Well-defined organometallic precursors for developing tailored catalytic materials.

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Abstract

Homo- and hetero-metallic complexes are used as building blocks of well-defined materials, which are employed in small molecules activation (such as H_2O, H_2 and O_2). In this regard, Water splitting is one of the key processes for many applications related to energy storage and conversion. Water oxidation or oxygen evolution reaction (OER) is still considered the most challenging step in water splitting since it is a more complex transformation than proton reduction. Cobalt-based metal organic frameworks (MOFs) have recently attracted great interest due to their notable electrocatalytic OER activity and the abundance of this metal in the earth.[1,2]

Herein, a new cobalt metal−organic framework (2D-Co-MOF) based on well-defined layered double cores that are strongly connected by intermolecular bonds has been developed (Figure 1a). In situ electrochemical activation of a 2D-Co-MOF@Nafion composite deposited on a graphite electrode produces a well dispersed and ligated nanostructuration of the composite promoting intimate interactions between both components, more abundant electrochemical active sites, where metal centers retain its coordinative chemistry thereby without affecting the intrinsic electrocatalytic properties of the active cobalt centers for OER. The so-activated 2D-Co-MOF@Nafion has been composite exhibits an outstanding electrocatalytic performance for the OER at neutral pH and a high robustness (Figure 1b). The particular coordination chemistry of the MOF consisting of a regular arrangement of multiple Co(II) redox metal sites connected by appropriate organic ligands can explain the higher catalytic activity of the present MOF.

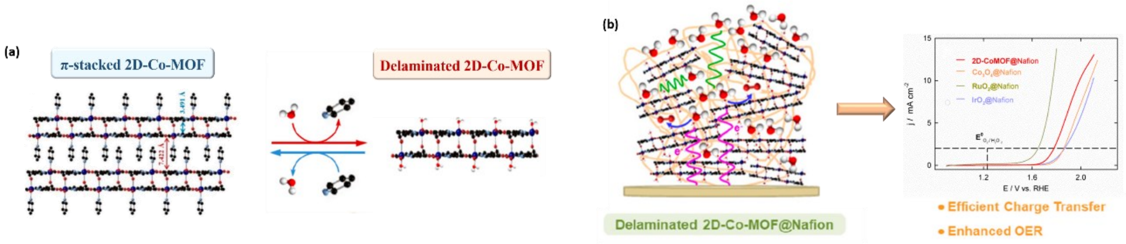


Figure 1. (a) X-Ray structure of 2D Cobalt-MOF and (b) its electrocatalytic OER performance.

The benchmark HER electrocatalysts are platinum (Pt)-based materials, but these are not good for OER, whereas iridium and ruthenium oxides are the state-of-art OER electrocatalysts. Unfortunately, they show insufficient activity toward HER. Indeed, we report a straightforward, efficient and robust synthesis of mono- and bimetallic nanoparticles, promoted through a commercially available metallic source. For instance, the Wilkinson complex in order to prepare Rh_2P nanoparticles, which have high crystallinity and are coated with graphitic carbon patches.[3] The resulting materials have been tested in electrocatalytic HER and OER processes at acid, alkaline and neutral media, providing superb HER activity and competitive OER performance, particularly at neutral and alkaline media, compared to the benchmark HER and OER electrocatalysts Pt and RuO_x/IrO_x, respectively (Figure 2a).[4] Moreover, supported Fe-doped Pd-nanoparticles (NPs) have been prepared via soft transformation of a PdFe-MOF.[5] The thus synthesized bimetallic PdFe NPs are supported on FeOx@C layers, which are essential for developing well-defined and distributed small NPs. The application of this material (PdFe@FeOx-C) as a multifunctional nanocatalyst for the electrocatalytic water splitting process has been investigated with promising results, compared with those obtained for previously mentioned benchmarking catalysts, in terms of favorable intrinsic activity, wide pH window and high stability (Figure 2b).[6]

Figure 2a. HER for Rh_2P@Carbon@Nafion catalysts.

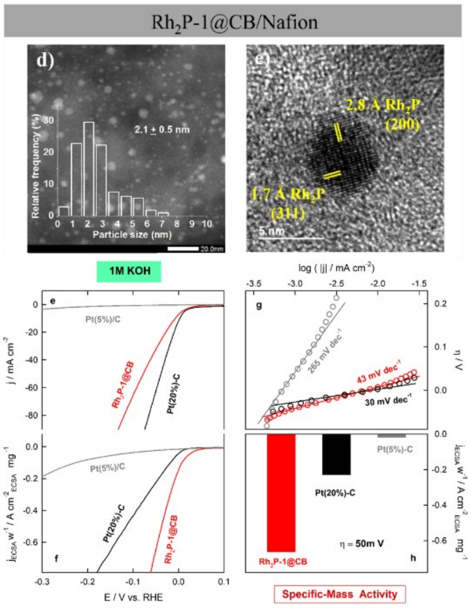
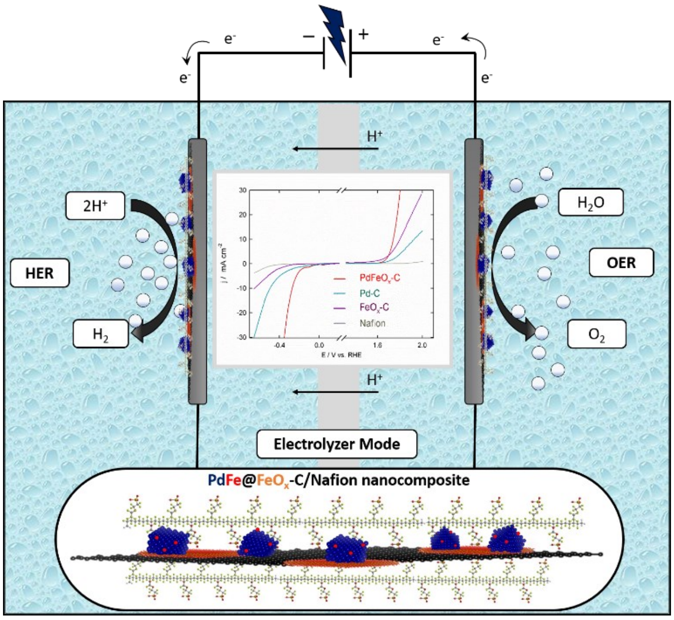


Figure 2b. HER and OER for PdFe@FeOx-C@Nafion catalysts.



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