

# Electronic Structure Evolution in Tricomponent Metal Phosphides with Reduced Activation Energy for Efficient Electrocatalytic Oxygen Evolution

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**Non-noble metal catalysts for high-active electrocatalytic oxygen evolution reaction (OER) are essential in large-scale application for water splitting. Herein, tricomponent metal phosphides with hollow structures are synthesized from cobalt-contained metal organic frameworks (MOFs), i.e., ZIF-67, by tailoring the feeding ratios of Ni and Fe, followed by a high-temperature reduction and a subsequent phosphidation process. Excellent OER activity and long-time stability are achieved in 1 M NaOH aqueous solution, with an overpotential of 329 mV at 10 mA cm<sup>-2</sup> and Tafel slope of 48.2 mV dec<sup>-1</sup>, even superior to the noble metal-based catalyst. It is evidenced that the formed (oxyhydr)oxide/phosphate species by in situ electrochemical surface oxidation are responsible for active OER. Accordingly, the simultaneous introduction of external Ni and Fe elements significantly influences the electronic structures of the parent metal phosphides, leading to the in situ electrochemical formation of surface active layer with decreased OER activation energy for greatly improved water oxidation performance. This electronic structure tuning strategy by introducing multicomponent metals demonstrates a versatile method to use MOFs as precursors for synthesizing high-efficient water splitting electrocatalysts.**

## 1. Introduction

Global energy consumption has been increasing rapidly in the past decades, with over 80% consumable source derived from fossil fuels, leading to serious energy crisis and greenhouse effect.<sup>[1,2]</sup> These issues motivate researchers and governments to

exploit environment-friendly and sustainable energy sources, in which hydrogen produced from solar energy by water splitting has been regarded as a promising candidate with high energy output and carbon-neutral combustion products.<sup>[3]</sup> Generally, this solar-to-hydrogen (STH) process can be realized through a hybrid system by using photovoltaic (PV) electrolysis, in which a solar cell powers an electrolyzer with STH efficiencies over 10%.<sup>[4]</sup> Such PV-electrolysis systems, with high STH efficiencies, have been thus considered of great potential for practical application in the near future. As the essential components in these hybrid systems, except for the highly developed PV cells (especially perovskite solar cells),<sup>[5,6]</sup> electrocatalysts for water splitting have also attracted intense attentions,<sup>[7-9]</sup> where the four-electron involved oxygen evolution reaction (OER) usually occurs as the rate determining step, as compared to the hydrogen evolution reaction (HER). To


this end, it is of great importance to explore excellent OER electrocatalysts for the demonstration of high-efficient PV-electrolysis systems.

Noble metal oxides (e.g., RuO<sub>2</sub>, IrO<sub>2</sub>) have been evidenced as the most active catalysts for electrocatalytic OER. However, their large-scale application is greatly limited due to the high cost and unsatisfactory durability.<sup>[10]</sup> To fulfill the practical application in water splitting, non-noble catalysts toward OER with high activity, good stability, and nontoxicity, are highly desired. Recent studies highlighted transition metal-based materials as promising electrocatalysts in OER, including phosphides/phosphates, oxides, sulfides, selenides, and hydroxides.<sup>[8,11,12]</sup> Among these materials, phosphides have attracted much concentration due to the high electrocatalytic activity, excellent stability, and promising potential in a wide pH scale.<sup>[13-16]</sup> Du and co-workers synthesized novel FeNiP solid-solution nanoplate arrays on nickel foam by a solvothermal method and followed by phosphidation, which performed an exceedingly low overpotential of 180 mV at 10 mA cm<sup>-2</sup> in alkaline solution with an excellent stability after 1000 cyclic voltammetry (CV) cycles, due to the increased active sites and the uniform 3D binder-free architecture.<sup>[17]</sup> Brock and co-workers reported monodisperse and homogeneous CoMnP nanoparticles (~5 nm in diameter) synthesized from a solution-phase reaction of

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manganese and cobalt carbonyl complexes with trioctylphosphine, with an overpotential of 330 mV at 10 mA cm<sup>-2</sup> and a Faradaic efficiency of 96% for efficient water oxidation.<sup>[18]</sup> Mn–Co coordination polymer-based multishell mixed-metal oxyphosphide particles, with an electrochemical-activated Mn–Co oxide/hydroxide species in the nanoshells, were prepared by Lou and co-workers through a phosphidation reaction,<sup>[19]</sup> showing greatly enhanced OER activity with an overpotential of 320 mV at 10 mA cm<sup>-2</sup>. Despite of these achievements, there is still significant room for further improvement in the performance for OER.

Recently, metal organic frameworks (MOFs) have been demonstrated as excellent electrocatalyst precursors for the remarkable advantages in structural optimization and component adjustment.<sup>[1,20]</sup> As a cobalt-contained MOFs, ZIF-67 has acted as precursors for the synthesis of cobalt oxides,<sup>[21]</sup> selenides,<sup>[22]</sup> sulfides,<sup>[23]</sup> phosphides,<sup>[24]</sup> and metal nanoparticles<sup>[25]</sup> by various derivative methods. For example, Zheng and co-workers synthesized Co<sup>3+</sup>-rich Co<sub>0.85</sub>Se nanoparticles coated with carbon shell via a hydrothermal reaction of ZIF-67 with NaHSe followed by a high-temperature treatment, which exhibited excellent OER performance with an overpotential of 360 mV at 10 mA cm<sup>-2</sup>, resulting from its abundant active sites, high conductivity, and superior OER kinetics.<sup>[22]</sup> Yu and co-workers developed a general phosphidation approach to fabricate a family of Co-based bimetallic phosphide ultrathin nanosheets by introducing external metal ions into ZIF-67, which performed an excellent OER activity with an overpotential of 209 mV at 10 mA cm<sup>-2</sup> in 1 M KOH aqueous solution, superior to the noble metal-based catalysts.<sup>[26]</sup> Yu and co-workers reported a versatile strategy for the controllable synthesis of CoO@Co/N-doped porous carbon arrays on Ni foam by pyrolyzing 3D Ni@CoO@ZIF-67 hybrid arrays, with an overpotential of 309 mV at 10 mA cm<sup>-2</sup> achieved for OER.<sup>[27]</sup>

Given tunable components and OER-active transition metal element (i.e., Co) contained in frameworks, herein, transition metal phosphide nanomaterials as efficient OER catalysts were prepared using hollow ZIF-67 spheres as the precursor with components tuned by introducing Ni and Fe ions into framework, via a high-temperature reduction and then a phosphidation process. The obtained tricomponent metal phosphide showed excellent performance and good stability for OER, even superior to the typical noble metal oxide (RuO<sub>2</sub>). The in situ formed (oxyhydr)oxides/phosphates by electrochemical surface oxidation were responsible for OER. Thereafter, the simultaneous introduction of external elements (Ni and Fe) significantly altered the electronic structure of the parent metal phosphides, contributing to the reduced OER activation energy of the electrochemically surface-oxidation formed active layer for the greatly improved water oxidation performance. This electron structure tuning strategy by introducing external metal ions demonstrates a versatile method to use MOFs as precursors for the synthesis of high-efficient water splitting electrocatalysts.

## 2. Results and Discussion

The hollow ZIF-67 (denoted as Z67) spheres were synthesized through a room-temperature solution method by mixing

cobalt sulfate and 2-methylimidazole (MeIm) in methanol. The obtained Z67 demonstrates a hollow structure with a diameter of about 500 nm (Figure 1a). After adding nickel nitrate, the obtained Ni doped ZIF-67 (denoted as CoNi<sub>x</sub>-Z,  $x = 0.04, 0.2, 1$ , here  $x = 0.2$ ) exhibits similar hollow sphere structures with diameters and color unchanged (Figure 1b). In comparison, the introduction of ferric nitrate caused significant changes in color and morphology. The obtained Fe doped ZIF-67 (denoted as CoFe<sub>0.05</sub>-Z) shows an atropurpureus color and a polyhedral shape with diameter much increased to  $\approx 5 \mu\text{m}$  (Figure 1c). As discovered from the transmission electron microscope (TEM) image and energy-dispersive X-ray spectroscopy (EDS) mapping profiles (Figure S1, Supporting Information), the small particles on the solid polyhedron should belong to cobalt–iron complexes. Interestingly, with simultaneous introduction of Ni and Fe elements, the obtained Ni/Fe co-doped ZIF-67 (denoted as CoNi<sub>0.2</sub>Fe <sub>$\gamma$</sub> -Z,  $\gamma = 0.01, 0.05, 0.2$ , here  $\gamma = 0.05$ ) shows a hollow polyhedral structure, with color turned to be dark purple and size increased to be  $\approx 1 \mu\text{m}$  (Figure 1d), as compared to the pristine ZIF-67 (Z67). As demonstrated by X-ray diffraction (XRD) patterns (Figure S2, Supporting Information), all these samples, with or without Ni and/or Fe incorporation, keep in good crystallinity and hold the same crystal structure as ZIF-67.

To implement carbonization process and improve the reduction degree of metal ions, the Z67, CoNi<sub>0.2</sub>-Z, CoFe<sub>0.05</sub>-Z, and CoNi<sub>0.2</sub>Fe<sub>0.05</sub>-Z samples were annealed in Ar/H<sub>2</sub> flow at relatively high temperature (700 °C),<sup>[28]</sup> with black powders obtained, and denoted as Z67-H, CoNi<sub>0.2</sub>-Z-H, CoFe<sub>0.05</sub>-Z-H, and CoNi<sub>0.2</sub>Fe<sub>0.05</sub>-Z-H, respectively. As shown in Figure 1e–h, the hydrogen reduced samples became rougher with small particles formed on the surface. As demonstrated in XRD patterns (Figure S3, Supporting Information), all the samples had metal species (e.g., Co, Fe) partially or completely reduced to metal phases, without ZIF-67 peaks recognized, indicating a complete destruction of the ZIF framework during the high temperature reduction process. Nevertheless, with the spherical morphology maintained, the formed metals and/or metal oxides should be well supported on the carbon framework derived from the reduction of ZIF-67.

To obtain the final products for high-efficient OER catalysts, all the Ar/H<sub>2</sub> reduced samples were further conducted with a low temperature phosphidation process, with products denoted as Z67-H-P, CoNi<sub>0.2</sub>-Z-H-P, CoFe<sub>0.05</sub>-Z-H-P, and CoNi<sub>0.2</sub>Fe<sub>0.05</sub>-Z-H-P, respectively. As shown in Figure 1i–l, after phosphidation all the samples show morphology almost unchanged with surface reverting smooth, except CoFe<sub>0.05</sub>-Z-H-P. In the sight of XRD patterns, after phosphidation the CoP phase can be identified in Z67-H-P and CoNi<sub>0.2</sub>-Z-H-P (Figure S3a,b, Supporting Information). The TEM images and EDS mapping profiles demonstrate the hollow structures for both Z67-H-P and CoNi<sub>0.2</sub>-Z-H-P, and an additional Ni<sub>3</sub>P phase is formed in CoNi<sub>0.2</sub>-Z-H-P due to the introduction of Ni element (Figures S4, S5, and S6, Supporting Information). With the Fe element introduced, a partially phosphatized Co<sub>2</sub>P phase emerges while metal phases (i.e., Co, Fe, Co<sub>0.7</sub>Fe<sub>0.3</sub>) still exist (Figure S3c, Supporting Information), implying an inadequate phosphidation process. The overlapped elemental distributions of P, Fe, and Co further confirm the phosphidation happening to the metal phases (Figure S7, Supporting Information). Interestingly, with the

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