Morphological and Electronic Dual Regulation of Cobalt–Nickel Bimetal Phosphide Heterostructures Inducing High Water-Splitting Performance

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ABSTRACT: Electrocatalytic water splitting (EWS) is a key technology for generating clean and sustainable hydrogen, which can store abundant energy but is impeded by the insufficient efficiency of the anode and cathode catalyst. Designing and constructing non-noble metal composite bifunctional electrocatalysts for promoting both the cathodic hydrogen evolution (HER) and anodic oxygen evolution reactions (OER) is clearly of great importance for EWS. Thus, the chemical composition and morphology of cobalt–nickel bimetal phosphide (Ni, Co)2P nanoparticles (NPs) encapsulated in nitrogen-doped carbon nanotube hollow microspheres (NCNHMs) can regulate the redox-active sites and enhance the electron transfer, resulting in superior splitting efficiency. Contributing to the synergistic effects between highly active Co–Ni bimetal phosphide NPs and NCNHMs, the obtained Co–Ni bimetal phosphide/NCNHMs display remarkable electrochemical performance for water splitting compared with Ni,P/NCNHMs. Therefore, the Ni1.4Co0.6P/NCNHMs catalysts achieved through a nitriding–phosphidation strategy derived from a hollow Ni1.4-Co0.6-based metal organic framework (MOF) exhibit superior HER catalytic activity (87.9 mV at 10 mA cm−2 tested in 0.5 M H2SO4 and 64.4 mV at 10 mA cm−2 tested in 1 M KOH) and OER catalytic activity (320.0 mV at 10 mA cm−2 tested in 1 M KOH). The Ni1.4Co0.6P/NCNHMs deliver excellent water-splitting catalytic activity (1.55 V at 10 mA cm−2 tested in 1 M KOH), which is competitive with that of current non-noble metal electrocatalysts. Density functional theory (DFT) simulations and related experimental results suggest that the electron transfer from Co doping and coating with NCNHMs improves the electronic states, which would enhance the binding strength with H-bonds and then promote the electrocatalytic activity.

Innovative energy conversion and storage technologies for use with new energy sources are greatly required to alleviate the increasing global energy crisis and environmental problems in the 21st century.1,2 Motivated by the challenges associated with the intermittent nature of renewable energy technologies such as tidal, wind, and solar energy, electrocatalytic production of hydrogen based on electrochemical electrocatalytic water splitting (EWS) will effectively mitigate these issues.3−7 Briefly, the operational efficiency of EWS is strongly dependent on the activity of the electrocatalysts for two fundamental half-reactions, namely, the hydrogen evolution reaction (HER) in the cathode and the oxygen evolution reaction (OER) in the anode.8−10 In recent years, numerous highly efficient noble metal-based HER and OER catalysts have been reported (Pt-based and Ru/Ir-based), respectively. However, these catalysts suffer from high cost, inadequate resources, and low durability, severely restricting their practical applications.11−15 Significant effort has been devoted to fabricating highly efficient and nonprecious metal bifunctional EWS electrocatalysts, including some promising nonprecious metal-based materials and some nonmetal electrocata-

1−4,8,9,16−23 Thus, constructing inexpensive and highly effective bifunctional electrocatalysts to replace these noble metal-based electrocatalysts for real application of EWS is highly urgent.

Recently, transition-metal phosphides (TMPs; M = W, Mo, Cu, Co, Fe, Ni) with similarity to hydrogenase have received special attention in view of their nontoxicity, low cost, and catalytic activity toward HER and OER.23−30 Among them, nickel phosphides obtained a better HER catalytic activity,14,15,31 Nevertheless, the efficiency of OER for nickel phosphide electrocatalysts is still inferior to that of noble metal-based catalysts and faces great challenges.

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owing to unsatisfactory surface activity and conductivity. To maximize the catalytic activity, the nanostructure and composition of the nickel phosphide catalysts can be optimized to exhibit more synergistically active sites and stability and to promote the reductive and oxidative proton-coupled electron transfers for water splitting. Therefore, optimizing the surface atomic coordination and electronic structure by introducing other metal atoms into the crystal lattices of nickel phosphides is a highly attractive and effective strategy. After this, the kinetic energy barriers of the catalytic reaction were reduced, thus leading to the enhanced electrochemical catalytic activity. For example, Liu and co-workers revealed low-electronegativity Mn-doped nickel phosphide matrices could effectively increase the charge density around the Ni center and reduce the rate-determining Gibbs free energy $\Delta G_{\text{OOH}} - \Delta G_{\text{O}}$ difference for the OER, which can benefit $\text{O}_2$ evolution. Wang and co-workers report the fabrication of Ni$_x$FeP@NPC heterostructures, and superior electrocatalytic OER performances can be obtained via the introduction of Fe into Ni$_x$P matrices. Even though TMP-based OER electrocatalysts have advanced, further improvement of the OER performance is restricted by their unsatisfactory electronic conductivity and an inadequate number of active sites. In situ grown nitrogen-doped carbon nanotubes covering active TMP NPs forming hollow porous carbon nanostructures could enrich the active sites, supply the efficient well-defined inner channels for efficient mass and charge transport, and then promote the sluggish OER. Therefore, it is a great challenge to fabricate and construct advanced bimetal TMPs with regulated electron states, abundant exposed active sites, and high conductivity to display satisfactory catalytic activity for overall EWS.

Motivated by the above considerations, we for the first time designed and fabricated a bifunctional catalyst composed of uniform disperse Co–Ni bimetal phosphides nanoparticles (NPs) encapsulated in NCNHMs through an in situ nitriding–phosphidation method from uniform Ni and Co atom dispersed hollow MOFs as templates. Compared with Ni$_3$P alone, Co substitution in the primitive Ni$_3$P lattices effectively regulates the electronic structure to govern the binding energies, enhancing the electrocatalytic performance. Notably, the Ni$_{1.4}$Co$_{0.6}$P/NCNHMs present low overpotentials of 87.9 and 64.4 mV at 10 mA cm$^{-2}$ for HER (0.5 M H$_2$SO$_4$ and 1 M KOH) and 320.0 mV at 10 mA cm$^{-2}$ for OER (1 M KOH), respectively. Consequently, for the overall EWS, the Ni$_{1.4}$Co$_{0.6}$P/NCNHMs show a voltage of 1.55 V at 10 mA cm$^{-2}$ along with high stability. Experimental observations demonstrate that the excellent HER or OER performance of Ni$_{1.4}$Co$_{0.6}$P/NCNHMs bifunctional catalyst, which can produce sufficient localized reactive sites by Co doping and in situ growth of TMP-encapsulated N-doped carbon nanotubes (NCNTs), thereby enhancing its EWS kinetics.  

### Scheme 1. Synthetic Route of Ni$_{1.4}$Co$_{0.6}$P/NCNHMs

[Diagram showing the synthetic route of Ni$_{1.4}$Co$_{0.6}$P/NCNHMs]

The synthesis and characterization of Ni$_{1.4}$Co$_{0.6}$P/NCNHMs illustrate the feasibility of fabricating such bifunctional catalysts. First, the hollow Ni$_{1.4}$Co$_{0.6}$BTC microspheres were fabricated via a simple hydrothermal method with nickel nitrate, cobalt nitrate, and BTC as metal source and organic ligand reagent, respectively. Polyvinylpyrrolidone (PVP) was applied as the stabilizing component to demonstrate a spherical hollow structure for the fabrication of MOFs. The crystal structure of Ni$_{1.4}$Co$_{0.6}$BTC microspheres is similar to that of the previously reported Ni-BTC microspheres. The powder X-ray diffraction (XRD) analysis reveals that the crystal structure of Ni$_{1.4}$Co$_{0.6}$BTC microspheres is similar to that of the previously reported Ni-BTC microspheres. It should be noted that the difference between the nominal and real Ni/Co molar ratios in the MOF precursors refers to the hollow MOF formation mechanism. The molar ratio of Ni:Co in Ni$_{1.4}$Co$_{0.6}$BTC is about 1.4:0.6, as confirmed by inductively coupled plasma mass spectrometry (ICP-MS). Subsequently, by temperature-programmed annealing and nitriding treatment of such precursors at 800 °C under N$_2$ atmosphere, the Ni$_{1.4}$Co$_{0.6}$/NCNHMs sample was obtained. In this process, the Ni and Co ions within the hollow framework were gradually transformed into uniform nickel and cobalt nanoparticles while the BTC were in situ carbonized.
formatted to porous carbon hollow microspheres. With the gradual increase of the calcination temperature, the nitrogen-doped carbon nanotubes are gradually extruded from the hollow carbon spheres under the catalysis of the metal nickel and cobalt nanocrystals.42,44

As shown in the XRD pattern of Ni$_{1.4}$Co$_{0.6}$/NCNHMs (Figure S2), three sharp peaks appear at 44.38°, 51.72°, and 76.15° between those of Ni (JCPDS No. 04-0850) and Co (JCPDS No. 15-0806), which should be related to the (111), (200), and (220) facets for the Co or Ni FCC structure, demonstrating that the Ni−Co alloy NPs are...

Figure 2. (a and b) SEM images, (c) TEM image, (d) HAADF-STEM elemental mapping, (e) magnified SEM image, and (f and g) high-magnification TEM images for the Ni$_{1.4}$Co$_{0.6}$/NCNHMs HMs.

Figure 3. (a) XRD pattern; (b) Brunauer–Emmett–Teller (BET) surface area measurement; (c) Co 2p, (d) Ni 2p, (e) P 2p, and (f) N 1s XPS spectra for Ni$_{1.4}$Co$_{0.6}$/NCNHMs electrocatalyst.

As shown in the XRD pattern of Ni$_{1.4}$Co$_{0.6}$/NCNHMs (Figure S2), three sharp peaks appear at 44.38°, 51.72°, and 76.15° between those of Ni (JCPDS No. 04-0850) and Co (JCPDS No. 15-0806), which should be related to the (111), (200), and (220) facets for the Co or Ni FCC structure, demonstrating that the Ni−Co alloy NPs are...
embedded on N-doped carbon hollow microspheres. The broad peak at 25.91° was related to the (002) plane of graphitic carbon. The SEM and TEM images (Figure S3a−c) confirm that the Ni1.4Co0.6/NCNHMs display hollow microspheres with a rough surface endowed with numerous NCNTs, and the Ni1.4Co0.6 nanoparticles are inside the N-doped carbon shells of hollow microspheres and the tips of NCNT. Further, Ni1.4Co0.6/NCNHMs can be indicated by the HRTEM lattice graph in Figure S3d; the marked d-spacing of 0.202 nm matches well to that of the (111) plane of Ni1.4Co0.6 nanoparticles. Additionally, the energy-dispersive spectrometry (EDS) mapping images (Figure 2d) also indicate that C, N, Ni, Co, and P elements were uniformly distributed into the Ni1.4Co0.6P/NCNHMs. By integration calculation, the molar ratio of Ni, Co, and P elements is about 1.4:0.6:1, indicating that the Ni1.4Co0.6P component may exist in the sample. The Ni1.4Co0.6P nanoparticles with ultrasmall size (ranging from 10 to 20 nm) are imbedded into the tips of NCNTs and hollow N-doped carbon microspheres (Figure 2e). The high-resolution TEM images (Figure 3f,g) show the distinct lattice fringes with the d-spacing of about 0.221 nm, which is similar to the (111) planes of Ni1.4Co0.6P. Interestingly, some twin crystal defects and grain boundaries (marked by white dashed lines) are presented in the Ni1.4Co0.6P nanoparticles. We propose that the thermal and emitted gases can lead to high stresses, which may support the fabrication of defects in Ni1.4Co0.6P nanoparticles, especially for formation of the twin crystal structures. These exposed defects at the crystalline catalyst surface could provide more electroactive sites and be beneficial for catalytic application (Figure S9).

The component and phase structures of Ni1.4Co0.6P/NCNHMs were further investigated by XRD (Figure 3a). The diffraction peaks centered at 40.79°, 47.44°, and 47.44° correspond to (111), (220), and (311) planes of the hexagonal...
phase for Ni$_2$P (PDF 65-3544). Compared with pure Ni$_2$P/NCNHMs, after the substitution of Co atoms, the positions of XRD peaks for Ni$_{1.4}$Co$_{0.6}$P/NCNHMs shift toward the higher angles, illustrating the successful doping of Co into the lattice of the Ni$_2$P matrix (Figure S6c). These results confirm the fabrication of a ternary Ni$_{1.4}$Co$_{0.6}$P compound rather than the mixture phase of two materials. The Ni adsorption-desorption measurements (Figure 3b) suggest that the Ni$_{1.4}$Co$_{0.6}$P/NCNHMs possess a large specific surface area of 131.5 m$^2$ g$^{-1}$, with a total pore volume of 0.261 cm$^3$ g$^{-1}$. The presence of abundant mesoporous structure facilitates the easy entry of reactant molecules to the inner surface of the catalyst, which can favor the increase of active sites.$^{51,52}$ Because surface chemistry governs the electrochemical activity of the electrocatalyst, it is vital to detect the surface chemical states of as-prepared samples by X-ray photoelectron spectroscopy (XPS) measurement. As displayed in the high-resolution Co 2p XPS results (Figure 3c), the two peaks at 794.1 and 779.2 eV relate to the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ of Co$^{2+}$ species in Co–P, which have a larger partial positive charge compared with Co metal (777.9 eV).$^{53,54}$ The peaks at 798.5 and 782.1 eV are indexed to partial Co$^{2+}$ oxide species, while the two broad peaks at 803.6 and 785.8 eV are related to the shake up satellite peak (Sat).$^{54}$ Similarly, as for the Ni 2p XPS results, the obvious peaks located at 871.2 and 853.6 eV are related to the Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ of Ni$^{2+}$ species, respectively, along with two broad satellite peaks located at 875.2 and 861.84 eV. It is worth noting that the binding energy (853.6 eV) for Ni species in Ni$_{1.4}$Co$_{0.6}$P/NCNHMs is positively shifted in comparison with the value (853.3 eV) in Ni in Ni$_2$P, indicating the electron transformation from Ni to Co in the Ni$_{1.4}$Co$_{0.6}$P/NCNHMs electrocatalyst.$^5$ The charge redistribution will be obtained from this strong interaction, which could favor the OH$^-$ adsorption.$^{24,51}$ Regarding the XPS spectrum of P 2p (Figure 3e), the three obvious peaks at 129.7, 130.3, and 134.9 eV could be related to the P 2p$_{3/2}$, P 2p$_{1/2}$ in metal phosphide, and oxidized P species, respectively. Four N types (Figure 3f), containing pyridinic (398.6 eV, 27.4%), pyrrolic (400.2 eV, 25.5%), graphitic N (400.6 eV, 23.5%), and quaternary N (401.1 eV, 23.6%), could be observed from the N 1s XPS spectrum. The presence of the pyrrolic N and pyridinic N in the Ni$_{1.4}$Co$_{0.6}$P/NCNHMs catalyst can enhance the electrocatalytic efficiency via interacting with H$^+$ for the HER.$^5$ The above analysis demonstrates that as-prepared Ni$_{1.4}$Co$_{0.6}$P/NCNHMs possess a novel porous nanostructure, charge redistribution, and rich boundary defects, which are excited to achieve remarkable electrocatalytic performances.

**Hydrogen Evolution Catalysis.** The HER of Ni$_{1.4}$Co$_{0.6}$P/NCNHMs catalyst was first demonstrated in an acidic environment (0.5 M H$_2$SO$_4$) and alkaline environment (1 M KOH) applying the three-electrode system. Meanwhile, the electrocatalytic performances of Ni$_{1.4}$Co$_{0.6}$P/NCNHMs, Ni$_{1.4}$Co$_{0.6}$P/HMs, Ni$_3$P/NCNHMs, Ni$_{1.4}$Co$_{0.6}$P/NCNHMs, and commercial Pt/C (20%) catalysts were also investigated. From Figure 4ac, the linear sweep voltammetry (LSV) results indicate that the Ni$_{1.4}$Co$_{0.6}$P/NCNHMs catalyst exhibits superior catalytic performance with lower overpotentials of 87.9 mV and 64.4 mV at 10 mA cm$^{-2}$ current density for HER in acidic and alkaline solution compared to Ni$_{1.4}$Co$_{0.6}$/NCNHMs (196.9 and 159.1 mV), Ni$_{1.4}$Co$_{0.6}$/HMs (114.8 and 91.7 mV), and Ni$_3$P/NCNHMs (137.5 and 107.8 mV), respectively, which can be comparable to the 20% Pt/C catalyst. In addition, the related Tafel slopes of Ni$_{1.4}$Co$_{0.6}$/NCNHMs (61 and 64 mV dec$^{-1}$) are also lower than those of Ni$_{1.4}$Co$_{0.6}$/NCNHMs (117 and 138 mV dec$^{-1}$), Ni$_{1.4}$Co$_{0.6}$/HMs (70 and 93 mV dec$^{-1}$), and Ni$_3$P/NCNHMs (75 and 119 mV dec$^{-1}$) in acidic and alkaline media, respectively, suggesting the superior electrocatalytic kinetics on the Ni$_{1.4}$Co$_{0.6}$/NCNHMs catalyst for HER performance (Figure 4b).

The Ni$_{1.4}$Co$_{0.6}$/NCNHMs catalyst displays HER electrocatalytic activity higher than that of other reported catalysts (Table S2–3, Supporting Information). Additionally, the Nyquist plots (Figure S10) also suggest that the Ni$_{1.4}$Co$_{0.6}$/NCNHMs show a smaller semicircle diameter than the other prepared catalyst, confirming an advantageous charge-transfer resistance ($R_d$) for Ni$_{1.4}$Co$_{0.6}$/NCNHMs in both acidic (8.5 Ω) and alkaline (12.7 Ω) media. Further, we also investigate the electrochemical active surface area (ECSA) of the catalyst by testing the double-layer capacitance ($C_d$) in acidic solution (0.5 M H$_2$SO$_4$) (Figure S11). The $C_d$ of the Ni$_{1.4}$Co$_{0.6}$/NCNHMs (13.41 mF cm$^{-2}$) is much greater than that of the Ni$_{1.4}$Co$_{0.6}$/NCNHMs catalyst Ni$_{1.4}$Co$_{0.6}$/NCNHMs (2.85 mF cm$^{-2}$), Ni$_{1.4}$Co$_{0.6}$/HMs (10.05 mF cm$^{-2}$), and Ni$_3$P/NCNHMs (4.09 mF cm$^{-2}$) (Figure S11e), which indicates that the Ni$_{1.4}$Co$_{0.6}$/NCNHMs catalyst has a large ECSA, suggesting high exposed active sites for the HER.$^5$ In addition, the Ni$_{1.4}$Co$_{0.6}$/NCNHMs catalyst displays a greater $C_d$ value in alkaline (1 M KOH) media (16.6 mF cm$^{-2}$) than in 0.5 M H$_2$SO$_4$ (Figure S12). The stability of the Ni$_{1.4}$Co$_{0.6}$/NCNHMs catalyst is further confirmed by the long-term chronoamperometry at 10 mA cm$^{-2}$. In addition, the current–time results (insets, Figure 4cf) show that the electrocatalytic activities of the Ni$_{1.4}$Co$_{0.6}$/NCNHMs catalyst were maintained for at least 24 and 22 h in acidic and alkaline media, respectively. From Figure 4cf, barely any change was found by comparing LSV results tested before and after long cycles. In addition, the SEM and TEM images reveal that the hollow microspheres composed of the N-doped carbon nanotube morphology of the Ni$_{1.4}$Co$_{0.6}$/NCNHMs catalyst displayed no obvious change after the long-term test (Figure S13). After electrochemical testing of Ni$_{1.4}$Co$_{0.6}$/NCNHMs in 1 M KOH solution, XPS analysis was conducted (Figure S14). When compared with the original spectra in Figure 3, the intensities and positions of the peaks relating to Ni 2p, Co 2p, and P 2p show no obvious changes, demonstrating that Ni$_{1.4}$Co$_{0.6}$/NCNHMs nanocrystals homogeneously encapsulated in nitrogen-doped carbon nanotubes have no chemical state conversion during the HER process.$^{56}$

To confirm the fundamental mechanism of the remarkable HER performance of the Ni$_{1.4}$Co$_{0.6}$/NCNHMs catalyst, the $\Delta G_{\text{H}^*}$ values on pristine Ni$_3$P and Ni$_{1.4}$Co$_{0.6}$/NCNHMs (Figure 4gh) with Co substitution at the atomic level were calculated (the calculation details are described in the Supporting Information). The $\Delta G_{\text{H}^*}$ is good descriptor of HER performance for the catalyst. A $\Delta G_{\text{H}^*}$ value close to 0 eV will cause the optimal HER performance, which can enhance the proton–electron-transfer process and is beneficial to the absorption and desorption steps between H$^+$ and the catalyst surface.$^{54}$ Noticeably, the Ni$_3$P with a negative $\Delta G_{\text{H}^*}$ of 0.38 eV is far from the ideal zero value and demonstrates the weak H-binding on the catalyst surface. After Co atom substitution for the lattice with 30% Ni atoms in Ni$_3$P, the $\Delta G_{\text{H}^*}$ of Ni$_{1.4}$Co$_{0.6}$/NCNHMs reduces to 0.25 eV, suggesting the strengthened H-binding is due to the abundant vacancies (Figure 4i). Thus, the highly
active HER performance is obtained on the Ni$_{1.4}$Co$_{0.6}$P/NCNHMs.

**Oxygen Evolution Catalysis.** Because the OER also plays a vital and significant role for overall EWS, the electrocatalytic OER performance of the Ni$_{1.4}$Co$_{0.6}$P/NCNHMs catalyst was then measured in 1 M KOH with a three-electrode configuration. For comparison, Ni$_{1.4}$Co$_{0.6}$/NCNHMs, Ni$_{1.4}$Co$_{0.6}$P/HMs, Ni$_{2}$P/NCNHMs, Ni$_{1.4}$Co$_{0.6}$P/NCNHMs, and commercial RuO$_{2}$ were also conducted. Figure 5a shows the LSV results of all the samples. The Ni$_{1.4}$Co$_{0.6}$P/NCNHMs show the highest electrocatalytic performance with the lowest overpotential of 320.0 mV at the 10 mA cm$^{-2}$ current density, which is better than those of Ni$_{1.4}$Co$_{0.6}$/NCNHMs (414.1 mV), Ni$_{1.4}$Co$_{0.6}$P/HMs (330.5 mV), and Ni$_{2}$P/NCNHMs (375.8 mV) catalysts and commercial RuO$_{2}$ (336.3 mV), further demonstrating the remarkably catalytic activity for OER of the Ni$_{1.4}$Co$_{0.6}$/NCNHMs catalyst.

Further, the Nyquist plots (Figure S15) also display that the Ni$_{1.4}$Co$_{0.6}$/NCNHMs catalyst ($R_{ct}$ = 14.5 Ω) shows lower charge-transfer resistance than the Ni$_{1.4}$Co$_{0.6}$/NCNHMs catalyst ($R_{ct}$ = 96.7 Ω), Ni$_{1.4}$Co$_{0.6}$/HMs catalyst ($R_{ct}$ = 25.4 Ω), and Ni$_{2}$P/NCNHMs ($R_{ct}$ = 73.2 Ω), suggesting high conductivity, remarkable mass transport, and mechanical properties in the OER test. The above results prove that the remarkable Ni$_{1.4}$Co$_{0.6}$/NCNHMs catalyst outperforms many of the reported Ni-based or Co-based nonprecious electrocatalysts for OER in 1 M KOH (Table S4, Supporting Information). To reveal the stability for OER, a chronopotentiometry long-term measurement was conducted at 10 mA cm$^{-2}$.

![Figure 5](https://dx.doi.org/10.1021/acs.jpclett.0c00851)

**Figure 5.** (a) LSV and (b) Tafel curves of obtained samples for OER (1 M KOH). (c) LSV of the Ni$_{1.4}$Co$_{0.6}$/P/NCNHMs sample before and after long cycles for OER (1 M KOH). (d) Polarization curves of Ni$_{1.4}$Co$_{0.6}$/P/NCNHMs and RuO$_{2}$/Pt/C for overall EWS. (e) Comparison of overall EWS performance between Ni$_{1.4}$Co$_{0.6}$/P/NCNHMs and compared electrocatalysts. (f) Chronopotentiometric curve for Ni$_{1.4}$Co$_{0.6}$/P/NCNHMs. The inset in panel c displays the time-dependent current density curves over the Ni$_{1.4}$Co$_{0.6}$/P/NCNHMs catalyst during electrolysis at 1.60 V.

Given the excellent activity and good stability for HER and OER of the Ni$_{1.4}$Co$_{0.6}$/P/NCNHMs catalyst, it is highly considered as an ideal bifunctional electrocatalyst for overall EWS. We further utilized the Ni$_{1.4}$Co$_{0.6}$/P/NCNHMs catalyst in a two-electrode (both anode and cathode) configuration for the overall EWS in 1 M KOH electrodes (Figure 5d). Remarkably, the Ni$_{1.4}$Co$_{0.6}$/P/NCNHMs catalyst displays superior overall EWS activity with a relatively low cell voltage of 1.55 V to afford a 10 mA cm$^{-2}$ current density. As displayed in Figure 5e, the low cell voltage for Ni$_{1.4}$Co$_{0.6}$/P/NCNHMs catalyst is competitive with recently reported bifunctional electrocatalysts for overall EWS performance, such as Cr-Doped FeNi-P (1.50 V),$^{58}$ FeNiP/NCH (1.59 V),$^{59}$ Ni$^{2-}$/Co$^{2-}$/P HNBs (1.62 V),$^{33}$ Ni$_{3}$/Ni$_{2}$P (1.67 V),$^{60}$ Co/P/NCNHP (1.64 V),$^{34}$ C-(Fe$^{2-}$/Ni$^{2-}$/P@PC)/(Co$^{2-}$/Ni$^{2-}$/P@CC (1.63 V),$^{23}$ (Ni, Fe)$_{2}$S$_{3}$/MoS$_{2}$ (1.56 V),$^{61}$ and Ni$_{3}$/FeN/r-GO (1.60 V) at a 10 mA cm$^{-2}$ current density. Further, the Ni$_{1.4}$Co$_{0.6}$/P/NCNHMs catalyst exhibits noticeable deterioration at 10
and 50 mA cm$^{-2}$ current densities, demonstrating the outstanding stability during overall EWS (Figure Sf). Meanwhile, a large number of bubbles can be easily observed from both the cathode (hydrogen gas) and anode (oxygen gas) during electrochemical tests (inserted image of Figure Sf).

Overall, the enhanced OER and HER performance of the as-prepared Ni$_{1.4}$Co$_{0.6}$P/NCNHM catalyst is related to the following aspects: (1) The hollow structure with nanosized subunits could reduce charge transport distances and provide rich active sites and high stability against agglomeration. (2) In situ grown N-doped carbon nanotubes could enrich the active sites, supplying efficient well-defined inner channels for efficient mass and charge transport for catalytic reactions. (3) Cobalt doping to the Ni$_3$P lattice matrix could regulate the active sites, supplying efficient well-defined inner channels for efficient mass and charge transport for catalytic reactions. (4) The rich boundary defects in Ni$_{1.4}$Co$_{0.6}$P could afford exposed active sites and also contribute to electron transfer. Thus, the optimal Ni$_{1.4}$Co$_{0.6}$P/NCNHM catalyst displays excellent electrocatalytic activity for HER, OER, and the overall EWS.

In summary, we report a facile route to fabricate a novel Ni$_{1.4}$Co$_{0.6}$P/NCNHM catalyst with N-doped carbon and cation substitution through a nitriding–phosphidation strategy using hollow Ni$_3$Co$_{0.6}$BTC MOF as the precursor. The derived Ni$_{1.4}$Co$_{0.6}$P/NCNHM catalyst by Co-doping and in situ growth of NCNTs could modify the electronic interactions and create more active sites, which favored electrocatalytic activity. Owing to the synergistic regulation of the components and the structural and electronic properties, the Ni$_{1.4}$Co$_{0.6}$P/NCNHM catalyst exhibits highly effective electrocatalytic performance and superior stability for HER catalytic activity and OER catalytic activity, respectively. Consequently, simultaneously working as two electrodes (both cathode and anode), the optimal Ni$_{1.4}$Co$_{0.6}$P/NCNHM catalyst shows a voltage of 1.55 V at 10 mA cm$^{-2}$ current density, along with good stability. The DFT simulations and experimental results suggested that the significant synergistic interaction between active Ni$_{1.4}$Co$_{0.6}$P NPs and hollow microspheres with NCNTs effectively enhances the electrocatalytic activity. This work sheds novel insight into the fabrication of efficient and unique designed TMP/carbon hierarchical nanostructures for electrocatalytic performance.

■ ASSOCIATED CONTENT

$\bullet$ Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c00851.

Experimental and computational details; XRD pattern, XPS analysis, and SEM and TEM images of samples (PDF)

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Notes
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