

Galán-Mascarós Research Group



Group Leader: José Ramón Galán Mascarós

Laboratory coordinator: Vanesa Lillo

Administrative support: Paula Segovia

Project laboratory technician: Samantha Grand (

Postdoctoral researchers: Cristina Sáenz de Pipaón / Felipe Andrés Garcés / Jesús González / Álvaro Reyes / Mabel Torréns / Irene Sánchez-Molina / Marta Blasco

PhD students: Javier Fonseca (until April) / Pilar Maldonado (until June) / Bárbara Rodríguez (until July) / Marta Blasco (until Oct.) / Franziska Hegner / Lijuan Han / Andrea Moneo / Mabel de Fez / David Nieto

Master students: Khalid Azmani

Visiting students: Bruno Morandi / Khalid Azmani

Project trainee: Sofía Shepherd (July-Sept.)

Abstract

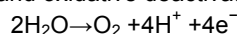
Our research team is devoted to the development of new molecule-based materials for applications in the fields of Renewable Energies and Materials Science. On the former, we are developing efficient and stable redox catalysts from Earth abundant metals, with

special interest in water splitting catalysts for the production of solar fuels. On the later, we target the design of novel multifunctional hybrid materials with co-existence of properties of interest (chemical, structural, magnetic, electrical, optical...) with control of the synergy between physical properties in the search for new phenomena.

Photocatalytic water oxidation with Prussian blue derivatives

Water oxidation catalysis is one of the biggest challenges that inorganic chemistry is facing nowadays. The discovery of a fast, robust, and cost-effective catalyst would be key for the realization of artificial photosynthesis, an achievement that could probably solve the energy problem worldwide in the near future.

Oxygen evolution from water is a complex redox process. It occurs at high oxidation potentials, and it involves four electrons. An active water oxidation catalyst (WOC) for such a high-energy, multielectron process will probably need the participation of metal ions, as occurs in natural photosynthesis. It should also meet many important requirements to be technologically relevant: inexpensive, readily available, produced in large scale, and stable to air, light, water, heat and oxidative deactivation.



$$E = 1.229 - 0.059(\text{pH}) \text{ V vs NHE at } 25^\circ\text{C}$$

Lately, we have disclosed the excellent catalytic and electrocatalytic activity of the cobalt-derivative of the Prussian blue family: $\text{Co}_x[\text{Fe}(\text{CN})_6]$ (**CoHCF**, Figure 1) to promote the oxygen evolution reaction in a large pH range, including neutral conditions. The next step has been to incorporate this catalysts onto photoactive semiconductors to promote photocatalytic water splitting. During 2017, we reported the photocatalytic activity of BiVO_4 and Fe_2O_3 (hematite) electrodes decorated with **CoHCF**, along computational modeling (in collaboration with the group of Prof. N. López) of the interfaces to understand the experimental results. Indeed, the computational model we developed is able to predict the success of a given catalyst/semiconductor photoelectrode.

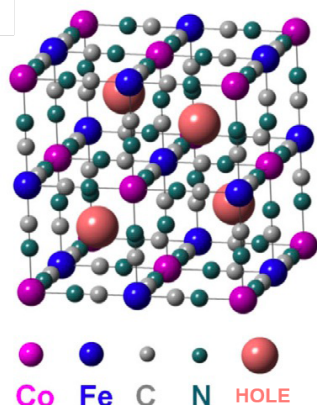


Fig. 1 – Representation of the idealized cubic unit cell of **CoHCF**.

We deposited thin layers of **CoHCF** on top of hematite electrodes via dip coating. The presence of our catalysts did not lead to a relevant enhancement in the photoelectrocatalytic performance (Figure 2). The small enhancement observed was assigned to longer lifetimes for surface recombination processes, as a result of the hole-scavenging character of the catalyst. Still, Water oxidation was occurring preferentially on the hematite surface. The computational model indicates that these two materials possess an intrinsic mismatch between their electronic levels, precluding efficient hole transfer between them, necessary to achieve efficient photocurrent enhancement.

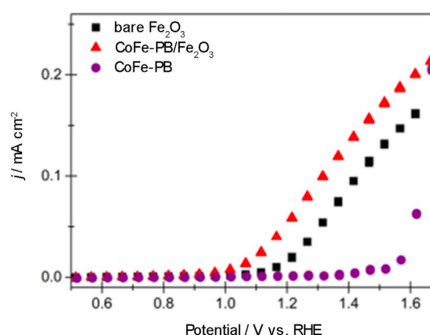


Fig. 2 – Steady-state j - V curve for electrochemical water splitting using hematite and/or **CoHCF** electrodes under light irradiation (1 sun).

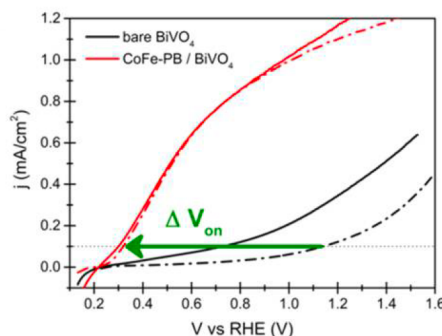


Fig. 3 – Steady-state j - V curve for electrochemical water splitting using BiVO_4 and/or **CoHCF** electrodes under light irradiation (1 sun).

The opposite behavior was expected in the case of **CoHCF**/ BiVO_4 photoelectrodes. The energy diagrams of both materials show an adequate alignment of the valence levels between light harvesting materials (BiVO_4) and the catalysts (**CoHCF**). As a result, these composite photoelectrodes exhibit excellent performance (Figure 3) with remarkable increase of photocurrent and significantly lower onset potential (0.8 V difference). All experimental data

(and computational models) support the genuine catalytic activity of **CoHCF** in these photoelectrodes.

Electrocatalytic water oxidation with polyoxometalates

Polyoxometalates (POMs) from earth-abundant metals are also promising electrocatalysts to promote the oxygen evolution reaction. Despite their intrinsic catalytic properties, there are some problems to be solved before they can be proposed for further applications. On one end, their chemical stability has been put into question; and on the other end, their insulating behavior requires the use of conducting support. During 2017 we participated in two studies to assess both challenges.

The genuine catalytic activity of $[\text{Co}_9(\text{H}_2\text{O})_6(\text{OH})_3(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3]^{16-}$ (**Co₉**, Fig. 4) was confirmed by fast laser flash photolysis experiments carried out in collaboration with Prof. M. Bonchio (University of Padova). Time dependent data showed no induction time (no evolution during the reaction) and multiple electron transfer events in the millisecond scale (Figure 5), demonstrating the powerful catalytic performance of this (and other) POMs.

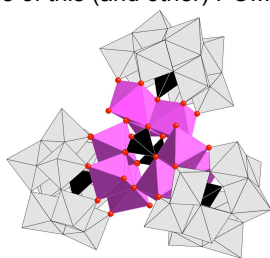
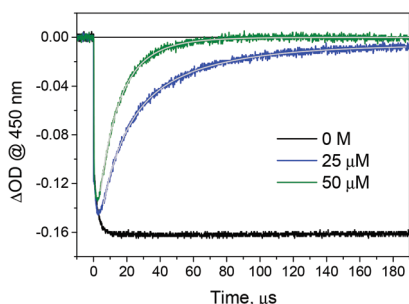


Fig. 4 – Structure of the polyanion **Co₉**.



Articles

“Conducting organic polymer electrodes with embedded polyoxometalate catalysts for water splitting”

ChemElectroChem (2017) 4, pages 3296–3301 (2017) M. Blasco-Ahicart, J. Soriano-López, J. R. Galan-Mascaros

Fig. 5 – Laser flash photolysis experiments in aqueous phosphate buffer (pH 8) containing persulfate, $[\text{Ru}(\text{bpy})_3]^{2+}$ and 0–50 μM **Co₉**.

We were able to use this same POM, as dopant for organic polymer films to obtain versatile organic polymer electrodes for water splitting. We incorporated **Co₉** into a conducting polypyrrole matrix, taking advantage of its high anionic charge (**Co₉¹⁶⁻**), yielding a heterostructure that combines the catalytic water oxidation features from the POM, together with the unique processability of polypyrrole. We optimized the electrocatalytic performance by studying the effect of several parameters, such as the POM content, film thickness, counter anions, and so forth. It is remarkable that less than 6% POM content in a polypyrrole film multiplies oxygen evolution reaction currents by one order of magnitude, reducing the required overpotentials by approximately 200 mV, and reaching current densities over 20 mA/cm^2 (Figure 6). Despite the moderate efficiency (ca. 65%), this strategy, being based on inexpensive and readily available raw materials, may be useful for the preparation of water splitting anodes that can be adapted to any surface, geometry, or support.

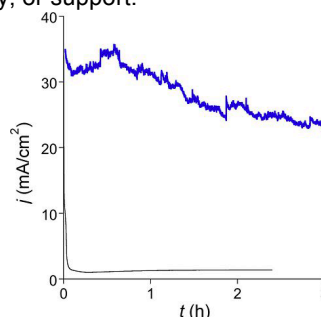


Fig. 6 – Chronoamperometry at 1.4 V vs NHE for a **Co₉**/ppy films (blue line), or TsOH/ppy films (black line) in KPi buffer (pH 7).

“Level alignment as descriptor for semiconductor/catalyst systems in water splitting: The case of hematite/cobalt hexacyanoferrate photoanodes”

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ACS Appl. Mater. Interfaces (2017) 9, pages 37671–37681

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