Facile formation of Fe-doped NiCoP hollow nanocages as bifunctional electrocatalysts for overall water splitting†

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Rational design of electrocatalysts with unique morphological structures and chemical compositions is crucial for electrochemical performance and energy storage capacity. In this work, an Fe-doped NiCoP hybrid hollow nanocage (denoted as Fe-NiCoP) was synthesized through the phosphorization of the product from [Fe(CN)₆]³⁻-intercalated NiCo-LDH (layered double hydroxide), where the original ZIF-67-Co was used as the template. Because of the hollow nanostructure and the synergistic effect between multiple components, the Fe-NiCoP catalyst exhibited promising hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) activities in 1.0 M KOH with low overpotentials of 147 and 235 mV at 10 mA cm⁻², respectively. Furthermore, the Fe-NiCoP catalyst only achieved a current density of 10 mA cm⁻² at the voltage of 1.60 V. Inspired by the excellent OER performance of the Fe-NiCoP catalyst, a Zn-air battery was built to explore the Fe-NiCoP catalyst for practical application. After 900 successive cycles, the Fe-NiCoP + Pt/C catalysts exhibited excellent cycling stability at 5 mA cm⁻², which was a much stronger performance than that of the RuO₂ + Pt/C catalysts. This work provides a practical strategy for the synthesis of high-performance and low-cost electrocatalysts.

1. Introduction

Electrochemical water splitting has been recognized as an attractive strategy to generate efficient, renewable, and clean hydrogen fuel, and consists of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).¹⁻⁵ Even though noble metal (Pt/Ir/Ru)-based catalysts have been considered as the most efficient HER and OER catalysts, their exorbitant cost and rarity limit their large-scale applications.⁶⁻⁸ Thus, continuous effort has been devoted to exploring and developing low-cost catalysts for the HER and OER with excellent performance and high stability.

It has been demonstrated that transition metal phosphides (TMPs) are potent substitutions for catalyzing the HER and OER due to their low cost and long-term stability.⁹⁻¹¹ For example, the Du group prepared porous Ni₃P nanosheets from a NiO-metal–organic framework (MOF)-74 precursor that exhibited the overpotentials of 168 mV and 320 mV for the HER and OER at 10 mA cm⁻², respectively.¹² The CoP nanowires synthesized by the Chen group possessed the overpotentials of 136 and 323 mV for the HER and OER at 10 mA cm⁻², respectively.¹³ Another Co₃P nanowire exhibited overpotentials of 125 mV and 360 mV for the HER and OER at 10 mA cm⁻², respectively.¹⁴ According to the reported cases, the single metal phosphides still exhibited large overpotential and sluggish kinetics.

The rational construction of multicomponent phosphides has been developed to improve water splitting performance.¹⁵⁻¹⁷ For instance, the Ni₃P-Co₃P-Fe₃P hollow nanoprism reported by our group exhibited a much smaller overpotential of 294 mV for the OER and remarkable stability for more than 12 h.¹⁸ Ni-Co-P hollow nanoribbons were fabricated by the Lou group as a bifunctional electrocatalyst, and the overall water splitting to deliver a current density of 10 mA cm⁻² required a voltage of 1.62 V.¹⁹ Multicomponent metal phosphides can highly enhance water splitting performance because of the existence of interfaces that are beneficial to the charge transfer.

The optimization of morphological structure is also an effective strategy to strengthen electrochemical performances. Compared with a solid structure, a hollow structure provides a much larger surface area and facilitates the diffusion of reagents, which will significantly enhance the electrocatalytic performance.²⁰⁻²² MOF materials have emerged as promising...
precursors for the synthesis of functional nanomaterials, due to their tunable porous structure and homogenous metal distribution.\textsuperscript{23-25} Low-cost multicomponent TMPs with a hollow structure would be excellent electrocatalysts for water splitting.

Herein, a Fe-doped NiCo hybrid hollow nanocage (denoted as Fe-NiCoP) was synthesized through the phosphorization of the product from [Fe(CN)\textsubscript{6}]\textsuperscript{3-}-intercalated NiCo-LDH (layered double hydroxide) at 350 °C with a heating rate of 2 °C min\textsuperscript{-1} for 2 h under N\textsubscript{2} gas flow. The Fe-NiCoP catalyst exhibited excellent HER and OER activities in 1.0 M KOH solution with low overpotentials of 147 mV and 235 mV at 10 mA cm\textsuperscript{-2}, respectively. The Fe-NiCoP catalyst only achieved a current density of 10 mA cm\textsuperscript{-2} at 1.60 V.

A Zn–air battery was built to explore the practical application of the Fe-NiCoP catalyst, where the Fe-NiCo + Pt/C catalysts exhibited excellent cycling stability even after 900 cycles at 5 mA cm\textsuperscript{-2}, with greater stability than that of a RuO\textsubscript{2} + Pt/C-based battery. The excellent electrocatalytic activity of Fe-NiCoP can be attributed to the co-contribution from the hollow nanocage structure, the synergistic interfaces from multicomponent phosphides, and the Fe-doping. This study provides a feasible strategy to prepare a low-cost electrocatalyst with promising performance for overall water splitting.

\section{2. Experimental section}

\subsection{2.1. Synthesis of ZIF-67-Co nanocages}

ZIF-67-Co nanocages were synthesized according to a procedure from a previous study.\textsuperscript{26} First, 1.16 g (4 mmol) of Co(NO\textsubscript{3})\textsubscript{2}-6H\textsubscript{2}O and 1.31 g (16 mmol) of 2-methylimidazole (2-MIM) were each separately dissolved in 100 mL methanol, mixed under vigorous stirring for 5 min, and then aged for 24 h. The purple precipitate was collected by centrifugation, washed several times with methanol, and then dried at 60 °C for another 24 h.

\subsection{2.2. Synthesis of NiCo-LDH hollow nanocages}

Next, 80 mg (0.275 mmol) of Ni(NO\textsubscript{3})\textsubscript{2}-6H\textsubscript{2}O and 40 mg of ZIF-67-Co were dissolved in 40 mL ethanol, and the reaction mixture was stirred and refluxed at 90 °C for 30 min. The green precipitate was collected by centrifugation, washed several times with methanol, and then dried at 60 °C for 24 h.

\subsection{2.3. Synthesis of Fe-NiCo-LDH hollow nanocages}

For synthesis, 40 mg of NiCo-LDH and 40 mg of K\textsubscript{3}[Fe(CN)\textsubscript{6}] were each separately dispersed in 20 mL deionized water. After pouring the K\textsubscript{3}[Fe(CN)\textsubscript{6}] solution into a NiCo-LDH solution, the mixture was stirred for another 30 min. The brown-green precipitate was collected by centrifugation, washed several times with methanol, and then dried at 60 °C for 24 h.

\subsection{2.4. Synthesis of Fe-NiCoP, NiCoP, and CoP hollow nanocages}

Additionally, 10 mg of Fe-NiCo-LDH and 100 mg of NaH\textsubscript{2}PO\textsubscript{4}-H\textsubscript{2}O were placed in a tube furnace and heated at 350 °C for 2 h at a heating rate of 2 °C min\textsuperscript{-1} under N\textsubscript{2} gas flow. The control samples of NiCoP and CoP were synthesized under the same conditions except that the Fe-NiCo-LDH precursor was replaced with NiCo-LDH and Co\textsubscript{3}O\textsubscript{4}, respectively.

\subsection{2.5. Characterization}

Powder X-ray diffraction (PXRD) patterns were utilized to obtain the crystal structure from a Model D/Max-tC X-ray diffractometer using a Cu k\alpha radiation source. Scanning electron microscopy (SEM) images were obtained with Hitachi S-4800 scanning. Transmission electron microscopy (TEM) images were determined with a JEOL JEM-2010F. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo VG Scientific ESCALAB 250 spectrometer. The Barrett–Emmett–Teller (BET) specific surface area was characterized on the Micromeritics ASAP 2050. The amounts of Ni, Co, and Fe in the Fe-NiCoP catalyst were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Leeman Prodigy).

\subsection{2.6. Electrochemical measurement}

The electrochemical measurements were performed on a CHI 660 three-electrode system. The working electrodes were prepared by first mixing as-prepared catalyst (70 wt%), carbon black (20 wt%), and polyvinylidene difluoride (PVDF, 10 wt%) in an N-methyl-pyrrolidone (NMP) solvent to form a homogeneous suspension that was coated onto cleaned Ni foam (NF) substrates and then dried at 80 °C for 12 h. All the electrochemical measurements were obtained after purification with N\textsubscript{2} for 30 min. Electrochemical impedance spectroscopy (EIS) experiments were performed under an AC voltage with 5 mV amplitude and a frequency ranging from 0.01 Hz to 100 kHz. The linear sweep voltammetry (LSV) was performed at a rate of 5 mV s\textsuperscript{-1} in 1.0 M KOH solution. All of the potentials were calibrated with respect to the reversible hydrogen electrode (RHE): E (RHE) = E (SCE) + 0.0591 pH + 0.242 V, and all polarization curves were iR corrected.

\subsection{2.7. Zinc–air battery test}

A primary Zn–air battery was constructed with a Zn foil anode, Fe-NiCoP catalyst, and Pt/C (mass ratio of 1:1) air cathode and electrolyte (0.2 M ZnCl\textsubscript{2} + 6.0 M KOH). The performance of the batteries was tested using a Land CT2001A system. For comparison, the Zn–air battery with a mixed Pt/C and RuO\textsubscript{2} air cathode was also tested under similar conditions.
3. Results and discussion

3.1. Synthesis and characterization

The synthetic procedure for constructing the Fe-NiCoP catalyst is shown in Scheme 1. Complex ZIF-67-Co was used as the template. The phase purity of ZIF-67-Co was verified by PXRD (Fig. S1a†), and the SEM image further revealed that the ZIF-67-Co template possessed a rhombic dodecahedral shape with a uniform length of 600 nm and a smooth surface (Fig. S2†).

A NiCo-LDH hollow nanocage was prepared by etching the ZIF-67-Co template with Ni(NO₃)₂·6H₂O in ethanol under reflux conditions. The diffraction patterns of synthesized NiCo-LDH were in good agreement with the standard NiCo-LDH (JCPDS card no. 33-0429), which suggested the successful synthesis of NiCo-LDH (Fig. S1a†).27,28 The hollow structure of NiCo-LDH was confirmed by the SEM and TEM images, where NiCo-LDH maintained the rhombic dodecahedral shape and particle size as that of the ZIF-67 template (Fig. S3a†). The shell thickness of NiCo-LDH was approximately 15 nm, as observed from the TEM images (Fig. S3b†).

The NiCo-LDH hollow nanocage underwent a second ion exchange step by reaction with [Fe(CN)₆]³⁻ at room temperature to produce Fe-NiCo-LDH. The diffraction peaks of Fe-NiCo-LDH were in agreement with the standard XRD profiles of NiCo-LDH (JCPDS card no. 33-0429), and no diffraction peaks indexed to Fe species were detected. The SEM image of the Fe-NiCo-LDH sample showed almost no significant morphological change as compared to NiCo-LDH (Fig. S4a†). The hollow structure of NiCo-LDH was also transferred to Fe-NiCo-LDH (Fig. S4b†).

The phosphorization of Fe-NiCo-LDH by NaH₂PO₂ at 350 °C for 2 h under an N₂ atmosphere generated the resultant complex Fe-NiCoP. The SEM and TEM images revealed that the hollow rhombic dodecahedral morphology for the Fe-NiCoP complex was well-retained from the phosphorization of Fe-NiCo-LDH (Fig. 1). The PXRD patterns for the Fe-NiCoP complex were similar to the patterns obtained for NiCoP (JCPDS card 71-2336), which demonstrated that successful phase transformation occurred after phosphorization (Fig. S6a†). No Fe-related phase was observed for Fe-NiCoP, suggesting that elemental Fe was successfully incorporated into the NiCoP lattices. The Fe-NiCoP catalyst exhibited a large BET of 134.4 m² g⁻¹, and the average pore sizes of the Fe-NiCoP catalyst were 0.25 nm, further confirming its mesoporous structure (Fig. S7†). This hollow structure accelerated the oxygen release and the electrolyte diffusion, further facilitating the OER performance.

As for comparison, complexes CoP and NiCoP were also synthesized through the direct phosphorization of Co₃O₄ and NiCo-LDH under the same reaction conditions as those used for Fe-NiCoP. The PXRD patterns of CoP and NiCoP were consistent with the standard patterns for CoP (JCPDS card no. 29-0497) and NiCoP (JCPDS card no. 71-2336) (Fig. S1b and S6a†). Compared to the hollow nanocage of Fe-NiCoP, a slight collapse and aggregation appeared in the NiCoP complex (Fig. S6a†).

The morphology and structure of Fe-NiCoP were further identified by high-resolution TEM (HRTEM) images (Fig. 1). Two inter-planar spacings of 0.21 nm and 0.19 nm were defined in the HRTEM image, which could be ascribed to the (111) and (210) plane of the Fe-NiCoP complex, respectively (Fig. 1d). Elemental mapping images (Fig. 1e–h) revealed the uniform distribution of Ni, Co, Fe, and P elements in the Fe-NiCoP complex. The EDX line scanning profile further indicated the hollow rhombic dodecahedral shape and the even distribution of Ni, Co, Fe, and P elements in the Fe-NiCoP complex (Fig. S8†). The ICP-MS measurement confirmed that the molar ratio of Ni, Co, and Fe atoms in Fe-NiCoP are 5.8 : 2.7 : 1.

The surface composition and chemical state for complexes NiCoP and Fe-NiCoP were investigated by XPS measurements. The Ni 2p spectra in Fig. 2a of Fe-NiCoP exhibits two peaks at 862.5 and 880.6 eV, which are two satellite peaks. The peaks located at 856.6 eV and 874.5 eV were attributed to NiII in the Ni 2p 3/2 region and Ni 2p 1/2 region, and those centered at 858.8 eV and 876.4 eV were ascribed to the NiIII state.30,31 For the Co 2p spectra (Fig. 2b), both peaks at 778.9

![Scheme 1](image-url)
eV and 797.8 eV corresponded to Co$^{3+}$ in Co 2p 3/2 region and Co 2p 1/2 region, and those centered at 782.5 eV and 799.8 eV were ascribed to the Co$^{2+}$ state, along with two satellite peaks at 786.5 and 804.8 eV, respectively.\textsuperscript{4,32,33} For the Fe 2p spectra (Fig. 2c), the peaks located at 711.1 and 717.9 eV were associated with the Fe$^{2+}$ state, and the other
two peaks centered at 714.3 and 724.3 eV corresponded to the Fe$^{3+}$ states, respectively. For the P 2p spectra (Fig. 2d), the peak at 134.3 eV was assigned to oxidized phosphorus species, while the P 2p1/2 binding energy at 129.7 eV indicated the presence of M-P.

In contrast, the XPS spectra for NiCoP were also collected (Fig. 2). The peaks in the Ni 2P 3/2 and Co 2P 3/2 region for complex NiCoP were negatively shifted around 0.2 eV and 0.1 eV, respectively. This shift demonstrated the influence of Fe-doping on the electronic structure of the Ni and Co centers, which had been modified and would be beneficial for water electrolysis.

3.2. Electrochemical performance

The electrocatalytic properties of CoP, NiCoP, Fe-NiCoP and commercial Pt/C for the HER were recorded using a three-electrode system in 1.0 M KOH solution. In Fig. 3a, the Pt/C catalyst presents the strongest HER activity with an overpotential of 37 mV at a current density of 10 mA cm$^{-2}$. For the other three catalysts, the Fe-NiCoP sample exhibited superior catalytic performance with only an overpotential of 147 mV at 10 mA cm$^{-2}$, which was much lower than those of CoP (226 mV) and NiCoP (186 mV) (Fig. 3c). The HER performance of Fe-NiCoP was much more optimal than the other Ni, Co, and Fe-based catalysts (Table S1†).

To gain further insight into the HER catalytic kinetics, the Tafel plots were evaluated, as shown in Fig. 3b. The Fe-NiCoP catalyst exhibited the lowest slope of 48.5 mV dec$^{-1}$, which was significantly lower than those of CoP (94.7 mV dec$^{-1}$) and NiCoP (87.0 mV dec$^{-1}$). This suggested that the integration of Fe into the NiCoP complex could greatly enhance the HER performance. The superior stability of the Fe-NiCoP catalyst for the OER was also demonstrated, where the current–time curve of the Fe-NiCoP catalyst only slightly decreased over 20 h (Fig. 3d).

The OER properties of the as-prepared CoP, NiCoP, and Fe-NiCoP catalysts and commercial RuO$_2$ catalyst were also investigated in Fig. 4. The Fe-NiCoP catalyst also displayed the best OER performance among the test complexes, with only an overpotential (235 mV) at 10 mA cm$^{-2}$. The overpotential of the Fe-NiCoP catalyst was much smaller than those of CoP (346 mV), NiCoP (281 mV), and RuO$_2$ (274 mV) (Fig. 4c) and those of several other recently reported non-noble catalysts (Table S2†). Fe-NiCoP exhibited a smaller Tafel slope (56.8 mV dec$^{-1}$) that was actually superior to the slope of CoP (68.3 mV dec$^{-1}$), NiCoP (62.7 mV dec$^{-1}$), and RuO$_2$ (66.4 mV dec$^{-1}$). The superior stability of the Fe-NiCoP catalyst for the OER was also demonstrated, where the current–time curve of the Fe-NiCoP catalyst only slightly decreased over 18 h (Fig. 4d). All the results demonstrated the excellent OER performance of the Fe-NiCoP catalyst.

To further understand the enhanced OER activity of the Fe-NiCoP catalyst, double-layer capacitance ($C_{dl}$) and electrochemical impedance spectroscopy (EIS) were also employed (Fig. 5 and S9†). The cyclic voltammetry (CV) curves obtained at different scan rates from 20 to 100 mV s$^{-1}$ for the CoP, NiCoP, and Fe-NiCoP catalysts are shown in Fig. 5. The electrochemical double-layer capacitances ($C_{dl}$) were measured in the range of 0.98–1.10 V (vs. RHE), with different
scan rates (scan rate: 20, 40, 60, 80, 100 mV s\(^{-1}\)). The current density at the middle potential with different scan rates was calculated, and the five differences were fitted to obtain the slope.\(^\text{39-41}\) The \(C_{\text{dl}}\) of the Fe-NiCoP (18.8 mF cm\(^{-2}\)) was much larger than those of CoP (8.1 mF cm\(^{-2}\)) and NiCoP (16.5 mF cm\(^{-2}\)), indicating that more active sites were exposed in the Fe-NiCoP catalyst. Furthermore, the Nyquist plot of the Fe-NiCoP catalyst exhibited a lower charge transfer resistance than those of CoP and NiCoP (Fig. S9†). This result illustrated that the Fe-NiCoP catalyst possessed the highest electrical conductivity and fastest electron transfer process during the electrochemical reaction.\(^\text{42}\)

To further investigate the compositional variation of the Fe-NiCoP catalyst after the OER test, XPS was performed (Fig. S10†). In the high resolution XPS spectra, all the dominant peaks were ascribed to the oxidized state of the Ni, Co, and Fe elements as Ni\(^{3+}\), Co\(^{3+}\), and Fe\(^{3+}\). The XPS results suggested that the surface of the Fe-NiCoP catalyst was converted into oxides or (oxy)hydroxides after the OER test.\(^\text{43-45}\) The XRD and SEM results demonstrated that the Fe-NiCoP catalyst maintained the initial phase and morphology structure after the HER and OER test (Fig. S11 and S12†).

Encouraged by the excellent HER and OER performances of the Fe-NiCoP catalyst, we determined that the Fe-NiCoP modified electrode could serve as both anode and cathode for overall water splitting in 1.0 M KOH solution (Fig. 6). The Fe-NiCoP electrode required 1.60 V at a current density of 10 mA cm\(^{-2}\), and the bubbles generated on the surface of the electrode could be clearly observed (Fig. 6). Compared to the...
recently reported Fe/Co/Ni-based electrocatalysts in alkaline electrolytes, there was similar or even greater overall water splitting capacity for Fe-NiCoP (Table S3†). The Fe-NiCoP catalyst maintained its capacity over 18 h with superior stability, and only minor potential decrease was observed (Fig. 6b).

Inspired by the excellent OER performance of the Fe-NiCoP catalyst, a Zn-air battery was built to explore the practical applications of the Fe-NiCoP catalyst.46,47 The Fe-NiCoP + Pt/C mixture (mass ratio, 1 : 1) was loaded in carbon paper to serve as the air-cathode, with a Zn plate anode and electrolyte (0.2 M ZnCl₂ + 6.0 M KOH) (Fig. 7a). For comparison, the Zn-air battery with a mixed Pt/C and RuO₂ air cathode was also tested under similar conditions. The open circuit voltage of the Fe-NiCoP + Pt/C battery was measured at approximately 1.405 V, indicating the excellent performance of the Fe-NiCoP catalyst (Fig. S13†). Moreover, the Fe-NiCoP + Pt/C-based battery exhibited even greater stability than the RuO₂ + Pt/C-based battery, where the potential of the Fe-NiCoP + Pt/C-based battery only slightly increased/decreased after 900 cycles at 5 mA cm⁻² vs. a dramatic increase/decrease of potential for the RuO₂ + Pt/C-based battery after 100 cycles (Fig. 7b). In this case, the Fe-NiCoP catalyst can be considered as a substitute for commercial RuO₂ for practicability.

4. Conclusion

In summary, we have demonstrated the use of an Fe-doped NiCoP hybrid hollow nanocage obtained from the phosphorization of [Fe(CN)₆]³⁻-intercalated NiCo-LDH. Because of the hollow nanostructure, a synergistic effect occurred between multiple components and Fe doping, and the Fe-NiCoP catalyst exhibited excellent HER and OER activities in 1.0 M KOH with low overpotentials of 147 and 235 mV at 10 mA cm⁻², respectively. The Fe-NiCoP catalyst only required a voltage of 1.60 V at 10 mA cm⁻² for electrocatalytic overall water splitting. A Zn-air battery based on Fe-NiCoP + Pt/C as the air cathode also showed greater stability than a RuO₂ + Pt/C-based battery. This work provides a new design principle for a low-cost electrocatalyst with promising performance for overall water splitting.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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