional theory in combination with an implicit solvent model to capture the effect of the photo-generated electrochemical potential.² Starting from the partially-sulfided Mo and S-terminated edges (referred to as Mo-edge and S-edge from here on) of stoichiometric MoS₂,³ we first determine the thermodynamic stability of hydrogen atoms on these edges as a function of the working electrode potential. Figure 1(a) shows that under mild reducing potentials vs. SHE, S-edge exhibits H coverage of 0.5 (with 1 H on each Mo atom), which further increases to 1 (1 H on each S and Mo atom) for potentials smaller than -0.43 V. The reaction free-energy profiles plotted at different H coverages for U = -0.6 V vs SHE (Figure 1 b) reveal that the reaction proceeds via the OCHO* intermediate, which is further hydrogenated into HCOOH*. Formic acid spontaneously desorbs to complete the catalytic cycle. Surprisingly, in contrast to that suggested by previous studies,⁴ the S-edge still retains its reactivity at very high H coverage and this reactivity differs from that of the non-hydrogenated S-edge (not stable under realistic conditions). Moreover, the activation of CO₂* via chemical adsorption requires an uphill rearrangement of S atoms, which is found to be less endothermic at high H coverage. This important aspect was also not addressed by previous DFT studies.⁴ By comparing these trends with those obtained on Mo-edge, we will discuss the full picture of the reactivity of the MoS₂. This analysis will provide guidelines for experimentalists regarding the surface states of the electro-/photo-active MoS₂ catalyst and the optimal MoS₂ edge.

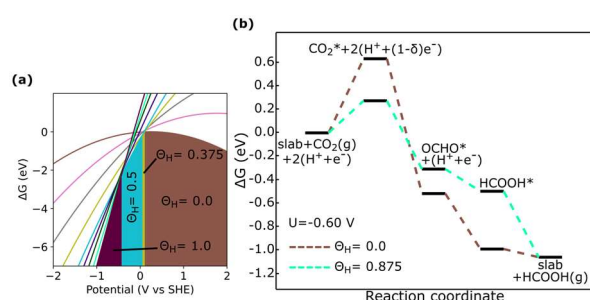


Figure 1: The (a) the predominance curves of different levels of hydrogenation vs electrode potential on the S-edge and (b) free-energy profile for conversion of CO₂ to HCOOH at two different H coverages on same edge for an electrochemical potential of U = -0.6 V corresponding to an overpotential of 0.53 V. The H coverage is defined as $\theta_H = N_H / (N_{Mo} + N_S)$ where N_H , N_{Mo} and N_S are the number of H, Mo and S atoms on S-edge in the chosen supercell.

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Photocatalytic performance of HKUST-1/TiO₂ composite towards hydrogen generation

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The boost in global energy consumption and environmental crises draws attention to utilize sustainable and renewable energy sources. Among renewable sources of energy, solar energy is the best as it is inexhaustible and widely distributed. On the other hand, hydrogen fuel has been considered a carbon-free alternative to fossil fuels due to its high energy content. There are numerous methods for generating hydrogen on a mass scale. However, all notable methods are characterized by high energy consumption, which drives the hydrogen production processes unfavorable on a mass scale. One of the simplest ways to produce green hydrogen from abundant solar energy and water molecules is by photocatalysis. However, it must be produced from green resources! Photocatalysis is a promising way to produce green hydrogen from water and sunlight. The ICP team developed highly active photocatalysts based on conjugated polymer nanostructures or TiO₂ (including composite nanomaterials) as well as metal cocatalysts for hydrogen generation and water treatment [1,2]. Also, it has been reported by ICP team that composite TiO₂/HKUST-1 shows good photocatalytic activity for generation of hydrogen by photo-reforming of a glycerol-water mixture under artificial sun light [3]. Encouraged by these observations, herein we developed composite nanomaterials based TiO₂ coupled with HKUST-1 (different mass ratios) for application in hydrogen generation by photocatalysis. We modified these nanomaterials with metal nanoparticles used as cocatalyst (Pt, Cu induced by radiolysis).

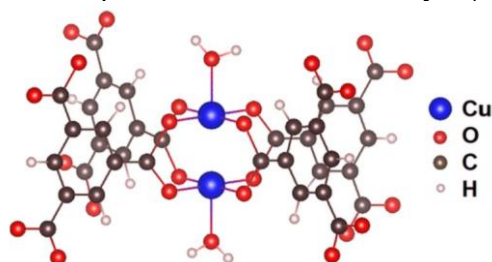


Figure 1 : Structure of HKUST-1 [4]

The photoactive composite materials obtained were further characterized by transmission electron microscopy (TEM), UV-Vis spectroscopy, time resolved microwave conductivity (TRMC), X-ray Photoelectron spectroscopy (XPS), FTIR, XRD and photoelectrochemical studies. Their activity for H₂ generation was studied using Micro Gas Chromatography (MicroGC). The composition of the composite has been optimized. These nanocomposites show high photocatalytic activity for hydrogen generation under UV-visible light and this activity is stable with cycling.

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Diamond nanoparticles: an alternative for photocatalysis under solar light?

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Compared to other nanoscale semiconductors, nanodiamond (ND) has not been really considered for photocatalytic reactions. This originates from the confusion with ideal monocrystalline diamond behaving a wide bandgap (5.5 eV) that requires deep UV illumination to initiate photoreactivity. At nanoscale, diamond particles enclose native defects that create energetic states decreasing the light energy needed to initiate charge separation. This is supported by very recent studies that involved our group with experimental results and DFT calculations [1, 2]. The presence of sp² carbon in hydrogenated detonation ND allows the emission of solvated electrons in water under visible light (400 nm) according to ultrafast transient absorption spectroscopy [2]. In addition, the diamond electronic structure can be strongly modified playing on its surface terminations (oxidised vs hydrogenated) [3]. Combining these assets, ND becomes competitive to other semiconductors toward photoreactions. Its potential needs to be deeply investigated.

In this context, this study reports on H₂ production by photocatalytic water splitting using ND alone under broad and moderate solar illumination conditions. Detonation nanodiamonds (DND), oxidized by an annealing in air leading to a predominance of carboxylic groups on their surface, were suspended in water. These particles also exhibited some sp² carbon reconstructions at their surface according to XPS and Raman spectroscopy. H₂ measurements were realized in dynamic mode, under N₂ flow (100 cc/min), in presence of a hole scavenger (1 vol.% TEOA) and sun-like illumination. P25 TiO₂ nanoparticles (Evonik) were studied under similar conditions as reference. After 50 min of stabilization, formation rate of H₂ reaches almost 3000 μmol.h⁻¹.g⁻¹, which is comparable to P25 TiO₂. Such effect is not observed for hydrogenated DND from the same source. H₂ production with oxidized DND was also evidenced in presence of methanol as hole scavenger. This study evidences the positive impact of ND for photocatalytic H₂ production by water-splitting without the addition of noble metal co-catalyst and with low amount of sacrificial agent (below or equal to 1 vol.%).

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Challenging the $[\text{Ru}(\text{bpy})_3]^{2+}$ sensitizer with Ru tris-diphenylsulfonate-phenanthroline for light-driven H_2 evolution in water

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The tris-bipyridine ruthenium complex, $[\text{Ru}(\text{bpy})_3]^{2+}$ (**Rubpy**; Fig. 1), and its derivatives have been widely used for decades as molecular photosensitizers (PSs) associated with a molecular catalyst (Cat) and a sacrificial electron donor (SD), for the photocatalytic reduction of protons to H_2 using visible light energy.^[1] However, the main drawback of this photosensitizer family is the poor stability of its oxidized and reduced forms, especially in water that causes relatively fast deactivation of the photocatalytic systems.

In this context, we were able to improve the stability and efficiency of a Ru based photocatalytic system for hydrogen production in water by using the water-soluble Ru tris-diphenylsulfonate-phenanthroline derivative, $\text{Na}_4[\text{Ru}((\text{SO}_3\text{Ph})_2\text{phen})_3]$ (**RuSPhphen**; Fig. 1) in place of the regular PS, **Rubpy**. **RuSPhphen** exhibits an absorption coefficient twice as high compared **Rubpy** and much longer lifetime of its excited-state, while keeping almost similar redox potentials, which favors efficient electron transfers between the three components of the system. Moreover, the groups of Castellano^[2a] and Brewer^[2b] have observed high photocatalytic activities with PS/Cat/DS systems using Ru tris-diphenyl-phenanthroline PSs, these performances having been attributed to the high stability of these PSs under photocatalytic conditions. **RuSPhphen** was thus tested by our group with the cobalt tetraazamacrocyclic complex $[\text{Co}(\text{CR14})\text{Cl}_2]^+$ (**Co**), one of the most efficient H_2 production catalysts in acidic water,^[3] and ascorbate (HA^-) as SD under visible-light

irradiation (Fig. 1). The redox and spectroscopic properties of **RuSPhphen** will also be presented, as well as a thorough photophysical study with the **RuSPhphen/Co/HA⁻** system, in order to explain its high stability which is related to the good photocatalytic activity of this system.

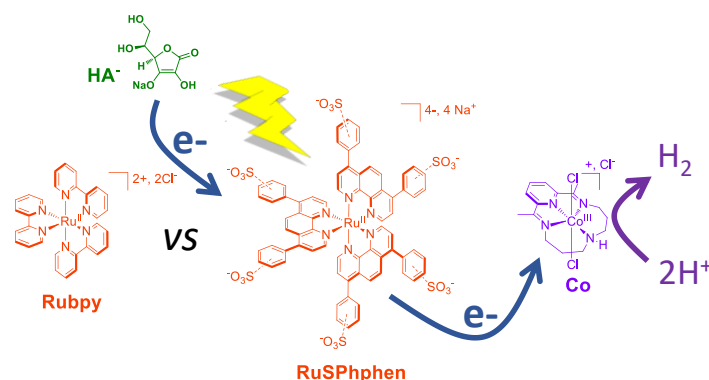


Fig. 1. Photocatalytic systems for H_2 evolution

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Nature of the Last Observable Intermediate in Biological Water Oxidation

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The conversion of solar energy to chemical energy in photosynthetic organisms begins with the light-driven four-electron water oxidation to molecular oxygen, catalyzed by the oxygen evolving complex (OEC) in Photosystem II (PSII). The Mn_4CaO_5 cluster of the OEC accumulates the four oxidizing equivalents by cycling through five states, S_0 – S_4 , and releases molecular oxygen during the $S_3 \rightarrow [S_4] \rightarrow S_0$ transition. The electronic structure of the S_3 state remains strongly debated. Spectroscopic studies suggest Mn-based¹ oxidation during the $S_2 \rightarrow S_3$ transition, whereas crystallographic studies suggest ligand-based oxidation.²

Here, we employ a highly accurate protocol³ based on the domain-based local pair natural orbital approximation to coupled cluster [DLPNO-CCSD(T)] to show that the oxo-hydroxo isomer, which results from Mn-based oxidation, is strongly favored energetically versus the peroxide isomer formed after ligand-based oxidation.⁴ Moreover, the models are evaluated against Mn K_α high energy resolution fluorescence detected (HERFD) X-ray absorption spectra (XAS) – the first XAS study of a homogeneous S_3 state sample. Our results conclusively preclude peroxide formation in the S_3 state, indicating metal-based oxidation in all observable S-state transitions of the OEC catalytic cycle. Understanding nature's unique water-oxidizing enzyme might provide invaluable guidelines for the development of artificial water-splitting catalysts.

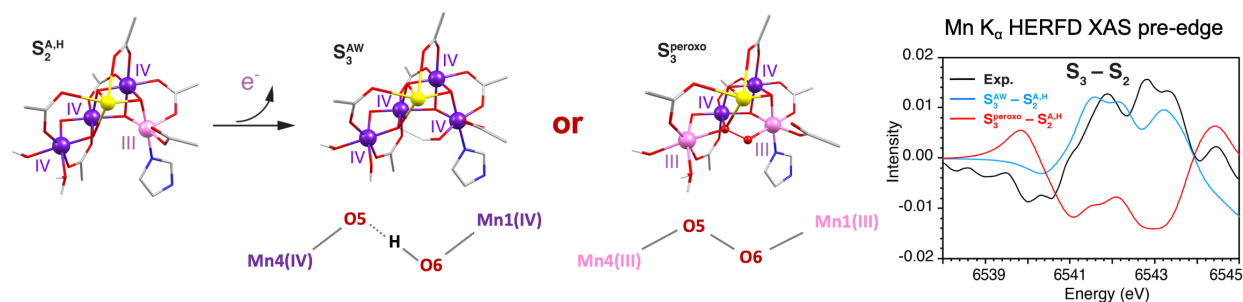


Figure 1: Left: Inorganic core of the OEC in the S_2 and S_3 states. Right: Experimental (black) and calculated (blue for S_3^{AW} , red for S_3^{peroxo}) Mn K_α HERFD XAS S_3 – S_2 spectral differences.

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The energy-mineral resources nexus in the context of energy transition

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The Paris Agreements (COP21) call for achieving global carbon neutrality by 2050. New energy production, storage, transport and use infrastructures will have to be built to replace those currently based on fossil fuels. These new infrastructures consume large quantities of base and rare metals, the availability of which is a matter of concern. In addition, the production of raw materials requires large amounts of energy, so issues related to raw materials and energy are inseparable and need to be addressed in a common framework. The expected shift towards low-carbon energy will take place in a context of growing global demand due to the rapid emergence of developing countries, increasing urbanization and the development of high technologies.

Some anticipate shortages resulting from the depletion of natural reserves during the century, while others argue that technological improvements and the exploitation of deeper or offshore resources and recycling will help maintain the increase in production at the level observed over the last century.

We will present and discuss the results of a dynamic model linking the expected demand in metals for different scenarios of GDP, population and energy with the production capacity constrained by geological and technological parameters. The results of modelling provide a better understanding of the coupling between reserves, mineral resources production, cost and price, energy and greenhouse gases emissions. The results are used to define the conditions for a sustainable supply of mineral resources in a changing world.

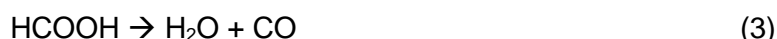
Photothermal Ru/TiO₂ catalysts for the gas-phase formic acid decomposition and CO₂ methanation

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Photothermal catalysis has been reported as an emerging process for sustainable energy applications [1]. The co-activation of the catalyst by light and heat energy sources may enhance the catalytic properties of the reaction [2]. Among the promising applications of photothermal catalysis, reactions related with the fields of H₂ production, transport, and chemical storage such as formic acid dehydrogenation (1) and CO₂ methanation (2) have been studied. However, in both cases we can have side reactions that harm the catalytic system such as dehydration (3) and reverse water gas shift (4) for HCOOH decomposition and CO₂ hydrogenation, respectively.



In this study, supported Ru nanoparticles on TiO₂ (P25) were under dual UV-A photonic/heat excitation for the gas-phase FA dehydrogenation and CO₂ methanation (Figure 1). It was observed an enhancement in the catalytic properties in terms of activity and selectivity under the dual excitation. In-situ DRIFTS results indicated possible alternative mechanisms under UV-A photons irradiation that they do not occur at dark conditions.

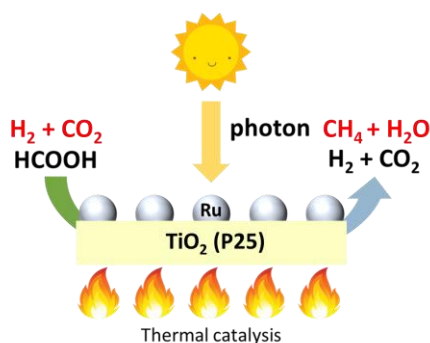


Figure 1: Scheme of a photothermal catalytic reaction (HCOOH dehydrogenation and CO₂ methanation) over Ru/TiO₂.

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Light-Induced CO₂ Reduction Promoted by Iron Porphyrin Derivatives: Photophysical Insights

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In naturally photosensitizing organisms, photonic absorption leads to multielectronic catalysis in carefully engineered photosystems^{1,2}. The lessons learned from these natural systems have allowed us to attempt at reproducing their subtleties in promising synthetic molecular mimics dedicated to solar-to-fuel conversion. In the photoinduced CO₂ reduction reaction, the thermodynamic challenges imposed by the multielectronic reduction can be bypassed by designing effective catalysts whose properties are tailored, by chemical functionalization, to bind and stabilize CO₂. Amongst these catalysts, modified iron tetraphenylporphyrins have gained attention for their efficiency, selectivity, and facility with which the second coordination sphere can be modified to tackle specificity in CO₂ capturing³⁻⁵ and compatible thermodynamic and kinetic properties. For such known systems, both charge accumulation steps and the catalytic cycle itself are yet not fully understood, and such knowledge may come from time-resolved spectroscopic measurements. In the present work, we apply nanosecond pump-probe techniques, both with optical absorption and resonant Raman probes, to understand the reversible dynamics of an active catalytic system in the presence of CO₂. Our photosystem is composed of an urea-modified iron porphyrin catalyst, which has been shown to be highly efficient towards the CO₂-to-CO reduction⁵, the prototypical [Ru(bpy)₃]²⁺ as a photosensitizer, and sodium ascorbate as a reversible electron donor. Light-induced charge accumulation measurements in inert atmosphere show that we can induce the sequential formation of charge-separated states, with up to 2-electron accumulations, and track their fate in solution in a reversible manner. In the presence of the substrate, the catalytic cycle is kick started at the formal Fe^I state, allowing us to obtain insights in terms of mechanistic steps of the cycle and isolate stable intermediates. In conclusion, the design of the next generation of active and selective catalysts strongly relies on the understanding of structure-activity relationships that can only be depicted by fundamental spectroscopic investigations.

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A Theoretical Insight into the Photophysics of Metal-Organic Framework-based Catalysts

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Photocatalysis appears as one of the most promising avenues to shift towards sustainable sources of energy, due to its capability to transform solar light into chemical energy, as for instance, in the production of chemical fuels as H₂ and CH₄ via overall water splitting (OWS) and CO₂ reduction (CO₂RR) reactions, respectively. Interestingly, metal-organic frameworks (MOFs) possess a tuneable crystalline porous structure which enhances the surface area exposed for reaction and mitigates the electron-hole recombination pathways, meanwhile offering the possibility to modify their properties via ligand functionalization or doping their inorganic structure. As a result, trinuclear copper pyrazoyl- (Cu-Pyr) and (TiO₂)-based (such as MIP-177) MOFs have demonstrated promising catalytic activities for OWS and CO₂RR reactions, respectively. On the top of that, when building a heterojunction by coupling MOFs with other co-catalyst (i.e. cation doped graphitic carbon nitride-based poly-heptazine imides (PHI) materials), it is possible to improve the interfacial charge separation and, more importantly, to set up a Z-scheme junction mimicking an artificial photosynthesis device. However, the performance exhibited by MOF-based materials is still limited due to the lack of the understanding of the photophysical processes driving the photocatalytic device operation. In this context, we have developed a multi-scale modelling approach based on classical Molecular Dynamics (MD) simulations and Quantum Mechanical (QM) calculations comprising GW formalism, Bethe Salpeter Equation (BSE) and Time-Dependent Density Functional Theory (TD-DFT) based techniques; with the aim of investigating the structural and opto-electronic properties of MOF-based materials and their heterojunctions.

On the one hand, we demonstrated that Cu-Pyr MOFs exhibited a suitable energetic alignment with respect to the OWS reaction potentials, where the hole injection driving forces can be further decreased by functionalization of the Pyr ligands with donor groups. More importantly, the charge separation driven by the coordination of hydroxyl group to the Cu(I) metal centres is at the origin of the long lifetimes and high photocatalytic activity measured experimentally. On the other hand, our MD simulations gave us the access to realistic MIP-177/PHI heterojunction structures and evidenced that the distortion of the PHI layers prompted by the presence of the doping cations yielded to an enhancement of their compatibility with the MOF surface. Afterwards, our QM calculations confirmed that the interfacial CT directionality and the absorption energy windows of the heterojunctions can be finely tuned by the choice of the dopants for both MOF and PHI components. Overall, our multi-scale modelling platform showed that the photoactivity of MOFs materials can be enhanced by chemical design of their structure based on reliable structure-property rules, which paves their way to the practical exploitation.

Photocatalytic CO₂ reduction activity of nickel-based polyoxometalates and POM@MOF-545 composites

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Polyoxometalates (POMs) can be described as molecular oxides based on high-valent metal centers (W^{VI}, Mo^{VI}, V^V...). They can incorporate in their structure transition metal centers such as Ni(II) ions and can be functionalized by organic ligands. They can play the role of catalyst and/or electron relays. Following a recent study on a Ni-containing POM (Ni₁₇, Figure 1) which exhibits one of the best CO production activities among POMs,¹ our group has decided to investigate the catalytic properties in homogeneous conditions of a series of Ni-based POMs (Figure 1) in order to apprehend the parameters that influence the catalytic activity. DFT calculations are in progress to give insight into the mechanism that governs the catalytic reactions.

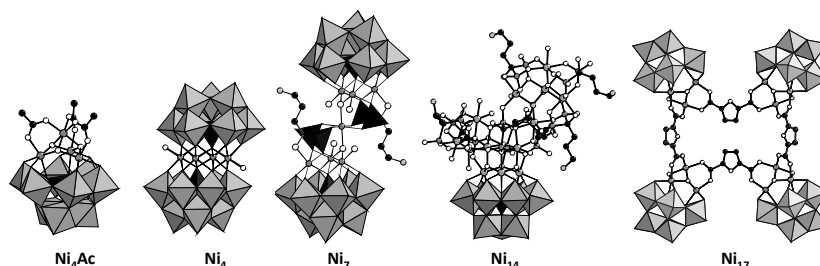


Figure 1: Representation of the POMs studied as catalysts, from left to right: [Na{(SiW₉O₃₄)Ni₄(CH₃COO)₃(OH)₃}₂]¹⁵⁻, [Ni₄(H₂O)₂(PW₉O₃₄)₂]¹⁰⁻, [{(PW₉O₃₄)Ni₃(OH)(H₂O)₂(O₃PC(O)(C₃H₆NH₃)PO₃)₂Ni}]¹⁴⁻, [(SiW₉O₃₄)Ni₁₄(Al₅H)₅(Al₂H)₂(H₂O)₁₁(OH)₇]¹²⁻, {Ni[{(SiW₉O₃₄)Ni₄(OH)₃}₄(OOC(C₄H₂O)COO)₆]}³⁰⁻

In the second part of the presentation, we will describe our first results on the role of POMs as electron relays for the photocatalytic activity of Zr-based porphyrinic metal-organic frameworks (MOFs). We previously reported that MOF-545 acts as a heterogeneous catalyst for the reduction of CO₂ to formic acid and proposed a mechanism.² We now show that the presence of electron-rich POMs in the MOF's cavities close to the Zr catalytic centers can enhance the catalytic performance of the composite. The influence of the impregnation conditions on the composition, the crystallinity and the photocatalytic properties was investigated and the stability of the composites was evaluated using recyclability tests.

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Multiple charges photoaccumulation on a hybrid polyoxometalate and catalytic application

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Polyoxometalates (POMs) are oxocluster of early transition metals in their highest oxidation state (Mo^{VI} , W^{VI} , V^{V} ,...). They display a wide diversity of structures, and some of them present quite interesting photophysical properties.^[1] In our team, we have specialized in the functionalization of POMs surfaces with organic function, generating hybrid organic-inorganic molecules.^[2]

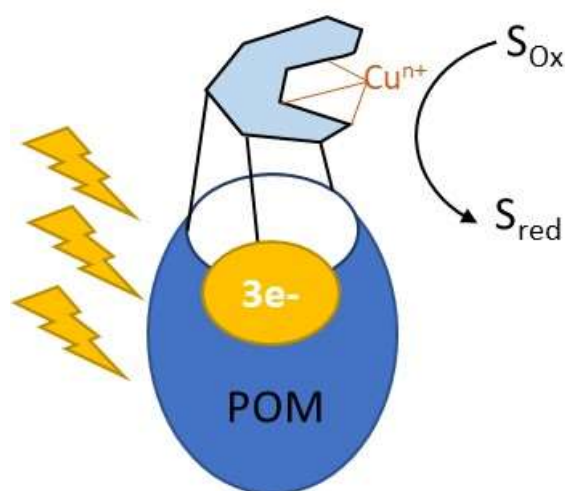


Figure 1: Schematic representation of the hybrid POM and its photoactivity

In this presentation, I will describe the synthesis of a new hybrid bearing a copper complex and its photophysical properties. This system is able to store, under visible light irradiation, up to three electrons. Moreover, its ability to release these electrons has been studied: photocatalytic generation of CF_3 radicals has been established, and the importance of a covalent link between the POM and the copper complex for efficient electron transfer was demonstrated.^[3]

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Mimicking Functional Features of CO dehydrogenase Toward Improved Catalyst Design for CO₂ Reduction

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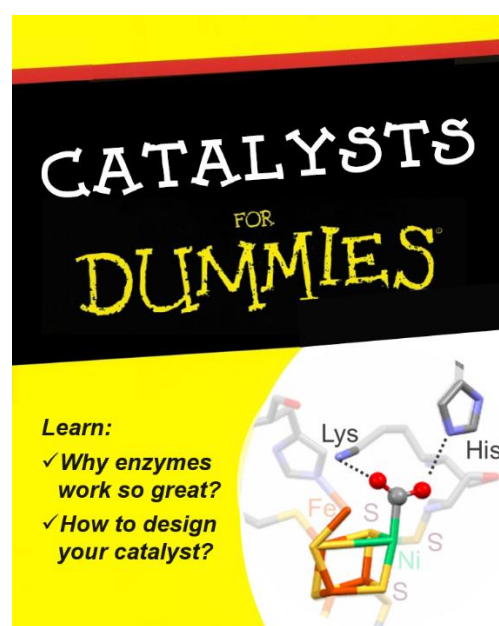
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Catalyst design primarily hinges on the elaboration of ligand scaffolds manipulating the electronic and structural properties to fine tune reactivity patterns.^[1,2] Nature has perfected this in the active sites of enzymes, providing design inspirations for chemists to control the challenging reactivity of carbon dioxide (CO₂) conversion. Herein, we present our efforts in the systematic advancement of the catalytic performance of the iron porphyrin molecular platform by mimicking functional features of the CO dehydrogenase (CODH) enzyme. This enzyme is known to reversibly reduce CO₂ to CO with high efficiencies at minimum overpotential. Taking into account lessons from the structure of the active state of the enzyme, we set forth methodical mimicry by playing on electronic effects, proton delivery, hydrogen bonding and electrostatic interactions.^[3-7] This provides incremental understanding as to which aspects of the enzyme are worthy to follow.



Learn:

- ✓ Why enzymes work so great?
- ✓ How to design your catalyst?

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Luminous textiles for carbohydrate photo-reforming

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Photo-reforming of glycerol to H₂ and CO₂ with irradiated Pt/TiO₂ suspension [1] is well known for decades. This reaction is classically study in quartz reactor with an external UV light source [2]. Our study is based on a new media with textile and microstructure optic fibres to support Pt/TiO₂ (by coating). With this technology, the UV light from the LED is brought directly inside the reactor by the optic fibres, so in one point we can regrouped the catalyst, the light and the reagents (Figure 1). This new media can be coupling by photovoltaic panels to convert solar energy into UV light by LEDs and at the end convert into hydrogen.

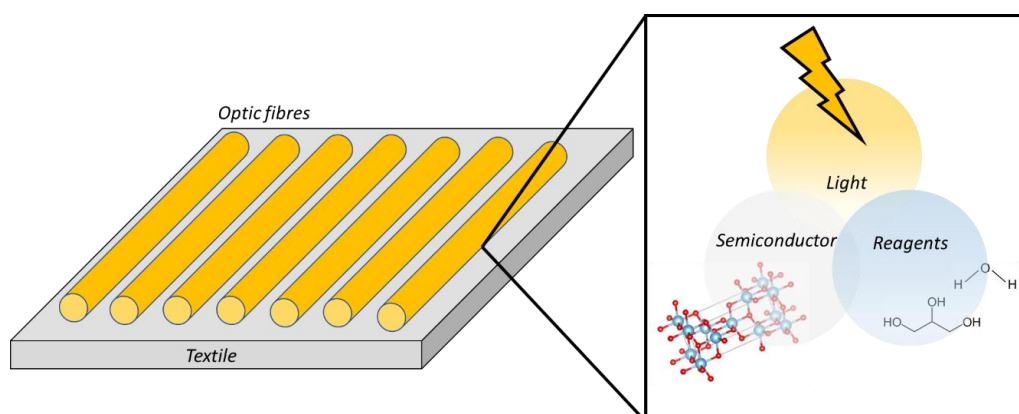


Figure 1: Principe of photo-reforming textiles.

This project is developed in the collaboration of IRCELYON and Brochier Technologies. We elaborated a photoreactor for carbohydrate photo-reforming with the luminous textile. We study the production of hydrogen through different reactors, to develop in the end a stainless-steel reactor to work under 10 bars of autogenous pressure.

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Photonic metasurfaces for the control of photocatalysis, some results of the IPPON project

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Photocatalysis is a key approach to achieve depollution, and energy conversion and storage. In order to use sunlight or inexpensive artificial light sources, the efficiency of the photochemical processes involved should be increased. Such an efficiency is expected to substantially benefit from the unprecedented potential of nanophotonics to trap and confine light. In the frame of the IPPON project¹, a key objective has been to develop novel concepts based on advanced micro- and nanostructured media enabling incoherent light confinement [1]. To achieve this, we have developed a complete methodology based on theoretical predictions, multi-domain and multi-scale modelling, chemical synthesis and micro-nanopatterning of functional materials, advanced characterization in optics and photochemistry. We will introduce dielectric metasurfaces based on 20nm thick TiO₂ layers conformally deposited onto a transparent wavelength-scale two-dimensional periodic photonic lattices (Figure 1), [2]. Such a metasurface has been designed to promote UV incident light trapping and absorption through slow light resonances. As a first illustration of the interest of this approach, we have demonstrated that these modes lead to a substantial increase of the NO pollutants degradation, compared to flat references. Similar metasurfaces are also developed to promote water splitting and artificial photosynthesis.

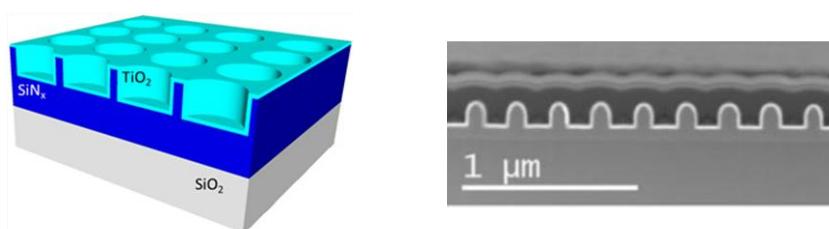


Figure 1: Schematic view and SEM cross-section view of the metasurface.

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One-step synthesis of Cu_xO_y/TiO_2 photocatalysts by laser pyrolysis for selective ethylene production from propionic acid

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Ethylene C_2H_4 is a major molecule for chemical industry and is needed in ton quantities. However, its synthesis pathways require high temperatures and/or pressures, leading significant energy consumption. In this context, we aim to use photocatalysis as an alternative method to produce ethylene at ambient temperature and pressure. Photo-decarboxylation of propionic acid (PA) mainly produces CO_2 , H_2 and ethane¹⁻⁴. In addition, ethylene traces were also detected with Pt/ TiO_2 or TiO_2 P25 catalysts^{3,4}. In this work, we show how the use of copper-modified TiO_2 nanoparticles (NP) applied for the first time to PA degradation allows promoting high selectivity towards ethylene photo-production without noble metals.

TiO_2 and Cu_xO_y/TiO_2 photocatalysts were synthesized by laser pyrolysis technique. This one-step method consists on an interaction between a CO_2 laser beam with a flow of precursors. Pure TiO_2 were synthesized from TTIP (Titanium Tetra Isopropoxide) precursor. Addition of $Cu(acac)_2$ in TTIP allowed obtaining copper-modified TiO_2 powders (Cu = 2 wt%). Besides the addition of Cu, only the effect of the atmosphere (He or Ar) during the synthesis was investigated. Samples were labelled TiO_2-X and Cu/TiO_2-X (X = He, Ar) depending on the atmosphere of synthesis.

The samples consist of a mix of anatase and rutile phases, with a higher rutile proportion in powders elaborated under Ar. STEM-HAADF coupled to EDX chemical analysis revealed rather homogeneous dispersion of copper species in Cu/TiO_2-He sample (~10 nm diameter) whereas Cu/TiO_2-Ar sample presented distinct copper species NP of 1-3 nm on larger TiO_2 support (~30 nm diameter). Such marked differentiation in terms of morphology is attributed to significantly different temperature in the reaction zone in presence of He or Ar..

Photocatalytic degradation of PA was explored under anaerobic conditions. Using pure TiO_2 , the main products were CO_2 and C_2H_6 . C_2H_4 ($C_2H_4/CO_2 = 1\%$) and H_2 were found in trace amounts. Modification of TiO_2 photocatalysts with copper/copper oxides lead to drastic changes in terms of levels of photo-generated products. Apart from CO_2 , Cu/TiO_2-He mostly produced C_2H_6 , but significantly enhanced C_2H_4 formation ($C_2H_4/CO_2 = 11\%$) up to 200 minutes. From this time, C_2H_4 production slows down, when on the contrary H_2 production considerably increases. With Cu/TiO_2-Ar , C_2H_4 was the major hydrocarbon product ($C_2H_4/CO_2 = 85\%$), Production of ethylene at 260 ppmv/h exceeded 130 times the production rate obtained from of pure titania.

This study shows both the laser pyrolysis flexibility for the synthesis of Cu/TiO_2 NPs with various morphologies, and the efficiency of these materials to achieve C_2H_4 selective production.

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Photocatalytic Hydrogen Evolution with Integrated Benzyl Alcohol Oxidation Working without Sacrificial Electron Donor

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The great promise of dihydrogen as a clean energy carrier in the future has stimulated scientists toward the development of cheap, eco-compatible and sustainable processes for H₂ production from sunlight. There are three main approaches to make solar fuels, namely : i) the combination of photovoltaic cells (PVs) with electrolyzers, which are mature technologies and currently give the highest performances; ii) the development of photoelectrochemical cells (PECs), requiring semiconductor combined with electrocatalysts grafted on their surfaces and lastly; iii) photocatalytic systems operating in solution, either in the form of a homogenous system made of molecules solubilized in a solution, or with colloidal semiconductor nanoparticles (SC NPs) dispersed in solution. A specific case of the latter approach, is dye-sensitized photocatalysis (DSP),¹ which is particularly attractive because it is less expensive, much simpler to prepare than a PV+electrolyzer and PEC. A typical dye-sensitized photocatalytic system (DSP) is composed of a dye and a hydrogen evolution catalyst (HEC) co-grafted onto n-type semiconductor (n-SC) nanoparticles (NPs), such as titanium dioxide (TiO₂).¹ However, all DSPs require an external sacrificial electron donor (SED) to operate,¹ representing a serious obstacle for the application, because they are expensive and polluting. Thus, no possible industrialization is expected following this approach. A real breakthrough would be achieved through the elimination of the SED by coupling the hydrogen evolution reaction with an oxidation reaction to upgrade abundant substrates into an added value products. Recently, we² and others³ have demonstrated that a dye chemisorbed on TiO₂ and associated with a TEMPO (2,2,6,6-tetramethyl-1-piperidine N-oxyl) catalyst can selectively oxidize alcohol into aldehyde in dye-sensitized photoelectrocatalytic cells (DSPECs). Inspired by these prior successes, we have successfully developed dual-functional hybrid photocatalytic systems that execute both a reduction and an oxidation reaction at the same time upon employing the photogenerated e⁻ and h⁺ pair to produce two valuable chemicals such as H₂ and aldehyde without SED (Figure 1). Scope and limitations of such systems will be discussed in the light of other approaches.

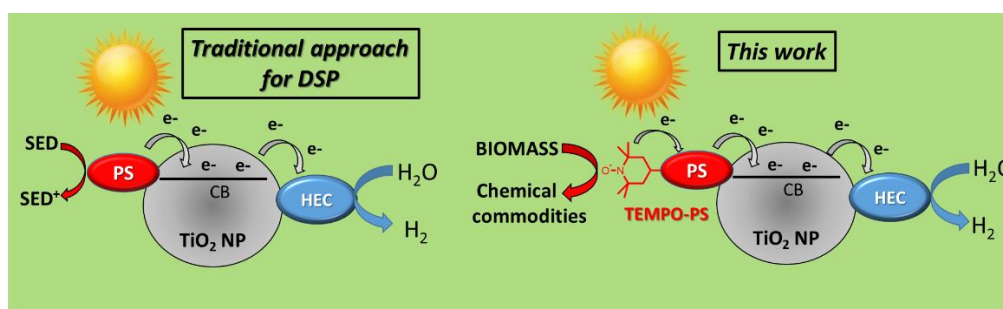


Figure 1. Schematic illustration of DSP studied in this presentation.

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Impact of the chemical composition and nanostructure of Mo oxysulfides based semiconductors on gas-phase photocatalytic reduction of CO₂

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The photocatalytic conversion of CO₂ is a complex process which still suffers from very low energy efficiency yield. To address some of the process limitations, we developed Mo oxysulfide based materials and explored the effects of the chemical composition (sulfur/oxygen ratio) and nanostructures (clusters, finite size 2 dimensional monolayers, stacked multilayers), that should impact the bandgap and band positions of the materials [1]. Moreover, we investigated two supports: Al₂O₃, optically inert, and TiO₂, a classical semiconductor to analyze if efficient heterojunctions could be built [2]. All materials were tested in CO₂ photocatalytic reduction in gas phase conditions, representative of the operating conditions of a plugged factory chimneys process.

A wide range of Mo oxysulfides based semiconductors were synthesized by a surface organometallic chemistry approach [3], followed by a temperature-controlled gaseous sulfo-reduction treatment. Characterizations show that the materials (1.3 Mo/nm²) exhibit S/Mo atomic ratio ranging from 0.2 to 2.2, with the presence of nanoclusters (~1 nm), and slabs (~4 nm) at high S/Mo. These variations lead to significantly different absorption properties and bandgaps ranging from 2.0 eV to 1.2 eV.

On Al₂O₃, the Mo oxysulfides materials exhibit activity and products selectivity (CO, CH₄, C₂H₆ and H₂) depending on the chemical composition of the oxysulfide. However, because of the competing HER which generates H₂, the carbonated products yield ((CH₄+CO+C₂H₆)/(CH₄+CO+C₂H₆+H₂)) is never higher than 65%, while the CH₄ selectivity (CH₄/converted CO₂) changes with the oxysulfide composition from 37% to 100%. On TiO₂, a heterojunction scheme is formed with the Mo oxysulfides. Figure 1 shows that the photocatalytic activity is modulated by the temperature of the sulfo-reduction treatment, which impacts the chemical composition and structure of the materials. The carbonated products yield is higher than 90%, which means that these materials are highly discriminatory toward CO₂ photoconversion. Additionally, at least 93% selectivity toward CH₄ formation is observed.

The results of the photocatalytic tests will be discussed in relation to the opto-electronic, chemical and morphological properties of the synthesized materials.

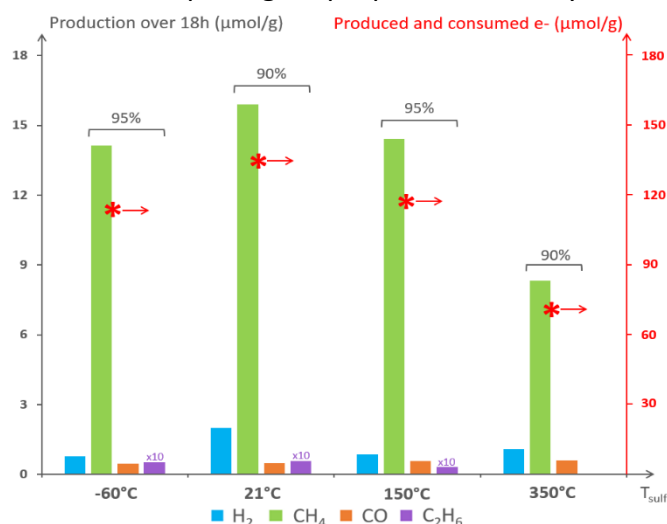


Figure 1: CO₂ photocatalytic activity of Mo oxysulfides supported on TiO₂ synthesized at various sulfo-reduction temperature (T_{sulf}). The left axis is for products production in μmol/g over 18h. The right axis is for the produced and consumed electrons in μmol/g over 18h (red stars). The percentages indicate the carbonated products yield (selectivity toward CO₂ photoreduction).

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Novel Bi-Based heterojunctions for the CO₂ photoreduction into CO

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Among the photocatalysts investigated to photoreduce CO₂, Bi-based materials have demonstrated their interest to selectively form CO, a molecular building block which can further be used to obtain methanol, acetic acid, aldehyde and even e-fuels... More recently, Bismuth oxyhalides BiOX (X= Cl, Br, I, F) show an interesting capacity to separate photogenerated charge, thanks to an internal electric field induced by their layered structure (comprised of [Bi₂O₂] and anion slabs)^[1]. They present then promising photocatalytic properties; even if, very few studies have been accomplished on Bi_xO_yF_z materials.

In this study, we succeeded to deposit heterojunctions of Bi and Bi-based compounds in thin films by a one-pot, eco-efficient, and industrial technique: the Reactive Magnetron Sputtering. With this unconventional technique, it is possible to tune the composition of the thin films by controlling the O₂ and CF₄ gas reactants flow rates injected during the sputtering of a pure bismuth target. We can then obtain various compounds (Bi₂O₃, BiO_{0.5}F₂, BiF₃...) alone or in mixture with a controlled content of metallic Bismuth. The composition and the structure of these materials were studied by XRD, Raman spectroscopy and XPS. Their optical properties, especially their band gap, were determined from UV-visible spectroscopy and ellipsometry. Experiments of photodegradation of pollutants into water shows that an optimum of metallic content has to be found to enhance the photocatalytic properties of the Bi-based materials^[2]. The CO₂ photoconversion measurements, performed at IFPEN, on these materials demonstrate a photon conversion efficiency close to the TiO₂ one, but with a high selectivity to form CO (= 90% and 10% of H₂). To go further, we now working on nanostructuring of these materials in order to increase the contact surface with CO₂ gas.

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Au-Pt plasmonic catalysts for methane artificial photosynthesis

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The use of most major fuels emits one of the main greenhouse gases, carbon dioxide (CO₂). Its overproduction is a key element causing global warming. One of the considered solutions is to recycle CO₂ into a useful chemical, methane, which can subsequently be used as a fuel. To reuse CO₂, we use the photoreduction with water in the gas phase, also known as artificial photosynthesis. These reactions are described in Figure 1. The reagent is at his highest oxidation state and has a particularly strong bond (the dissociation energy is around 750 kJ.mol⁻¹)^[1]. Furthermore, the reduction of CO₂ is in competition with the Hydrogen Evolution Reaction (HER). For these reasons in particular, a well-suited catalyst is required.

Metallic nanoparticles are great photocatalysts due to their peculiar interaction with light known as Localised Surface Plasmon Resonance (LSPR)^[2]. We have recently shown that alloy nanoparticles of gold (Au) and platinum (Pt) dispersed over titania (TiO₂) were active and selective for the photoreduction of CO₂ with water^[3]. We here show that the methane production rate can be optimized by designing smaller Au-Pt nanoparticles. By studying the effect of the composition of the nanoalloy on the photocatalytic performances, we also show that a synergy between gold and platinum can be found in Pt-rich compositions, which yield higher activity and selectivity than monometallic nanoparticles.

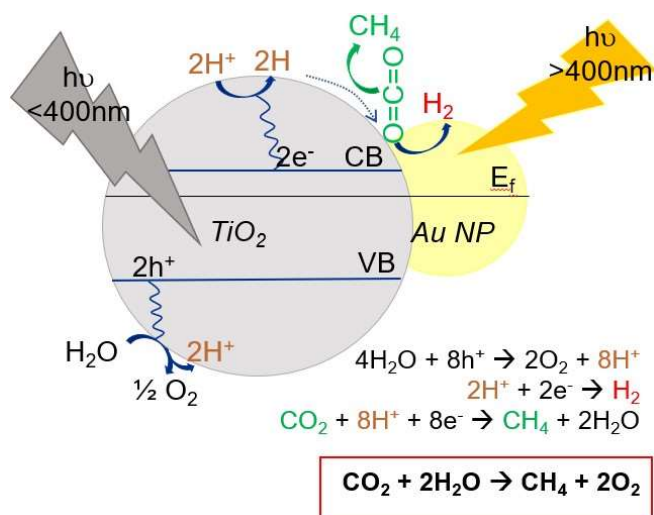


Figure 1: Scheme of the CO₂ photo-reduction process

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Présentations par poster

Combining CO₂ Reduction and H₂O Oxidation using P₂W₁₈Co₄@MOF-545(TM) Materials

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Developing photocatalytic methods to transform CO₂ into added-value carbon-based compounds (CO, formic acid, CH₄, etc.) is one of many strategies for valorizing CO₂ in the atmosphere. In this context, our group has focused on the development of Zr-based porphyrinic metal organic frameworks (MOFs) that have applications as fully noble-metal free, heterogeneous photocatalysts for the CO₂ reduction and H₂O oxidation half reactions.^[1,2] We have previously shown that MOF-545 can be impregnated with the polyoxometalate (POM) P₂W₁₈Co₄ to form a P₂W₁₈Co₄@MOF-545 composite material that can photocatalytically generate O₂ using sodium persulfate as a sacrificial electron acceptor.^[1] Moreover, we showed that metallated MOF-545(TM) (TM = transition metal, including Mn^{III}, Fe^{III}, Co^{II}, Cu^{II}, and Zn^{II}) materials are able to photocatalytically reduce CO₂ to formate in acetonitrile/triethanolamine (TEOA) solutions, wherein TEOA[•] radicals that are formed by the system are crucial for the hydride transfer that transforms CO₂ to HCO₂⁻.^[2]

As CO₂ reduction often requires proton-coupled electron transfers (e.g., CO₂ + 2 H⁺ + 2 e⁻ ⇒ HCO₂H), this reaction can be practically combined with H₂O oxidation (2 H₂O ⇒ O₂ + 4 H⁺ + 4 e⁻) to obtain a balanced, overall CO₂ reduction reaction (e.g., 2 H₂O + 2 CO₂ ⇒ 2 HCO₂H + O₂). In this poster, we present our work toward achieving concomitant H₂O oxidation and CO₂ reduction using P₂W₁₈Co₄@MOF-545(TM) composite materials, wherein light can be harvested by the MOF's porphyrin linkers, thereby permitting P₂W₁₈Co₄ to perform H₂O oxidation and MOF-545(TM) to perform CO₂ reduction (Figure 1). Notably, these reactions occur in pure water without the need for external sacrificial electron acceptors or donors.

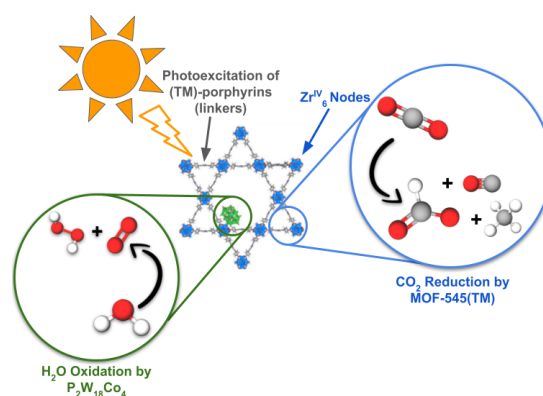


Figure 1: Schematic representation of the proposed reactions facilitated by the P₂W₁₈Co₄@MOF-545(TM) materials.

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Notes

Bimetallic catalysts for electrochemical CO₂ valorisation

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The electrochemical reduction reaction of CO₂ (eCO₂RR) has great potential to provide sustainable chemical feedstocks that do not rely on oil. However, significant selectivity challenges remain; from suppression of the competing H₂ evolution reaction, to controlling the distribution of products eg. CO, CHOO⁻, CH₄. There has been a recent interest in cooperative effects in many areas of catalysis and small molecule activation, where it is becoming clear that two metals can act synergistically to achieve different reaction pathways to metals in isolation.^[2] Applying this idea to electrocatalysis, a bio-inspired heterobimetallic Ni-Fe hydrogenase mimic was found to produce CH₄ as the sole carbon containing product of eCO₂RR, with the selectivity likely arising from the presence of the second metal.^[3] This work expands this concept to a new library of bimetallic complexes comprised of abundant, first row transition metals (Cu, Fe, Ni, Co). Both homo- and hetero- bimetallic complexes are presented. The electrocatalytic behaviour of these complexes towards CO₂ is described and the effect of metal-metal cooperativity on the product selectivity and reaction mechanism is explored.

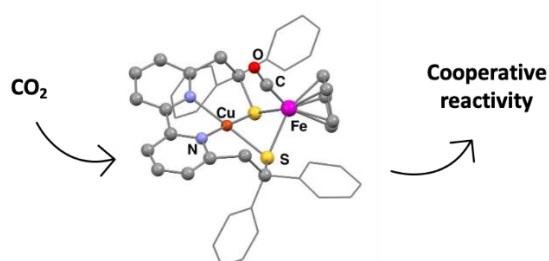


Figure 1: A heterobimetallic Cu-Fe complex for electrochemical CO₂ reduction

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Novel Bi-Based heterojunctions for the CO₂ photoreduction into CO

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Among the photocatalysts investigated to photoreduce CO₂, Bi-based materials have demonstrated their interest to selectively form CO, a molecular building block which can further be used to obtain methanol, acetic acid, aldehyde and even e-fuels... More recently, Bismuth oxyhalides BiOX (X= Cl, Br, I, F) show an interesting capacity to separate photogenerated charge, thanks to an internal electric field induced by their layered structure (comprised of [Bi₂O₂] and anion slabs)^[1]. They present then promising photocatalytic properties; even if, very few studies have been accomplished on Bi_xO_yF_z materials.

In this study, we succeeded to deposit heterojunctions of Bi and Bi-based compounds in thin films by a one-pot, eco-efficient, and industrial technique: the Reactive Magnetron Sputtering. With this unconventional technique, it is possible to tune the composition of the thin films by controlling the O₂ and CF₄ gas reactants flow rates injected during the sputtering of a pure bismuth target. We can then obtain various compounds (Bi₂O₃, BiO_{0.5}F₂, BiF₃...) alone or in mixture with a controlled content of metallic Bismuth. The composition and the structure of these materials were studied by XRD, Raman spectroscopy and XPS. Their optical properties, especially their band gap, were determined from UV-visible spectroscopy and ellipsometry. Experiments of photodegradation of pollutants into water shows that an optimum of metallic content has to be found to enhance the photocatalytic properties of the Bi-based materials^[2]. The CO₂ photoconversion measurements, performed at IFPEN, on these materials demonstrate a photon conversion efficiency close to the TiO₂ one, but with a high selectivity to form CO (= 90% and 10% of H₂). To go further, we now working on nanostructuration of these materials in order to increase the contact surface with CO₂ gas.

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Cerium titanates: An unexplored class of visible light active photoanodes for water splitting

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Photoelectrochemical water splitting is hoped to become a competitive source of green hydrogen, but there is still a need to discover novel photoelectrode materials [1]. Cerium titanates have been known for more than 50 years but only a handful of studies have investigated their potential applications [2]. Recent reports have shown that the CeTi_2O_6 brannerite phase was a promising photocatalyst under UV-visible light illumination [3]. To date, no study has used cerium titanates for photoelectrochemical water splitting and described their photo-electronic properties.

In this study, cerium titanates thin films were prepared by spin-coating on fluorine-doped tin oxide (FTO). The as-prepared photo-electrodes were characterized by SEM, XRD, and Raman spectroscopy. Photovoltammetry, DRS-UV-Vis, XPS, and UPS were combined to describe the band structure of this new material.

Raman spectroscopy and XRD showcased the successful formation of cerium titanate films on FTO at an annealing temperature of 700°C. The band gap of powdered CeTi_2O_6 was found to depend on the annealing temperature with values ranging from 2.4 and 2.6 eV. The presence of both Ce^{4+} and Ce^{3+} was observed by early XPS and UPS experiments. By optimizing the film thickness, a photoelectrochemical-response to UV-visible light was observed with a photo-current of $0.3 \text{ mA}\cdot\text{cm}^{-2}$ at a potential of 1.23 V vs. NHE.

A rational approach will be developed upon these results to develop a sound and rational optimization of the charge carriers' generation and transfer at the interface.

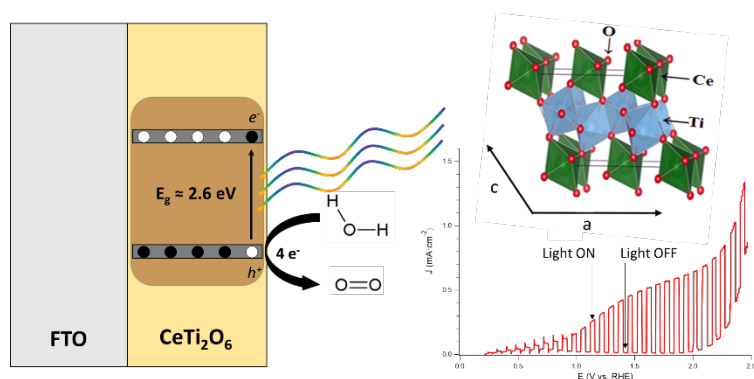


Figure 1: Photoelectrochemical activity of a CeTi_2O_6 brannerite thin film under UV-Vis light exposure

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Hybrid Semiconductor-Catalyst Devices for the Photoelectrochemical Conversion of CO₂

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In recent years, the use of hybrid photocathodes composed of a semiconductor and a molecular catalyst has emerged as a promising strategy for solar-driven fuels production from CO₂ and water.^[1] This approach combines the unique properties of semiconductors, such as their light-absorbing ability and charge separation, with the catalytic activity of molecular catalysts, allowing for great performance and selectivity. In this work, we explored the fabrication of hybrid photocathodes utilizing electrodeposited planar p-type cuprous oxide (Cu₂O) semiconductor and attaching iron porphyrins catalysts modified with urea functional groups as CO₂ substrate activators.^{[1] [2]} This provides a noble metal free hybrid system for CO₂ conversion.

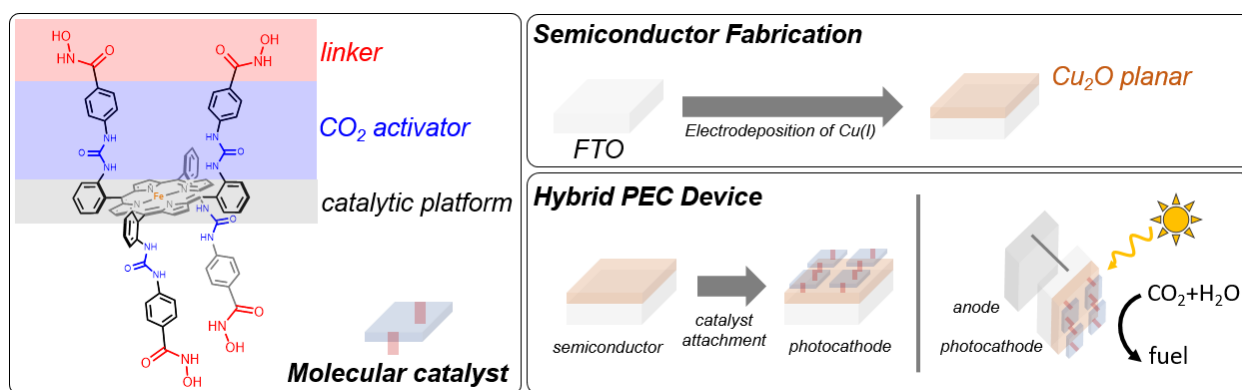


Figure 1: Hybrid PEC device incorporating tailored molecular catalysts on Cu₂O photocathodes.

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Investigation on Electron Transfer from Semiconductor to Metal in Photocatalytic H₂ Production

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Metal cocatalyst nanoparticles deposited on TiO₂ are known to improve photocatalytic activity of photocatalysts in alcohol dehydrogenation. What make metal cocatalysts useful in the photocatalytic mechanism are their chemical and electronic properties. Here we conclusively demonstrate that the photocatalytic activity is directly related to the probability of photogenerated electron transfer from semiconductor to metal. By studying a set of metal/TiO₂ samples it was possible to establish that the relative position of semiconductor Fermi level against metal workfunction governs the electron transfer. Experimentally, combinations of several photocatalysts (TiO₂ anatase, TiO₂ rutile, ZnO, WO₃) with several photodeposited metals (Pt, Os, Ir, Rh, Au, Cu, Ni, Ag) have been evaluated for the reaction $\text{CH}_3\text{CHOHCH}_3 \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}_2$ and more particularly the activation energy was systematically determined as the method described by Maheu *et al.* [1].

As Norskov's principal (volcano curve) [2], translation of Sabatier's principle [3], metal cocatalysts

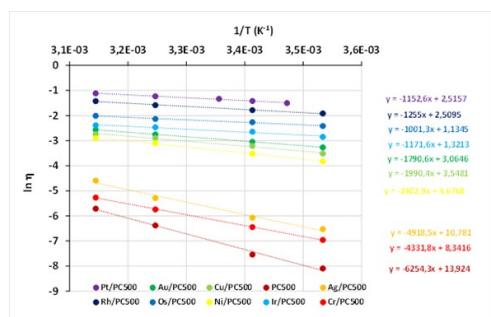


Figure 1 : Arrhenius plot of photonic yields for M/TiO₂ (M=Pt, Au, Cu, Ag, Rh, Os, Ni, Ir, Cr)

having a thermal-neutral of H₂ chemisorption energy (ΔE_H), should lead in produce high amount of H₂ [4]. However, Rh and Au do not follow this principle. On the other hand, considering minimum and maximum workfunction of the different metals, the trend seems to obey to a threshold function *ie* below a value, the metals have a low activity and above this value the activity increases rapidly with the increase of the work function.

By using Fermi-Dirac statistics, it was possible to predict that the apparent activation energy of the reaction is governed by the difference between the Fermi level of the semiconductor photocatalysts and the workfunction of the metal (Figure 1).

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Insights into Photocatalytic Hydrogen Peroxide Generation by Metal-Free Nanopolypyrrole under Visible Light

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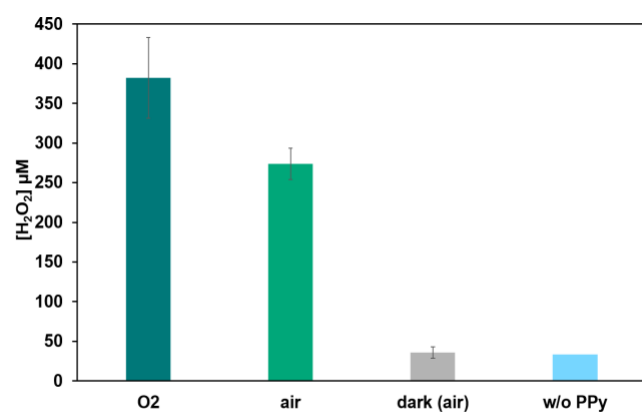


Figure 1. H₂O₂ production by nano-PPy at different conditions including PDPB nanowires and PPy, as active visible-light photocatalysts for water treatment and splitting^{3a,b,c}. This study investigates the in situ H₂O₂ generation of PPy during the photocatalytic process. Experiments were conducted using an Oriel 300 W Xenon lamp, and H₂O₂ was quantified with the KI method on an HP 8543 UV-Visible Spectrophotometer. Nano-PPy (1 mg/mL) produced approximately 2.18 µM H₂O₂/min under visible light irradiation ($\lambda \geq 420$ nm) and O₂ atmosphere without sacrificial agents. The process was tested across pH 2-7, varying light intensities and PPy concentrations. These findings could open opportunities for additional catalytic applications, such as Photo-Fenton reactions or oxidation of crucial organic compounds.

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Ligand Redox Non-Innocence in Low-Valent Octahedral Molybdenum Complexes: A DFT Study

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Two octahedral molybdenum complexes containing a bidentate ligand, a β -Diketonate substituted with dipivaloylmethanate (dpm) or dibenzoylmethanate (dbm), have been synthesized to catalyze the CO₂ carboxylation reaction. Our work aims at characterizing the electronic structure of the complexes after successive reductions and oxidations to evaluate the possible role of the ligand during the electrochemical processes. DFT calculations were employed making use of the crystallographic structures of the series of complexes to determine the molecular orbital diagrams and the spin states of the species. Our results suggest that the dbm ligand is involved during the second and third reductions that are best described as ligand-based processes. Thus, we can support that the dbm-substituted β -Diketonate ligand is non-innocent which will have direct implications for catalysis especially regarding the decarboxilation reactions.

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PAVIN Solaire: a collaborative research platform for the production of solar fuels

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The **PAVIN platform** is a 400 m² solar platform for indoor (technical building of 50 m²) and outdoor experimentations regarding engineering of photo-reactive processes (natural and artificial photosynthesis). It is equipped with heliostats and sun tracker systems (3.5 m² for TRL5 operations and 0.3 m² for TRL3 operations), different solar concentrator devices (Fresnel lenses, Schmidt-Cassegrain), main solar flux sensors (DNI, DHI, GHI), utilities and systems for liquid and gas phases analyses related to online rates measurement. It enables to work with **photoreactors, photobioreactors or photo-electrochemical cells** at different TRL using artificial or solar light from lab-scale to pilot-scale (Figure 1). It is then possible to design and test solar technologies at TRL 3-5 with different objectives like high volumetric biomass or fuel productivities or high surface productivities, synonym of high thermodynamic efficiency. This last objective assumes to develop dilution (until 50-100 m² for light distribution area) and hybridization systems for solar light collected [1, 2]. The solar PAVIN platform is the only one in Europe where this kind of technologies are developed, thanks to the establishment of solar photo-reactive processes knowledge models [3] used with optimization techniques (constructal theory, entropy generation minimization, evolutionary algorithms,...) for inverse design.



Figure 1: Some examples of the Solar PAVIN platform facilities at TRL 3-5.

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Deep Eutectic solvents for electroenzymatic CO₂-to-CO conversion by carbon-nanotube-supported CODHs

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A major challenge for our society is to tackle global warming by minimizing the concentration of greenhouse gases in the atmosphere. While the first solution seems to be to reduce their emission, a complementary solution is to recycle CO₂ (the most abundant greenhouse gas) by converting it into building blocks such as CO.

A promising approach is to take advantage of highly efficient and specific natural catalysts such as CO Dehydrogenase (CODH)^[1] enzymes, able to reduce CO₂ to CO by lowering the activation energy of the reaction. They rely on active sites comprised of abundant metals, iron and nickel, buried inside a protein scaffold. This structure is responsible for their high reversible catalytic activity with minimal overpotential. However, CODH is highly-oxygen sensitive and must be handled under strictly anaerobic conditions.

Key to achieving efficient bio-electrocatalysis is the design of tailored electrodes with a minimized enzyme-electrode distance in order to avoid electron transfer rate limitations and to design innovative and sustainable enzymatic devices. For this purpose, carbon nanotube (CNT)-based electrodes have proven ideally suited. Once modified with adapted anchoring groups^[2], they can accommodate a high enzyme loading on their surface and provide high film conductivity.

This study shows a new method for enhancing the catalytic activity under aerobic conditions through the development of CODH-modified electrodes in particular organic media. Deep Eutectic Solvents (DESs)^[3], a subclass of ionic liquids with low toxicity and low manufacturing cost, have diffusion and oxygen solubility limiting properties^{[4],[5]}. We have studied the electrocatalytic CO₂ reduction at CNT-supported CODH in DES with the aim of enabling an efficient CO₂-to-CO conversion in a non-natural environment as a means of increasing their oxygen tolerance.

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H₂ production by photocatalysis under solar light: development of nanocomposites based on Metal Organics Frameworks (MOFs)

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Sustainable society development is facing many challenges such as the transition from fossil to renewable fuels. To achieve this transition, solar fuels based directly on the conversion of sunlight into chemicals are among the most promising renewable fuels to supply and store energy due to the inexhaustible, cheap, and powerful character of the sun. Therefore, hydrogen (H₂) production by water splitting thanks to photocatalysis under solar light appeared rapidly as a relevant vector to produce green fuels. Indeed, H₂ generation by photocatalysis is only based on light activation of a photocatalyst, leading to the formation of an electron/hole (e⁻/h⁺) pair in the conduction and valence, respectively. Then, photo-induced e⁻ will react with H⁺ from water to produce H₂ and photo-induced h⁺ will react with a scavenger, which is most of the time an alcohol such as methanol, added in water to avoid water oxidation. Nevertheless, most of the time, the H₂ generation yield by photocatalysis is not good. To improve this yield, efforts are made to develop hybrid nano-heterostructured multi-phase materials as efficient new photocatalysts [1]. Metal organic frameworks (MOFs) are very promising candidates for developing these nanocomposites with traditional well-known photocatalyst as TiO₂ or ZnO [2,3]. MOFs are hybrid (organic/inorganic) porous ordered solids with high porosity and active surface. Besides, they can have photocatalytic activity and participate to ions and charge exchange. Finally, they are also relatively easy and cheap to synthesize in view of development at large scale. In this work, the aim is to develop and compare nanocomposites based on MOFs with TiO₂ or ZnO for efficient H₂ production by photocatalysis under UV-Visible light. In this study, binary and ternary nanocomposites with MOFs, TiO₂ and g-C₃N₄ were developed and studied. Preliminary results demonstrated that TiO₂ is more efficient and relevant than ZnO for H₂ production and for being coupled with MOFs. HKUST-1/TiO₂ (1:20 in mass) nanocomposite after 5h under Xenon lamp in water/methanol (3:1 in volume) leads to ~13 mmol/g of H₂ against only 0.015 mmol/g with HKUST-1/ZnO (1:20). Our results show that copper-based MOFs coupled with TiO₂ or TiO₂/g-C₃N₄ are promising for H₂ generation under UV-Visible light.

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Nuclearity influence on hydrogen evolution reaction with thiocarbohydrazone nickel complexes

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Facing the 21st century energy challenge, hydrogen production is a central theme in the field of renewable energy storage. Platinum possesses the best performances among catalysts able to reduce protons to hydrogen. Due to its scarcity and its cost, efforts to find alternative non-noble transition metal catalysts is the subject of intense research. A large number of molecular catalysts based on Earth-abundant metals have been developed in the recent years. Together with the introduction of proton relays in the second coordination sphere, redox-active ligands can be exploited to enhance catalytic activity. Transition metal complexes with thiosemicarbazone ligands have been studied for many years as these complexes present some interesting features for hydrogen evolution reaction. In that perspective, we have associated the electroactive thiosemicarbazone ligand with redox-active transition metals like nickel and cobalt.¹⁻⁴ The complexes, characterized at the experimental and theoretical levels, were evaluated as electrocatalysts for proton reduction in an effort to rationalize the catalytic performances. More recently, we have reported the synthesis and characterization of a trinuclear nickel-thiocarbohydrazone complex, displaying an improved turnover rate compared to its mononuclear counterpart. These results support the fact that the nuclearity as well as the ligand nature and the metal center influence the electronic and redox properties of the catalysts, which affect their catalytic performances..

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Light-driven charge accumulation on ruthenium tris-diimine photosensitizers featuring flavin-inspired π -extended ligands

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Photosynthesis is a fascinating source of inspiration to design innovative molecular devices for the conversion and storage of solar energy under a chemical form such as hydrogen or carbon-based fuels. These applications however rely on multielectronic catalytic processes whereas light-driven processes are inherently single-electron events. Nature perfectly overcomes this apparent antagonism thanks to specific cofactors acting as reversible multielectron relays. Taking inspiration from these systems, an increasing number of sophisticated light-harvesting units reversibly accumulating multiple redox equivalents has been studied over the last years.^[1] We contributed to the field with the design of original ruthenium tris-diimine photosensitizers reversibly storing two electrons coupled to two protons on quinone-inspired π -extended ligands, thus reproducing the mechanism of the PSII-plastoquinone couple.^[2] Yet, storing electrons at a sufficiently reducing potential to drive the catalytic processes of interest is a major challenge. We therefore decided to prepare a new series of complexes incorporating the alloxazine subunit found in the natural flavin cofactor FAD involved in the photosynthetic production of the strong reducing agent NADPH. A spectroscopic and electrochemical investigation of their electronic properties will be presented here in the context of light-driven charge accumulation.

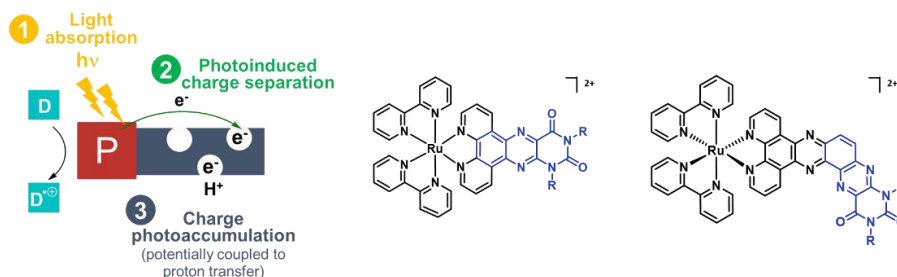


Figure 1: Representative structures of Ru photosensitizers featuring flavin-inspired π -extended ligands.

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Multi-Perylene Arrays for Photocatalytic Applications

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In the context of the current environmental crisis, the development of sustainable pathways for the production of commodity chemicals is a topic of increasing importance. Inspired from Nature, and more specifically from photosynthetic organisms, that are able to harvest solar energy to drive the primary reactions supporting their thriving, the development of molecular photocatalytic systems coupling light-harvesting systems to a desired catalyst is a great challenge. A specific point to consider is the development of efficient antennae able to activate the catalyst under low-light (solar) irradiation. To achieve this goal, the implementation of multichromophoric photosensitizers can provide an enhanced absorption capability. In this work, we will present our efforts toward designing multi-perylene arrays, based on a rigid triptycene scaffold and their coupling to well-established Ru-based catalysts able to promote 2-electron alcohols oxidation. The choice of the perylene cores was driven by their exceptional (photo)chemical stability, their good absorption properties in the visible range of the solar spectrum as well as their tuneable redox properties. The triptycene scaffold will provide a highly modular platform to specially organize 1 to 3 perylene moieties around the catalytic centers. Finally, the use of Ru-polypyridyl catalysts do provide stable systems with well-established reactivity as ideal models to investigate advanced photosensitizer designs for enhanced photocatalysis. In this poster, we will present the synthesis of various antenna architectures as well as our first attempt to graft these multi-perylene arrays onto an archetypal Ru-polypyridyl core (Figure 1). Preliminary photocatalytic tests for alcohol oxidation will be briefly discussed.

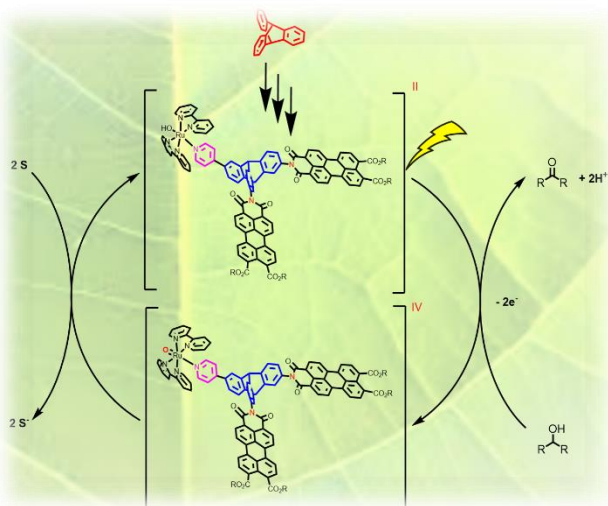


Figure 1: Ru-polypyridyl/antenna assemblies targeted in this work

SEMICONDUCTING CONJUGATED OLIGOMERS FOR PHOTO-DRIVEN WATER OXIDATION

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Conjugated polymer (CP) nanostructures appear as a new class of photocatalytic **nanomaterials** very active under visible light for water treatment and water splitting. Our group in ICP developed the synthesis of conjugated **polydiphenylbutadiyne** (PDPB) nanowires (using soft templates) ^{[1][2]} and studied their photocatalytic properties. These PDPB nanowires (synthesized by UV or γ irradiation in mesophases) are very active photocatalysts under visible light irradiation for water depollution and PSW, without the presence of any sacrificial electron donors/acceptors or any co-catalysts. Nanostructuring of CPs is a key factor for their photocatalytic activity ^{[3][4]}. In this study, a new monomer **bis(pyridyl)butadiyne** (BPB) containing pyridyl moieties, that can form hydrogen bonds with water molecules, was synthesized using Sonogashira and Glaser coupling reactions. Introduction of hydrophilic functions like pyridyl can enhance dispersity while maintaining or even improving the photocatalytic activity, compared with the previously investigated PDPB. The new monomer BPB was synthesized and characterized by UV-visible spectroscopy, nuclear magnetic resonance (NMR) and Fourier-transform infrared spectroscopy (FTIR). Using soft template method (hexagonal mesophases) and polymerization by UV or γ -irradiation, the monomer molecules were polymerized in the confined oil domain of the mesophase to give new conjugated nanostructures **poly(bis(pyridyl)butadiyne)** (PBPB). Herein, we developed different nanostructures of PBPBs that were characterized by UV-Vis spectroscopy, FTIR. The photocatalytic activity of these nanostructures under visible light was studied for H₂O₂ generation and water oxidation using Ghormley triiodide method.

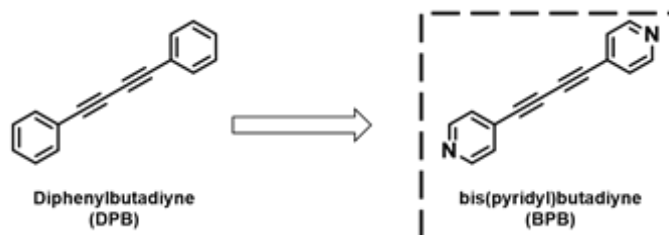


Figure 1. Structure of BPB monomer in this study.

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Proton relays in molecular electrocatalysis: how do they allow for reversible behavior?

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Catalysis in hydrogenases and other metallenzymes involved in CO₂ transformation only requires Earth-abundant metal centers, the reactivity of which is enhanced thanks to the presence of basic sites acting as proton relays [1] at their vicinity. Such active sites have been used as an inspiration to design new synthetic catalysts for H₂ evolution [2-4] and oxidation [5,6]. Specification, catalytic platforms with installed proton relays display bidirectional [7] and, in rare cases, reversible catalysis [5]. In this presentation we will show how a detailed molecular electrochemistry study can help understanding and quantifying the role of the protons relays related to these remarkable behaviors.[8]

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Graphene/TiO₂ anatase (101) interface for photovoltaic and photocatalysis applications: insights from hybrid DFT

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Due to their importance in photovoltaics and photocatalysis, the oxygen defective anatase (101) surface (A101) and graphene/anatase (101) interface (Gr/A101) were investigated using the HSE06 hybrid functional^[1,2] with both effective core pseudopotentials (ECP) and all-electron (AE) atom-centered basis sets, combined to additional empirical dispersion effects with the D2 and D3 models^[3,4]. For the defective surface, the oxygen vacancy formation energy of nine different vacancy positions at surface or subsurface were computed, considering both singlet and triplet spin states. In all cases, the surface twofold and threefold coordinated oxygen sites were found to be the most and least stable ones, respectively, with substantial relaxations of the neighbouring atoms. For the most stable vacancy sites, the computed offsets of the defect levels positions from the conduction band minimum range between 1.1 and 1.3 eV, in excellent agreement with the experimental value of 1.3 eV^[5]. The Gr/A101 interface was found to be held by weak van der Waals (vdW) forces with an adhesion energy of 1.03 eV, and to present a band gap opening of Gr with a value of 0.14 eV linked to a slight distortion of Gr. In addition, both the stoichiometric and the oxygen defective Gr/A101 interfaces were found to present very similar electronic structures, despite a weak destabilization of the later compared to the former, outlining the importance of both models for photovoltaic and photocatalysis applications.

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Mechanistic Studies of the Photodeoxygenation of N₂O with Rhenium Bipyridyl Carbonyl Complexes

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Nitrous oxide (N₂O) is a major greenhouse gas that is 300 times more powerful than CO₂ on a per molecule basis and remains the number one emission contributing to ozone depletion in the 21st century.^[1] Over the past few decades, the different reactivity modes of nitrous oxide have attracted much attention.^[2-3] Thermochemical methods usually require extreme conditions (high temperature or high pressure of H₂) and/or sacrificial oxophilic reducing agents.^[2] It is mandatory to develop selective, clean, and energy-efficient processes for N₂O reduction. Recently, transition metal complexes have been used for this purpose.^[3] However, little is known regarding the reaction mechanism.

Here, we present recent advances in our investigation of the mechanistic pathways for nitrous oxide photoreduction using rhenium bipyridyl triscarbonyl complexes [Re(bpy)(CO)₃Cl] (**Re-1**) as photocatalyst. The photocatalytic deoxygenation of N₂O efficiently generates dinitrogen and only water as a by-product (Figure 1). To get insights on the initial steps of the photocatalytic process as well as on short-lived transient species, time-resolved photochemical and photophysical studies have been performed using laser flash photolysis, UV-vis, and IR spectroscopy.

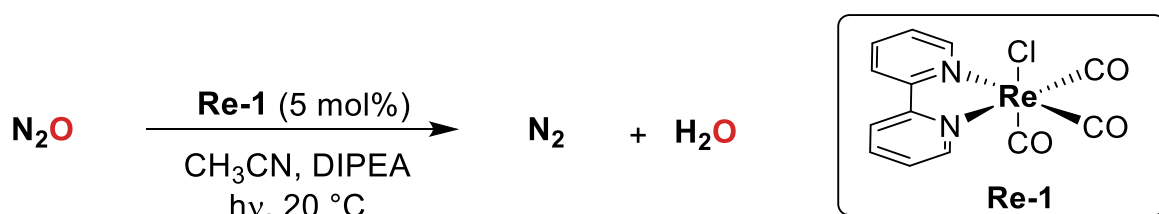


Figure 1: Photocatalytic deoxygenation of N₂O using **Re-1** complexe.

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