Nested hollow architectures of nitrogen-doped carbon-decorated Fe, Co, Ni-based phosphides for boosting water and urea electrolysis

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ABSTRACT

Tailoring the nanostructure/morphology and chemical composition is important to regulate the electronic configuration of electrocatalysts and thus enhance their performance for water and urea electrolysis. Herein, the nitrogen-doped carbon-decorated tricomponent metal phosphides of FeP₄ nanotube@Ni-Co-P nanocage (NC-FNCP) with unique nested hollow architectures are fabricated by a self-sacrifice template strategy. Benefiting from the multi-component synergy, the modification of nitrogen-doped carbon, and the modulation of nested porous hollow morphology, NC-FNCP facilitates rapid electron/mass transport in water and urea electrolysis. NC-FNCP-based anode shows low potentials of 248 mV and 1.37 V (vs. reversible hydrogen electrode) to attain 10 mA/cm² for oxygen evolution reaction (OER) and urea oxidation reaction (UOR), respectively. In addition, the overall urea electrolysis drives 10 mA/cm² at a comparatively low voltage of 1.52 V (vs. RHE) that is 110 mV lower than that of overall water electrolysis, as well as exhibits excellent stability over 20 h. This work strategizes a multi-shell-structured electrocatalyst with multi-compositions and explores its applications in a sustainable combination of hydrogen production and sewage remediation.

KEYWORDS

tri-metal phosphides, nested hollow nano-architecture, oxygen evolution reaction, urea oxidation reaction

1 Introduction

Hydrogen energy has been consumingly regarded as one of the foremost alternatives for unsustainable fossil fuels on account of the ever-increasing energy demand and the rising concerns about environmental issues [1–3]. Nowadays, water electrolysis is a promising technology to obtain renewable hydrogen energy [4, 5]. However, the anodic oxygen evolution reaction (OER), as the paramount half-reaction of water splitting, is a kinetically sluggish process and requires a fairly high overpotential due to the formation of high energy intermediates in the multi proton-coupled electron-transfer process [5–7]. This could be addressed by using anodic reactions based on other substances e.g., hydrazine [8], benzylamine [9], methanol [10], ethanol [11] and urea [12, 13], which are more prone to be oxidized than water molecules. Among there, the anodic urea oxidation reaction (UOR) is preferable because urea electrolysis requires a low potential to produce hydrogen and enables urea-rich sewage remediation. In alkaline electrolysis, the theoretical voltage (0.37 V vs. reversible hydrogen electrode (RHE)) of UOR is much lower than that of OER (1.23 V vs. RHE) [14, 15]. Therefore, urea electrolysis potentially enables a sustainable combination of pollution treatment and energy conversion. To achieve efficient

water and urea electrolysis, noble-metal catalysts with their low overpotentials and high proton mobility, e.g., IrO₂ and RuO₂, display excellent electrocatalytic performance [16]. Unfortunately, the scarcity and excessive costs limit their larger-scale application in industry. Therefore, the development of electrocatalysts with high efficiency, low cost, and high abundance is still urgent and challenging.

To date, transition metal phosphides (TMPs), such as Ni₂P [17, 18], Fe₂P [19], MoP [20] and CoP [21] have been attracted wide attention owing to their chemical stability, low-cost, and environmental friendliness [22]. Among them, nickel phosphide shows extraordinary electrocatalytic activity and stability for UOR [17, 19, 23]. Both experimental results and density functional theory (DFT) calculations have been demonstrated that the high-valence nickel species generated during the catalysis process plays a key role in improving the UOR activity [1, 19, 24]. Nonetheless, the inappropriate electronic structure and poor electronic conductivity still hinder the further improvement of catalytic activity of nickel-based electrocatalysts [23]. Thus, exploring effective approaches to overcome these defects has become the most critical step to improve the performance of Ni-based phosphides.

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In recent years, a variety of effective strategies have been used to boost the electrocatalytic activity of nickel-based catalysts, such as improving intrinsic activity by multi-metallization [25], exposing more active sites by modulation of nanostructures and morphologies [20] as well as enhancing electrical conductivity with the conductive matrix [19]. Thereinto, multi-metallization that incorporates one or more transition metals with a similar atomic radius and electron configuration into the host metal atoms is an effective strategy [24]. The interactions among different metal elements can effectively modulate the electronic structure of the 3d orbital, optimize the free energy of adsorption of the intermediates, and improve the electrocatalytic OER or UOR activity [26, 27]. For instance, Wang et al. fabricated heterometallic phosphide nanobox Co-Ni-Fe-P, which exhibited a remarkable OER activity with the abundant active sites and the optimized valence electrons [2]. Sha et al. prepared thorny leaf-like NiCoP via the *in situ* vertically grown on a carbon cloth (NiCoP/CC), which confirmed that the incorporation of Co into nickel-based phosphates can tune the electronic structure around Ni and P elements, enhance the charge transfer rate, and reduce the kinetic energy barriers in the UOR process [24]. These demonstrated that the corporation of Fe and Co that belong to the same group as Ni into Ni-based phosphides could optimize the electronic structure of the material, facilitate the formation of high-energy intermediates ($\text{OOH}^*/\text{CO}^*/\text{NH}_2^*$) and accelerate the combination of the adsorbed hydrogen intermediates (H^*) into H_2 [28–31]. However, there is still a severe challenge to produce multi-component TMPs with more accessible active sites and enhanced electron conductivity.

Structural and morphological modulation is now a popular and efficient way to maximize the exposure of active sites for boosting the activity of electrocatalysts [32–34]. Three-dimensional (3D) hierarchical hollow architectures have attracted great attention as they provide a larger surface area and better utilization of the sites from inner space for fast electron/mass transport [35]. Hitherto, different types of TMPs, e.g., multi-shelled Ni_2P [36], CoP@FeCoP/NC [37], FeCo-FeCoP@C [38] and CoP/NiCoP [39] have been fabricated and studied. Therein, metal-organic frameworks (MOFs) have been demonstrated as promising precursors to construct multi-shelled hollow architectures owing to the features of large specific surface areas, multi-porous hierarchical structures, diverse compositions, and well-defined metal centers [40–43]. For instance, Lou et al. reported $\text{Co}_3\text{O}_4/\text{NiCo}_2\text{O}_4$ double-shelled nanocages that were controllably transformed from ZIF-67/Ni-Co layered double hydroxide (LDH) [44]. In addition, Wang et al. demonstrated that ZIF-67/Ni-Co LDH is a rational intermediate to achieve conductive nitrogen-doped carbon decoration of phosphides without the damage of nanocage structures [45]. Importantly, during the phosphating process of Ni-Co LDH, the Ni-Co LDH nanosheets were converted to the Ni-Co-P nanoparticles and the assembly of the interlinked Ni-Co-P nanoparticles resulted in abundant pores, which could facilitate rapid electron/mass transport for the electrocatalysis [29].

Inspired by the abovementioned works, herein, we fabricate multi-component Fe-, Co-, and Ni-based phosphides as electrodes for efficient OER and UOR through a facile approach. Through the rational designs, Fe_2O_3 nanotube, Fe_2O_3 nanotube@ZIF-67, and Fe_2O_3 nanotube@Ni-Co LDH are successively produced as the precursors to achieve the final nested hollow nitrogen-doped carbon-decorated FeP_4 nanotube@Ni-Co-P nanocage (NC-FNCP). The synergistic interplay of multiple catalytic centers (Ni, Co, and Fe) provides proper electronic structure and local coordination environment improving the electrocatalysis performance for water and urea electrolysis. Additionally, the

nested double hollow structures of NC-FNCP facilitate the release of evolved gas bubbles that can activate the reaction interface and promote the adsorption of important intermediates. And the nitrogen-doped carbon can further accelerate the electron transfer rate. Therefore, the as-prepared NC-FNCP electrode exhibits great properties on both the OER and the UOR, with the potentials of 248 mV and 1.37 V to attain a current density of 10 mA/cm^2 , respectively. In addition, NC-FNCP shows great overall water and urea splitting performance and long-term stability.

2 Experiment

2.1 Materials synthesis

2.1.1 Synthesis of Fe_2O_3 nanotubes

All reagents were used directly after receipt without further purification. The synthesis of Fe_2O_3 nanotubes followed the previous work [46, 47]. In a typical procedure, 3.2 mL of FeCl_3 (0.5 mol/L) and 2.88 mL of $\text{NH}_4\text{H}_2\text{PO}_4$ solutions (0.02 mol/L) were mixed. Subsequently, deionized (DI) water was poured into the above solution to reach a total volume of 80 mL under stirring. The mixed solution was then sealed into a 100 mL Teflon-lined autoclave and maintained at a preheated oven at 220 °C for 48 h. After the Teflon-lined autoclave cooled down naturally, the product was collected by centrifugation and repeatedly rinsed with deionized water and ethanol three times, and finally dried at 60 °C in an oven.

2.1.2 Synthesis of Fe_2O_3 nanotube@ZIF-67 nanocomposite structure

Typically, 1.2 g polyvinylpyrrolidone (PVP) was dispersed in 50 mL Fe_2O_3 methanol mixture, and stirred at room temperature for 15 min, then maintained for about 10 min. The 50 mL cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) methanol solution with a molar concentration of 0.69 mmol/L and 100 mL 2-methylimidazole methanol solution with a molar concentration of 36 mmol/L were mixed into the above solution at the same time and stirred for 2 h at natural temperature. After being separated by centrifugation and washing with methanol several times, and dried at 60 °C, the resulting powder was obtained.

2.1.3 Synthesis of Fe_2O_3 nanotube@ZIF-67/Ni-Co LDH

First, 50 mg of as-synthesized Fe_2O_3 @ZIF-67 was ultrasonically dispersed in 30 mL of ethanol. Then 7.48 g nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was added into the above solution and stirred for 1 h. The obtained product was centrifuged and repeatedly cleaned with ethanol, and dried in a vacuum oven at 60 °C for 12 h.

2.1.4 Synthesis of NC-FNCP

The NC-FNCP was prepared by a facile low-temperature phosphatization process. Based on the phosphorous loading and electrochemical performance, the optimum ratio of phosphorous precursors to Fe_2O_3 @ZIF-67/Ni-Co LDH precursors was about 10:1. Briefly, 20 mg of Fe_2O_3 @NiCo-LDH and 200 mg of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ were put in the downstream and upstream side of the tubular furnace and then heated at 350 °C for 2 h under N_2 flow. For comparison, single hollow structure Ni-Co-P nanocages and Fe-P nanotubes were also prepared with a similar method.

2.2 Materials characterization

The phases and crystal structure of the synthesized samples were analyzed by X-ray diffraction (XRD, Rigaku D/max-2500, $\text{Cu K}\alpha$ ($\lambda = 0.1542 \text{ nm}$)) with the 2θ degree from 10° to 80° at a scanning

rate of 8 °/min. The morphology and microstructure of the samples were examined via scanning electron microscopy (SEM, JEOL JSM-6700F, 5 kW) and transmission electron microscopy (TEM, 200CX, 200 kV). High-resolution transmission electron microscopy (HRTEM) was performed on a JEOL JEM-2100F electron microscope operating at 200 kV. The surface analysis and the composition of samples were implemented by X-ray photoelectron spectroscopy (XPS) using an X-ray photoelectron spectrometer with a monochromatic Al K α radiation. The component of the samples were analysed by energy dispersive spectroscopy (EDS, Hitachi SU-70) and inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer ICP 2100). The surface area and porosity analyzer (Quantachrome, USA Qudrasorb SI) was used to assess pore volume, pore size and surface area of the samples via the Brunauer-Emmett-Teller (BET) surface areas and pore-size distribution curves.

2.3 Electrochemical measurements

All the half-cell electrochemical measurements were carried out using a standard three-electrode system on a CHI660E workstation. The Ni foam coated with catalysts, carbon rod, and standard Hg/HgO were used as working, counter, and reference electrodes, respectively. The water and urea splitting were performed at a two-electrode cell using the NC-FNCP as both the anode and cathode. The OER and water electrolysis were conducted in 1 M KOH, while UOR and urea electrolysis was exerted in 1 M KOH with 0.5 M urea. The catalyst ink was prepared by dispersing 6.0 mg of as-prepared catalysts in a mixed solution of 110 μ L of ethanol, 330 μ L of distilled water, and 40 μ L of naphthol. Then dropped 120 μ L of the catalyst ink on the NF substrate and dried at room temperature. All potentials reported were calibrated to the potential versus RHE using the Eq. (1)

$$E(\text{V vs. RHE}) = E(\text{V vs. Hg/HgO}) + 0.0592 \times \text{pH} + 0.098 \text{ V} \quad (1)$$

The linear scanning voltammetry (LSV) curves were measured with a sweeping rate of 5 mV/s. The polarization curve was replotted as voltage vs. log current density to obtain the Tafel plot. By fitting the linear portion of the Tafel plot to the Tafel equation

$$\eta = a + b \log |j| \quad (2)$$

η refers to the overpotential, b is the Tafel slope and a denotes the intercept. Cyclic voltammetry (CV) measurement was implemented at scan rates of 10–100 mV/s and the double-layer capacitance (C_{dl}) was calculated from the CV plot. Electrochemical impedance spectroscopy (EIS) was conducted at a frequency range from 10^5 to 0.01 Hz with an amplitude of 5 mV. Turnover frequency (TOF) was calculated according to the following equation

$$\text{TOF} = J \times A / (z \times F \times n) \quad (3)$$

where J is the current density at a specific potential (A/cm^2), A is the surface area of the Ni foam (1 cm^2), z is the number of electrons transferred in the OER and UOR ($z = 4$ in the OER, and $z = 6$ in the UOR), F is the Faraday constant ($96,485 \text{ C/mol}$), and n is the total number of moles of the active metal centers of the catalysts.

3 Results and discussion

The synthetic processes of NC-FNCP were schematically illustrated in Fig. 1. Firstly, Fe_2O_3 nanotubes were prepared by a facile hydrothermal method [48]. Secondly, the regular Fe_2O_3 nanotube@ZIF-67 composite nanostructure was formed by the nucleation and growth on the surface of PVP-modified Fe_2O_3

Figure 1 Schematic illustration of the synthesis of NC-FNCP.

nanotubes. Then the Fe_2O_3 nanotube@ZIF-67 was further used to react with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, where ZIF-67 acts as a self-sacrificing template. During this process, the generated protons from the hydrolysis of Ni^{2+} ions etch the ZIF-67 nanoparticles, meanwhile, the released Co^{2+} ions from ZIF-67 are partially oxidized. As a result, $\text{Co}^{2+}/\text{Co}^{3+}$ *in situ* co-precipitate with Ni^{2+} as Ni-Co LDH layers around the ZIF-67 dodecahedron. As Co^{3+} continues to flow outwards, the solid ZIF-67 becomes vulnerable and eventually generates the outer hollow nanocages [30]. Finally, the Fe_2O_3 @ZIF-67/Ni-Co LDH are chemically converted into NC-FNCP by $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ treatment at 350°C for 2 h in an inert atmosphere. As a result, the nested hollow NC-FNCP composed of Fe-Co-Ni tri-metal phosphides and nitrogen-doped carbon is achieved.

The precursors and the final product NC-FNCP were characterized by SEM and TEM images. The synthesized Fe_2O_3 displays a uniform hollow nanotube morphology with a smooth and tidy surface (Figs. 2(a) and 2(b)). The length of the nanotubes is about 200–400 nm, and the outer and inner diameters of the nanotube are 90–110 and 40–80 nm, respectively (Fig. 2(c)). Fe_2O_3 nanotube@ZIF-67 has an outer dodecahedral polyhedral structure with a very uniform size (ca. 400–600 nm) (Figs. 2(d)–2(f)), which is the same as that of the pure ZIF-67. Fe_2O_3 nanotubes and Fe_2O_3 nanotube@ZIF-67 were also further studied by XRD (Fig. S1 in the Electronic Supplementary Material (ESM)). After the etching of ZIF-67 and the coprecipitate process of $\text{Co}^{2+}/\text{Co}^{3+}$ ions with Ni^{2+} , the as-formed Fe_2O_3 nanotube@ZIF-67/Ni-Co LDH inherits the dodecahedron morphology and the dimension of Fe_2O_3 nanotube@ZIF-67 but shows rough surfaces (Fig. 2(g)). TEM unambiguously reveals that the ZIF-67 layers convert to the hollow dodecahedron nanostructures and the surface is assembled by LDH nanoflakes. As a result, with a hollow Fe_2O_3 nanotube inside, the etched product shows a unique nested hollow architecture (Figs. 2(h) and 2(i)). XRD patterns still show slight diffractions of ZIF-67 (Fig. S2 in the ESM), demonstrating that ZIF-67 was not thoroughly transformed into Ni-Co LDH during the etching process.

After phosphatization treatment, the SEM (Fig. 3(a)) and TEM (Figs. 3(b) and 3(c) images illustrated that the obtained NC-FNCP maintained similar morphologies with that of Fe_2O_3 nanotube@ZIF-67/Ni-Co LDH precursor. Similar phenomenon could also be found in the synthesis of FeP_4 nanotubes (Fig. S3 in the ESM) and Ni-Co-P nanocages (Fig. S4 in the ESM). However, careful observations indicated that the outer shell of NC-FNCP was composed of amorphous carbon-decorated nanoparticles with size of ca. 5 nm (Figs. 3(d)–3(f)). These nanoparticles were interconnected with each other, which was beneficial for the electron transfer. HRTEM measurements were further applied to give more detailed structural information of NC-FNCP. The

Figure 2 (a) SEM, (b) and (c) TEM images of the Fe_2O_3 nanotubes. (d) SEM, (e) and (f) TEM images of Fe_2O_3 nanotube@ZIF-67. (g) SEM, (h) and (i) TEM images of Fe_2O_3 nanotube@ZIF-67/Ni-Co LDH.

Figure 3 (a) SEM, (b) and (c) TEM images of NC-FNCP. (d)–(i) HRTEM images of NC-FNCP. (j) SAED image of NC-FNCP and (k) EDS mapping images of NC-FNCP.

interplanar spacings of 0.28, 0.20, and 0.19 nm were consistent with the (211) plane of CoP, (130) plane of FeP₄, and the (112) plane of Ni₃P, respectively (Figs. 3(g)–3(i)). Selected area electron diffraction (SAED) patterns (Fig. 3(j)) confirmed the existence of three phosphide phases, e.g., CoP, Ni₃P, and FeP₄. Elemental mapping images were obtained to further demonstrate the surface elements and their distribution. Figure 3(k) displays the EDS mapping images revealing those elements of Co, Fe, Ni, P, C, and N for NC-FNCP. Energy-dispersive X-ray spectroscopy (EDX) result showed that the Fe/Co/Ni mass ratio in the NC-FNCP yolk-shelled structure was about 1:0.45:0.72 (Fig. S5 in the ESM). The chemical composition of the sample was further measured using ICP-OES (Table S1 in the ESM). The Fe/Co/Ni atomic ratio was about 1:0.26:0.52, which was very close to the EDX result. Those results revealed that the homogeneous hybrid of the FeP₄ and Ni-Co-P phases. To evaluate the specific surface areas and the pore size distribution of NC-FNCP, N₂ adsorption-desorption isotherm was recorded in Fig. S6 in the ESM. The sample showed a nearly type-IV signal with the BET surface area of 14.4 cm²/g. The corresponding Barrett-Joyner-Halenda (BJH) curve delivered that NC-FNCP presented a well-defined mesoporous structure.

XRD analysis was revealed in Fig. 4(a), the peaks of the NC-FNCP are corresponding with the standard card CoP (JCPDS No. 29-0497), FeP₄ (JCPDS No. 32-0471) and Ni₃P (JCPDS No. 34-0501), respectively. Typical diffraction peaks located at 31.6°, 36.3°, 46.2°, 48.1°, 56.0° and 56.7° are corresponding to the crystal faces of CoP (011), (111), (112), (211), (020) and (301). Diffraction peaks at 31.8°, 35.8°, 38.2°, 39.5°, 43.4°, 46.0° and 53.9° can be attributed to the crystal faces of FeP₄ at (130), (131), (112), (201), (221), (132) and (241). And the remaining characteristic diffraction peaks centered at 41.8°, 45.2°, 46.6°, 50.6° and 52.7° represent lattice planes of (231), (112), (240), (141), (222), and (132) in Ni₃P, respectively.

XPS measurement was actualized to study the surface composition and bonding state of the final product NC-FNCP [49, 50]. The XPS survey spectra of NC-FNCP (Fig. S7 in the ESM) contain elements of Ni, Co, Fe, P, C, N, and O. The XPS spectra of each element are presented in Figs. 4(b)–4(f). As for Ni 2p (Fig. 4(b)), two peaks with a binding energy difference of about 17.7 eV, namely Ni 2p_{1/2} (870.9 eV) and Ni 2p_{3/2} (853.2 eV), confirming the predominance of Ni²⁺ valence [51]. The peaks at

856.6 and 875.5 eV belong to Ni³⁺, while the other two peaks around 857.0 and 882.6 eV are assigned to satellite peaks [52]. As for Co 2p (Fig. 4(c)), the peaks of 793.7 and 778.6 eV from Co³⁺, and the peaks 781.1 and 797.8 eV from Co²⁺ correspond to 2p_{1/2} and 2p_{3/2} of Co 2p, respectively [20]. The remaining peaks of 803.6 and 786.3 eV are satellite peaks [53]. Moreover, no peaks matched with zero-valence nickel and cobalt are confirmed, indicating that the outer shell of NC-FNCP is completely covered by Ni₃P and CoP. For the Fe XPS spectra (Fig. 4(d)), the peaks of Fe 2p_{3/2} (710.2 and 713.2 eV) and Fe 2p_{1/2} (724.3 and 727.8 eV) are observed, corresponding with the higher oxidation states of Fe²⁺ and Fe³⁺, respectively. The slight peak centered at 706.7 eV correspond to the Fe species in NC-FNCP [19]. Compared to Ni-Co-P, the binding energy of Co 2p and Ni 2p of NC-FNCP were negatively shift of 0.6 and 0.5 eV, suggesting the synergy interaction between FeP₄, Ni₃P and CoP (Fig. S8 in the ESM). The three peaks at 284.5, 285.7 and 288.8 eV of C 1s spectra (Fig. 4(e)) indicated the presence of C–C, C=N and O=C–O functional groups for NC-FNCP. In P 2p spectra (Fig. 4(f)), the fitting peaks centered at 129.6 and 129.1 eV corresponding to the P 2p_{1/2} and P 2p_{3/2} of metal phosphides, while the peak at around 133.6 eV belongs to the P–O bonds, which can attribute to partial oxidation of metal phosphides NC-FNCP [54].

The OER performance of NC-FNCP was assessed in 1.0 M KOH by using a traditional three-electrode cell. For comparison, hollow Ni-Co-P nanocages, Fe-P nanotubes, and commercial RuO₂ catalysts were also evaluated with the same condition. Figure 5(a) presents the LSV curves of different samples with IR correction. The NC-FNCP electrode shows a lower overpotential of 287 mV at 50 mA/cm² for OER, which is superior to RuO₂ (306 mV), Ni-Co-P (339 mV), and FeP₄ (368 mV) electrodes. As shown in Table S2 in the ESM, compared to the other related materials, the OER performance of NC-FNCP is outstanding. Moreover, the catalytic activity of NC-FNCP is also higher than all compared samples at the high current density. Such excellent performance may result from the synergistic combination of tricomponent metal catalytic centers (Fe, Co, and Ni) effectively facilitating the charge transfer efficiency. Tafel slope was calculated according to the LSV curves to describe the kinetics of OER (Fig. 5(b)). Tafel slope for NC-FNCP is 51.2 mV/decade, smaller than those for Ni-Co-P (77.1 mV/decade) and FeP₄ (96.1

Figure 4 (a) XRD patterns; XPS spectra (b) Ni 2p; (c) Co 2p; (d) Fe 2p; (e) C 1s and (f) P 2p of NC-FNCP.

Figure 5 Electrochemical measurements for the OER in 1 M KOH solution. (a) LSV curves and (b) corresponding Tafel plots of the RuO₂, FeP₄, Ni-Co-P and NC-FNCP samples. (c) The fitted C_{dl} of the above samples, (d) Nyquist plots and (e) TOF values of the above samples. (f) The Chronopotentiometry curves of the NC-FNCP at 25 mA/cm² inset of (f) showing LSV curves of the NC-FNCP before and after 1,000 CV cycles.

mV/decade), hinting at the favorable OER reaction kinetics of NC-FNCP. The double-layer capacitances (C_{dl}) were analyzed from CV curves to estimate the electrochemically active surface areas. Derived from the CV at different scan rates (Fig. S9 in the ESM), the extracted C_{dl} of NC-FNCP, Ni-Co-P and FeP₄ were 12.36, 7.35 and 2.84 mF/cm², respectively (Fig. 5(c)). The larger C_{dl} of NC-FNCP further confirms the advantage of the nested hollow architectures. The Nyquist plots derived from EIS were applied to reveal the charge transfer resistance (R_{ct}) at the electrolyte/catalyst interface (Fig. 5(d)). As shown in Table S3 in the ESM, the R_{ct} of NC-FNCP is the smallest among all the samples. This result demonstrated that NC-FNCP has a faster charge transfer rate and favorable OER kinetics. TOF as a considerable kinetic parameter can be used to depict the intrinsic activities of electrocatalysts [17]. It was supposed that all the metal sites in NC-FNCP are electrocatalytically active. According to the TOF equation, the TOF results are described in Fig. 5(e), NC-FNCP shows the highest TOF (0.041 s⁻¹ at $\eta = 1.55$ V) in the OER process. These results are identified with the Tafel slope analysis. To investigate the stability of the NC-FNCP electrode for practical applications, coherent CV and long-term chronopotentiometry were performed. Two LSV curves show slight differences and the performance even improved after the 1,000 CV cycles (Fig. 5(f)). In addition, the chronopotentiometry measurements demonstrate the outstanding stability of the NC-FNCP electrode after continuous OER operation for 18 h at the current density of 25 mA/cm².

To ensure the genuine active species of NC-FNCP during the OER and UOR processes, the electrodes after OER/UOR long-term stability measurement were evaluated by XPS analysis. As shown in Figs. S10(b)–S10(d) in the ESM, all peaks in the regions of Co 2p, Ni 2p, and Fe 2p XPS spectra clearly showed that trivalent oxyhydroxide became a predominant metal species after OER electrolysis. Compared with the original sample, all the peaks (Co 2p, Ni 2p, and Fe 2p) shift toward more positive binding energies, and the area ratio of the relative peaks of Co³⁺/Co²⁺, Ni³⁺/Ni²⁺, and Fe³⁺/Fe²⁺ increase, indicating that those metals were oxidized to higher valence states. Meanwhile, those metal phosphides disappear, which is consistent with the disappearance of metallic P with binding energy of 129.1 and 130.2 eV (Fig. S10(e) in the ESM) signal and the appearance of lattice oxygen signal with a binding energy of 529.5 eV (Fig. S10(f) in the ESM).

Thus, we conclude that at least the surface of the catalyst is oxidized to oxide/(oxy) hydroxide species after the electrochemical process, and the *in-situ* phase transformation may contribute to the high OER activity and good stability of the heterometallic phosphide catalyst. The surface layer of these oxide/(oxy) hydroxide species was in amorphous forms (Fig. S11 in the ESM), which was in good agreement with previous studies. Additionally, the SEM image recorded after the OER stability test exhibits that the original architectures of the catalyst are still well maintained (Fig. S12 in the ESM), which in part justify the cycle stability of NC-FNCP.

To assess the main active centers of the as-prepared phosphides, DFT calculations were further performed to calculate the adsorption/desorption energies of oxygen-containing intermediates (OH*, O*, and OOH*) at the interface of catalysts. In consideration of the HRTEM results, the facets of (130), (112), and (211) were employed for FeP₄, Ni₃P, and CoP, respectively (Figs. S13–S15 in the ESM). Based on the diagram in Fig. S16 and Table S4 in the ESM, the rate-determining step for the three catalysts was the conversion of O* to OOH* species during the OER process. It can be seen that the CoP exhibited a significantly smaller ΔG value of 1.762 eV for the rate-determining step (RDS) than that of Ni₃P (2.536 eV) and FeP₄ (2.704 eV), confirming a more favorable OER kinetics on the CoP model. Moreover, one can found that all four steps on the surface of CoP are thermodynamically uphill at potential $U = 0$ V. When U increases to 1.815 V, the highest ΔG value of the OER elementary steps decreases to 0 eV, which implied that the entire OER process could proceed spontaneously over this potential. Based on these results, we speculate that the Co sites may be the main active metal centers of NC-FNCP.

The above results indicate that NC-FNCP shows obvious potential toward OER, which motivates further study on NC-FNCP for UOR. UOR was carried out using the same three-electrode setup as OER except that the different concentrations (0, 0.33 and 0.5 M) of urea were added to 1.0 M KOH as the electrolyte. LSV curves show that the anodic current increased extensively after adding urea (Fig. S17 in the ESM). Moreover, the needed operation voltage is 1.41 V to drive 50 mA/cm² with 1.0 M KOH + 0.5 M urea, which is 111 mV smaller than that of the OER process in the same condition. This means that UOR consumes less energy [55]. For the comparison, the further experiments were

measured in the condition of 1 M KOH + 0.5 M urea. As depicted in Fig. 6(a), the NC-FNCP electrode only needs operation voltages of 1.37, 1.44, and 1.48 V (vs. RHE), to attain current densities of 10, 100, and 200 mA/cm², respectively, which are far superior to the control cases by using Ni-Co-P (1.41, 1.49, and 1.54 V) and FeP₄ (1.44, 1.54, and 1.57 V). The performance of NC-FNCP is also preferable to those of the recently-related electrocatalysts (Table S5 in the ESM). As an important parameter to evaluate kinetics, the Tafel slope also supports the above results (Fig. 6(b)) [23]. The Tafel slope of NC-FNCP is 35.79 mV/dec, which is smaller than that of Ni-Co-P (75.85 mV/dec) and FeP₄ (97.26 mV/dec). Compared with OER, these low Tafel slope values indicate that the energy efficiency of hydrogen generation is improved for UOR [53]. The larger C_{dl} (Fig. 6(c)) derived from CV of NC-FNCP (Fig. S18 in the ESM) compared to those of control samples indicated that the nested hollow NC-FNCP could afford more accessible active reaction sites for UOR. It was further verified by the favorable charge transport process of NC-FNCP revealed by EIS measurement (Fig. 6(d)). A smaller R_{ct} (25.4 Ω) is found for the NC-FNCP electrodes by fitting the Nyquist plot (Table S3 in the ESM). These results indicated that the nitrogen-doped carbon can accelerate electron transfer and the nested hollow architectures are beneficial to promote electrolyte transfer. In addition, the TOF of NC-FNCP was identified as 0.82 s⁻¹ at η = 1.36 V (Fig. 6(e)), larger than those of the controls, demonstrating the synergistic effects of the combination of tricomponent metal catalytic centers. Furthermore, chronopotentiometry measurement was obtained to assess the UOR durability for the NC-FNCP electrode (Fig. 6(f)). The potential of 95% was maintained after 12 h continuous urea electrolysis at 10 mA/cm², suggesting the excellent UOR stability for the NC-FNCP electrode. To further investigate genuine species during the catalytic UOR, XPS analysis was also employed to evaluate the catalyst after the UOR stability test (Fig. S19 in the ESM). It was found that the change trends in the binding energies of Co 2p, Ni 2p, Fe 2p, P 2p, and O 1s were similar to the case of OER, which implies that the surface oxidation also occurred during UOR, and this surface layer is amorphous as seen in the HRTEM image (Fig. S20 in the ESM). In addition, as shown in Fig. S21 in the ESM, the structure of the catalyst also remains well. It was then convinced that the synergistic effects of these active species and well-maintained structures

ensure the UOR performances.

The hydrogen evolution reaction (HER) performance of NC-FNCP was also obtained in 1.0 M KOH with and without 0.5 M urea, and the results are depicted in Fig. S22 in the ESM. It was found that the potentials required for HER have a difference of 41 mV to reach the current density of 50 mA/cm² in 1.0 M KOH with and without 0.5 M urea. However, with the increase of current density, the presence of urea shows little effect on HER performance. According to Figs. S23(a) and S23(c) in the ESM, the NC-FNCP electrode at 10 mA/cm² requires relatively low potentials of 145 and 157 mV in 1.0 M KOH with and without 0.5 M urea, respectively. The potentials of NC-FNCP were also lower than those of Ni-Co-P and FeP₄ electrodes. Additionally, Tafel slopes obtained from LSV curves are shown in Figs. S23(b) and S23(d) in the ESM, the NC-FNCP electrode exhibits the smallest Tafel slope compared with Ni-Co-P and FeP₄ electrodes, indicating its favorable HER kinetics.

All the above results imply that NC-FNCP has potential for overall water and urea electrolysis. In consideration of the practical application and energy conversion, a two-electrode electrolyzer was set up using NC-FNCP as both anode and cathode in 1 M KOH with and without the addition of 0.5 M urea. As shown in Fig. 7(a), to deliver the current density of 10 mA/cm², the cell voltage of urea electrolysis is 1.52 V, which is about 110 mV lower than that of water electrolysis. The required cell voltages to attain higher current densities (20, 50, and 100 mA/cm²) are also much lower than those required for water electrolysis (Fig. 7(b)), implying the urea electrolysis process consumes less energy. In addition, the long-term durability of water (Fig. 7(c)) and urea (Fig. 7(d)) electrolysis was examined by chronopotentiometry measurements. As for urea electrolysis, the NC-FNCP/NC-FNCP electrode maintained a high voltage of 96% after 20 h at 10 mA/cm². Those results demonstrate that NC-FNCP has superior performance overall water and urea splitting as well as good stability.

The high performances of nested hollow architectures of NC-FNCP for water and urea electrolysis mainly due to the following reasons: (1) The synergistic combination of tricomponent metal catalytic centers (Fe, Co, and Ni) effectively altering the electronic structure and facilitating the charge transfer efficiency. (2) The nested porous hollow architectures with large specific surface areas

Figure 6 Electrochemical measurements for the UOR in 1 M KOH and 0.5 M urea solution. (a) LSV curves and (b) corresponding Tafel plots of the FeP₄, Ni-Co-P and NC-FNCP samples. (c) the fitted C_{dl} of the above samples, (d) Nyquist plots and (e) TOF values of the above samples. (f) The Chronopotentiometry curves of the NC-FNCP at 10 mA/cm².

Figure 7 (a) LSV curves for the NC-FNCP|NC-FNCP electrode in 1.0 M KOH with (blue line) and without (red line) 0.5 M urea. (b) Comparison of the required voltage at different current densities for overall water and urea electrolysis. (c) Chronopotentiometry plots of water electrolysis implemented at different current densities. (d) Chronopotentiometry plots of urea electrolysis implemented at the current density of 10 mA/cm².

are conducive to the full contact of the electrolyte/electrode and facilitate the release of bubbles. (3) The existence of N-doped carbon composition can improve electronic conductivity and facilitate rapid electron/mass transport. Thus, the strategy of building the nested hollow architectures with multicomponent TMPs could be extended to other metal phosphides for electrocatalysis.

4 Conclusions

In summary, nested hollow architectures of NC-FNCP were successfully fabricated through a facile method. Due to the unique structural features and trimetallic compositions, NC-FNCP shows superior boosting electrocatalytic activities by reducing the resistance for ion transportation, accelerating the diffusion of gases, and enhancing the utilization of electroactive species compared to the single hollow Ni-Co-P nanocages and FeP₄ nanotubes. As a result, NC-FNCP requires a low overpotential of 248 mV and 1.37 V (vs. RHE) to achieve the current density of 10 mA/cm² for OER and UOR, respectively. When used as a bifunctional catalyst toward urea-assisted hydrogen generation, the NC-FNCP requires a cell voltage of 1.52 V to deliver 10 mA/cm² with long-term electrochemical durability for 20 h. This work exhibits an inexpensive catalyst system with multiple-component and multi-shell hollow nanostructures, thus paving a path to devise the high-performance bifunctional electrodes for the energy-efficient combination of hydrogen generation and sewage treatment.

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