2016 Annual Scientific Report



Galán-Mascarós Research Group



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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.



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Catalytic water oxidation with Prussian blue derivatives: Enhanced performance

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.

 $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$



Fig. 1 - FESEM images of CoO_x (a) and its transformation into a CoFe PB film by chemical etching with potassium hexacyanoferrate after 0.5 (b), 1 (c), 1.5 (d), 2 (e) and 3 hours (f).

In 2013 we disclosed the promising WOC activity of cobalt-containing Prussian blue analogues (PBAs). This open metal-organic frameworks (MOFs) are robust and stable in a large pH range, including acidic and neutral conditions, exhibiting catalytic activities comparable to those of metal oxides for the oxygen evolution reaction (OER). Despite their robust performance, essential parameters such as current densities and mechanical resistance were still far from being competitive. We

assigned these weaknesses to poor interfacial matching with electrode surfaces.

Finally, we have been able to establish a novel synthetic protocol for the preparation and processing of cobalt hexacyanoferrate (**CoFe**) thin films. Using as starting materials Co(OH)₂, the **CoFe** films can be obtained by chemical etching in a solution of hexacyanoferrate. The cubic **CoFe** nanocrystals as grown from the hydroxide fibers (Figure 1) form a rugged and compact network with much improved catalytic features.

These films promote orders of magnitude higher electrocatalytic currents than previously reported and excellent long and short-term stability, even at current densities over 10 mA cm^{-2} (Figure 2). Furthermore, this catalyst also possesses excellent pH stability, remaining active in a large pH range (1 < pH < 12). The activity is comparable to that of transition metal oxides, whereas abundant oxides rapidly and irreversibly deactivate in acidic media. Structure and activity persist even in concentrated sulfuric acid. These CoFe represents the first heterogeneous non-noble metal WOC, active and corrosion resistant in acid media, where hydrogen production is preferred for a water splitting platform.



Fig. 2 - Overpotential versus time data, under a constant current density of 10 mA cm⁻² in pH 7 phosphate buffer, of **CoFe** (red curve) and CoO_x (blue curve). Before and after being treated with a pH = 1 sulfuric acid solution (indicated by the dotted green line).

Record energy barrier in a bi-stable spin crossover Fe^{ll} complex

Spin crossover (SCO) compounds are a paradigmatic example of bistability at the molecular level, where the electronic state of a metal complex can be switched from a low-spin (LS) to a low-lying metastable high-spin (HS) configuration through external stimuli: thermally, under light irradiation or pressure. In such compounds, cooperativity and memory effect may appear in bulk, when a structural phase



transition is associated to the electronic transition.

Following our work with polyanionic Fe^{2+} trimers (Figure 3) with the anionic ligand 4-(1,2,4-triazol-4-yl)ethanedisulfonate (L1) we have studied in detail the thermodynamic and kinetic behavior of [(NH₂(CH₂)₂]₆[Fe₃(µ-L1)₆(H₂O)₆].



Fig. 3 - Two views of the molecular structure of $[Fe_3(\mu-L1)_6(H_2O)_6]^{6-}$ (H-atoms omitted for clarity). Color code: Fe =purple; S = yellow; O = red; N = blue; C = black.

Multiple relaxation experiments were performed after trapping the HS state by rapid cooling (Figure 4). This material needs several hours to decay into the ground state. The kinetics of this relaxation process, as a function of temperature, allowed us to estimate an activation barrier over 6000 cm^{-1} (> 8000 K). This compound is the highest barrier ever found for a spin transition compound, and it explains the extremely slow kinetics. It is worthy to mention that this barrier has a pure molecular origin, since all experimental data suggests the system is noncooperative. With this in mind. dilution experiments are underway in order to proof that SCO compounds can act as molecular switches at room temperature.



Fig. 4 - Relaxation of the trapped high spin fraction (γ_{HS}) of [(NH₂(CH₂)₂]₆[Fe₃(μ -L1)₆(H₂O)₆] at different temperatures after cooling down the sample at 10 K/m in from its saturation value at 400 K.

A novel polymerization reaction on coinage metal surfaces

On-surface synthesis is a promising strategy for engineering heteroatomic covalent nanoarchitectures with prospects in electronics, optoelectronics and photovoltaics. In collaboration with the group of Dr. David Écija (IMDEA Nanoscience, Madrid), we have discovered the thermal tunability of a novel surface-assisted organic reaction.

Deposition of tetra-aza-porphyrin species bearing ethyl termini on Au(111) at room temperature results in a close-packed assembly (Figure 5a). Upon annealing at 275 °C, the molecular precursors undergo a series of covalent reactions via their ethyl terminal groups, giving rise to phthalocyanine polymers and tapes (Figures 5b-c). However, if the annealing is carried out at 300 °C, the result is completely different, yielding the formation of monomeric phthalocyanines (Figure 5d). A systematic scanning tunneling microscopy study of reaction intermediates, combined with density functional calculations, suggests а [2.2] cycloaddition as responsible for the initial linkage between molecular precursors, whereas the monomeric reaction is rationalized as an electrocyclic ring closure. Both mechanisms are initiatited via dehydrogenation of the ethyl moieties by the coinage metal.



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Fig. 5 – High-resolution STM images on Au(111): (a) OETAP molecules ; (b) OETAP dimer after annealing at 275 °C ; (c) OETAP polymers of higher dimensions and histogram of average polymeric lengths ; (d) Phthalocyanine

molecules obtained after annealing at 300 °C the OETAP.

Our results open avenues to thermally control reaction pathways on surfaces, selecting intermolecular versus intramolecular reactions. This strategy may facilitate the preparation of desired polymers from monomers, or the growth of 1D or 2D nanoarchitectures on surfaces.

Articles

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