Bimetallic phosphides embedded in hierarchical P-doped carbon for sodium ion battery and hydrogen evolution reaction applications

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ABSTRACT Transition metal phosphides have been explored as promising active materials for sodium-ion batteries (SIBs) and hydrogen evolution reaction (HER) applications owing to their unique physical and chemical characteristics. However, they suffer from the drawbacks such as severe agglomeration, and sluggish reaction kinetics. Herein, bimetallic phosphides ($\text{Ni}_2\text{P}/\text{ZnP}_4$) embedded in P-doped carbon hierarchical microspheres are demonstrated with robust structural integrity, fast charge transfer, and abundant active sites. As expected, the optimally structured $\text{Ni}_2\text{P}/\text{ZnP}_4$ composite exhibits good electrochemical performance as an anode material in SIBs, including high specific capacity, good cycling stability and rate capability. Meanwhile, the $\text{Ni}_2\text{P}/\text{ZnP}_4$ composite also exhibits excellent electrocatalytic performance for HER with a small overpotential of 62 mV, a Tafel slope of 53 mV dec^{-1} , as well as excellent stability.

Keywords: metal organic frameworks, phosphating, bimetallic composite, sodium-ion battery, hydrogen evolution reaction

INTRODUCTION

Nowadays, the fast consumption of fossil fuels and the accompanying serious environmental issues have forced researchers to explore clean, inexpensive, efficient, and sustainable energy storage and conversion technologies [1–4]. Sodium-ion batteries (SIBs) and hydrogen generation through electrocatalytic water splitting have been considered as two main alternatives due to their availability and environmental benignity [5–7]. Nevertheless, great challenges still hinder the further development of SIBs due to the inferior electrochemical performance, as

well as the hydrogen evolution reaction (HER) owing to the rarity and prohibitive cost of the electrocatalysts (e.g., platinum group metal) [8–10]. In this respect, strategies need to be employed to improve sodium storage capability and quest inexpensive electrocatalysts, in which the most effective way is to engineer novel functional materials with unique micro-/nano-structures, complex chemical compositions, and natural abundance [11–15]. For example, Lu *et al.* [16] have developed a sequential etching, coordination reaction and pyrolysis strategy to synthesize Ni-doped FeP/C hollow nanorods with excellent HER activities in all-pH media owing to their component and structural benefits. We have recently synthesized bimetallic sulfides ($\text{Co}_9\text{S}_8/\text{ZnS}$) embedded in hollow nitrogen-doped carbon nanosheets *via* a sulfidation of cobalt-zinc metal-organic frameworks (MOFs) and subsequent calcination [6]. We found that the abundant phase boundaries induced by two-phase construction may create numerous active sites and extrinsic defects for fast electron transportation and ion diffusion, which suggested that mixed-metal sulfides with complex compositions may improve the electrochemical activity compared with single-component ones. However, reasonable design of mixed-metal phosphides and further investigation of their performance in catalysis and batteries are rarely reported.

Recently, earth-abundant transition metal phosphides (TMPs) have shown great potential in batteries [17,18], photocatalysis [19], electrocatalysis [20–22], due to their low cost, high electrical conductivity and activity. However, such kinds of materials suffer from large volumetric

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strain, sluggish ion diffusion. Even worse, the structures of host materials are distorted due to the severe stacking and agglomeration, thus limiting their electrochemical durability and catalytic activity. Many effective strategies have been explored to enhance the performance of TMPs, such as nanostructure designed to buffer volume strain (e.g., Ni_2P nanoarrays on nickel foam [21], and Ni-Co mixed metal phosphide nanoboxes [23]), hybrid with carbon matrix to improve the conductivity (e.g., Cu_3P nanoparticles coated by a N,P-codoped carbon [24], and monodisperse Ni_2P immobilized on N, P-codoped carbon nanosheets [25]), engineering of mixed-metal phosphides (e.g., Ni-Co-P hollow nanobricks [26], and CoP/FeP porous microcubes [27]) to improve charge transfer. However, either of these strategies alone has a limited effect on the performance improvement for TMPs. Simultaneous integration of morphological design, conductive carbon modification, and compositional manipulation is expected to achieve better electrochemical performance and remedy these shortcomings.

In order to integrate the above-mentioned considerations, MOFs can be used as self-sacrificed templates to fabricate multicomponent phosphides which can effectively improve the conductivity of the material while retain its due activity [28,29]. At the same time, annealing at high temperature in inert atmosphere can effectively transform the organic framework into highly ordered three-dimensional (3D) porous carbon skeleton [30]. Herein, we report the *in-situ* formation of bimetallic phosphides nanocrystals embedded in hierarchical P-doped carbon *via* a facile phosphatization of Zn-doped Ni-MOF [31]. The synthesis process is schematically shown in Fig. 1. Bimetallic Ni-Zn MOF was applied as both self-sacrificing template and the precursor for the synthesis of bimetallic hybrid phosphides (designated as NZP@PC). Phosphorus-doped carbon matrix was formed

simultaneously during high temperature carbonization. Benefiting from the abundant phase boundaries, robust structure, and highly conductive carbon skeleton, the composites show enhanced performance in both SIBs and HER. As SIBs anode materials, NZP@PC delivers a good rate capability with a specific capacity of $132.4 \text{ mA h g}^{-1}$ at high current density of 2000 mA g^{-1} , and excellent cyclic stability over 500 cycles at 500 mA g^{-1} . As an electrocatalyst for HER, NZP@PC exhibits a small overpotential of 62 mV and a Tafel slope of 53 mV dec^{-1} .

EXPERIMENTAL SECTION

Synthesis of Zn-doped Ni-MOF and pure Ni-MOF

In typical synthesis of Zn-doped Ni-MOF, 1 mmol of *p*-benzenedicarboxylic acid, 0.33 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.33 mmol of ZnCl_2 were dissolved in 20 mL of *N,N*-dimethylformamide (DMF) with stirring at room temperature. After the solution became light green, uniform, and transparency, 2 mL of 0.4 mol L^{-1} NaOH solution was added dropwise with continually stirring for 10 min. After the solution became uniform, the mixture was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 40 mL and kept in an electric oven at 100°C for 8 h. After cooling down to room temperature, the product was collected and thoroughly washed several times with DMF and ethanol, respectively, and then dried under vacuum at 80°C for 12 h. Then the Zn-doped Ni-MOF was obtained, denoted as Zn/Ni-MOF. For comparison, the pure Ni-MOF was prepared through a similar procedure mentioned above except for without adding ZnCl_2 .

Synthesis of $\text{Ni}_2\text{P-ZnP}_4$ composite (NZP@PC) and Ni_2P (NP@PC)

Firstly, the ground light green powders of Zn/Ni-MOF

Figure 1 Schematic illustration of the formation of $\text{Ni}_2\text{P-ZnP}_4$ composite coated by a P-doped porous carbon matrix (NZP@PC).

and Ni-MOF were placed in a tube furnace and annealed at 370°C for 1 h with a heating rate of 5°C min⁻¹ under a flowing Ar. After pre-sintering, the MOFs initially decomposed and the samples were denoted as Zn/Ni-MOF-C and Ni-MOF-C, respectively. The phosphorization process was then conducted by using NaH₂PO₂·H₂O as phosphorus source in a tube furnace. The mass ratio of Zn/Ni-MOF-C (or Ni-MOF-C) to NaH₂PO₂·H₂O was about 1:10. Typically, Zn/Ni-MOF-C (or Ni-MOF-C) and NaH₂PO₂·H₂O were placed at two separate positions of the tube furnace, in which NaH₂PO₂·H₂O at the upstream and Zn/Ni-MOF-C (or Ni-MOF-C) at the downstream. The samples were then subjected to heat treatment in tubular furnace at 300°C for 1 h under an ultrahigh purity Ar atmosphere with a heating rate of 1°C min⁻¹ to obtain the final Ni₂P-ZnP₄ composite (or Ni₂P). The obtained P-doped carbon encapsulated phosphides are denoted as NZP@PC or NP@PC, respectively.

Materials characterization

The crystallographic information of the obtained samples was recorded by X-ray powder diffraction (XRD, Regaku D/Max-2500 with nonmonochromated Cu K α radiation, λ =1.5418 Å). Carbon content in the product was determined by using LECO CS-600 C/S analyzer. The property of carbon layer was analyzed by Raman spectrometer (LabRAM HR800). The microstructure and morphologies of the samples were characterized by field-emission scanning electron microscope (FESEM, FEI Nova NanoSEM 230) at 10 kV with energy dispersive X-ray. And the transmission electron microscopy (TEM) images of these samples were observed by FEI Tecnai G2 F20 electron microscope working at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS, VG Escalab-250xi) measurements were also conducted to probe the electronic states of elements in the surface. The Nitrogen adsorption-desorption isotherms (Quantachrome Instruments) were recorded at 77 K for calculating the Brunauer-Emmett-Teller (BET) surface area and pore size.

Electrode fabrication and electrochemical measurement

Stainless-steel coin cells (CR2016) were made for electrochemical measurements. The working electrode was made by dispersing the as-prepared phosphides (NZP@PC or NP@PC) (85 wt.%), conductive Super P (5 wt.%), and polyvinylidene fluoride (PVDF) (10 wt.%) in *N*-methyl-2-pyrrolidone (NMP) solution to form a slurry. The homogeneous slurry was casted onto a copper current collector, and then was dried in a vacuum oven at

100°C overnight. The typical thickness of the electrode was ~30 μ m with a mass loading of about 1.5 $\pm$ 0.2 mg cm⁻². 1 mol L⁻¹ NaClO₄ in propylene carbonate (PC) with 5% fluoroethylene carbonate (FEC) was chosen as the electrolyte and the glass fiber membrane with thickness of 0.5 mm was used as the separator. All the cells were assembled in a glovebox (Mbraun, Germany) with ultra-high purity argon. Galvanostatic charge/discharge measurements were carried out in the potential range of 0.01–3.0 V at different current densities using a multichannel battery testing system (LAND CT2001A, China). Both the charge and discharge current density and specific capacity were calculated based on the mass of P-doped carbon encapsulated phosphides. Cyclic voltammetry (CV) curves were recorded using an electrochemical workstation (CHI660E, China) between 0.01 and 3.0 V. The electrochemical impedance spectroscopy (EIS) data of the electrodes were recorded on an electrochemical workstation (Metrohm Autolab-M204, Switzerland) in the frequency range of 100 kHz to 0.01 Hz.

The electrocatalytic activity of HER was evaluated in a typical three-electrode system attached to a CHI660C workstation at ambient temperature. A saturated calomel electrode (Hg/HgCl₂ in saturated KCl, SCE) was used as the reference electrode and a platinum foil electrode was used as the counter electrode. The preparation method of the working electrodes containing investigated catalysts was as follows. The catalysts and PVDF powder were mixed in a weight ratio of 9:1 and dispersed in NMP to form uniform ink. Then the mixture was ultrasonicated for 20 min and spread homogenously onto Ni foam substrate of ~1.0 cm² in area. Finally, the as-prepared working electrode was dried at 60°C in vacuum. The loading amount of catalysts for each electrode was about 0.15 mg. Linear sweep voltammetry (LSV) was recorded at a scan rate of 5 mV S⁻¹ to obtain the polarization curves. The polarization curves were replotted as overpotential vs. log current density to get Tafel plots for assessing the HER kinetics of investigated catalysts. The long-lifetime test was carried out by *i*-*t* curve at a constant working potential of -1.27 V for 18 h. All the data presented were corrected for *i*R losses and background current. The electrochemical double-layer capacitance was determined from the CV curves measured in a potential range without redox processes according to the following equation: $C_{dl} = I_c/v$, where C_{dl} , I_c , and v are the double-layer capacitance (mF cm⁻²) of the electroactive materials, charging current (mA cm⁻²), and scan rate (mV s⁻¹), respectively.

Figure 2 The chemical and physical characterizations of the as-prepared NZP@PC. (a) XRD patterns with Rietveld refinement. (b) Raman scattering spectrum. (c) FTIR spectrum. (d) Nitrogen adsorption-desorption isotherms and corresponding pore size distribution curve (the inset).

RESULTS AND DISCUSSION

The crystallographic information of Zn/Ni-MOF and NZP@PC were recorded by powder XRD measurement. As shown in Fig. S1, all the diffraction peaks of the Zn/Ni-MOF correspond well to the layered topology of $[\text{Ni}_3(\text{OH})_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ (CCDC # 638866), which is highly consistent with the previous report [31]. Meanwhile, the XRD pattern with Rietveld refinement of the as-prepared NZP@PC composite is shown in Fig. 2a with all diffraction peaks well indexed to the hexagonal Ni_2P phase (ICSD # 43395), and tetragonal ZnP_4 phase (ICSD # 40428). The mass fractions of Ni_2P , and ZnP_4 are 83.85 and 16.15 wt.%, respectively, and the refined unit cell lattice parameters of these two phases are shown in Table S1. The carbon in NZP@PC was investigated by the Raman scattering spectrum (Fig. 2b). Two characteristic bands of carbonaceous materials located at ~ 1327 and 1571 cm^{-1} can be assigned to the D-band and G-band, respectively, indicating the presence and partial graphitization of carbon in the composite. Moreover, C-S analysis shows the mass content of carbon is about 33.28%. Additionally, Fourier transform-infrared (FT-IR) spectrum was recorded as shown in Fig. 2c. The characteristic

bands for P–O/P=O stretching (around 1068 cm^{-1}) and C–P stretching (around 726 cm^{-1}) are in accordance with the previous reports [24,32]. As-prepared composite shows characteristic –COOH/–CN band centered at wavenumbers of around 1690 cm^{-1} , indicating the existence of the functional groups in carbon skeleton [33]. Furthermore, nitrogen isothermal adsorption/desorption measurement was also carried out to further characterize the porous structure of the NZP@PC composite (Fig. 2d). The isotherm can be described as type II with type-H3 hysteresis loop, which can be linked to slit-shaped pores. The BET surface area of NZP@PC is measured to be $40.3 \text{ cm}^3 \text{ g}^{-1}$ with mainly pore diameter below 30 nm. The large surface area and narrow pore size distribution can provide substantial active sites for electrochemical reactions, and enhance electrolyte penetration for fast kinetics [34–36].

The detailed morphological and crystallographic properties of the products are elucidated through FESEM and TEM. As demonstrated in Fig. 3a, the prepared NZP@PC composite well inherits the hierarchical microsphere morphology of the Zn/Ni-MOF (Fig. S2) and the microspheres have an average diameter of $\sim 8 \mu\text{m}$.

Figure 3 The morphological and microstructural characterizations of the as-prepared NZP@PC. (a, b) FESEM images. (c, d) TEM images. (e) HRTEM image and the corresponding FFT images of the selected regions, respectively. (f) STEM-EDX spectrum. (g) HAADF-STEM image and the corresponding EDS elemental maps.

The enlarged FESEM image (Fig. 3b) further reveals the detailed feature of the microsphere, which is composed of interconnected nanoflakes with apparent open spaces between them. The energy dispersive X-ray (EDX) elemental mapping images (Fig. S3) confirm the existence of Ni, Zn, and P. The TEM images (Fig. 3c, d) demonstrate the solid and dense interior of the Zn/Ni-MOF microspheres. The continuous nanoflakes are radially oriented and serve as building blocks to construct the hierarchical structure. The high-resolution TEM (HRTEM) image (Fig. 3e) was collected to further reveal the two-phase property. The fast Fourier transformation (FFT) image (inset of Fig. 3e) of the selected regions shows the diffraction spots of Ni_2P , and ZnP_4 , respectively. In addition, the lattice fringes in the nanocrystalline domains can be labeled by (100), (002) planes for Ni_2P crystal, and (112) plane for ZnP_4 crystal, respectively. Notably, a uniform thin carbon layer of around 3 nm is well decorated on the surface of the hybrid phosphides nanocrystals. The large amount of lattice mismatch and distortion between the Ni_2P and ZnP_4 crystalline domains may create more crystal defects and accessible active sites for ions storage and catalytic activity [37–39]. Furthermore, the high an-

gle annular dark field scanning transmission electron microscopy (HAADF-STEM) image and the corresponding EDS elemental maps (Fig. 3g) show the homogenous distribution of Ni, Zn, P, C, and O elements in the independent nanoflake. The corresponding EDX spectrum (Fig. 3f) also confirms the existence of Ni, Zn, P, C, and O elements with low atomic percentage of Zn species, well consistent with the XRD results.

XPS was applied to ascertain the surface chemical composition and electronic structure of the as-prepared NZP@PC. Based on the survey spectrum in Fig. 4a, the NZP@PC composite is mainly composed of Ni, Zn, P, C, and O elements, corresponding well with the element mapping images (Fig. 3g). As depicted in Fig. 4b, the Ni 2p spectrum shows five prominent bands, corresponding to Ni 2p_{3/2} (853.5 eV) of Ni–P, and Ni 2p_{3/2} (856.1 eV) and Ni 2p_{1/2} (874.1 eV) of Ni–O, respectively, with the bands at 861.6 and 879.4 eV related to satellite bands [26]. As presented in the high-resolution Zn 2p spectrum (Fig. 4c), the two main peaks at around 1021.4 and 1045.2 eV should be assigned to Zn 2p_{3/2} and Zn 2p_{1/2} of Zn^{2+} , respectively [40]. The high resolution XPS of P 2p spectrum in Fig. 4d is deconvoluted into three peaks

Figure 4 XPS spectra of the as-prepared NZP@PC. (a) XPS survey spectrum. (b) Ni 2p spectrum. (c) Zn 2p spectrum. (d) P 2p spectrum. (e) C 1s spectrum. (f) O 1s spectrum.

at 129.3, 133.6, and 133.9 eV, assigned to C–P, P–O, P=O bonds, respectively [24]. The high resolution XPS of C 1s spectrum (Fig. 4e) can be resolved into three components centered at 284.8, 286.2, and 288.7 eV. The main peak located at 284.8 eV corresponds to the graphite-like sp^2 C [24]. The small peaks at 286.2 and 288.7 eV can be ascribed to the C–P and CO type bonds, respectively, which originate from the substitutional doping of P [24,25]. The P-doped carbon matrix can improve the electronic conductivity of electrode material and provide more active sites [41]. The oxidized species (Fig. 4f) associated with the Ni–O, P–O, P=O, and CO-type bonds can be ascribed to the incomplete phosphorization or/and slightly oxidized surface of NZP@PC under ambient conditions, which are consistent well with the previous reports [21,25,26,36].

For comparison, similar experiments without adding $ZnCl_2$ were carried out and pure Ni-MOF was obtained. After the sequential pre-decomposition and phosphatization, a P-doped carbon encapsulated Ni_2P (designated as NP@PC) was obtained. In the absence of $ZnCl_2$, only bulk particles morphology was obtained (Fig. S4d, e). The chemical and physical characterizations of the NP@PC are shown in Fig. S4a–c. Pure Ni_2P with good crystallinity was obtained and Raman characteristic peaks of carbonaceous material were detected. The single-crystalline nature of Ni_2P was confirmed (Fig. S4f) and the uniform

distribution of Ni, P, C, and O was demonstrated by the HAADF-STEM image and the corresponding EDS elemental maps (Fig. S4g).

The NZP@PC or NP@PC was assembled into half-cells to evaluate the electrochemical performance as anode materials for SIBs as shown in Fig. 5. Fig. 5a shows the cycling performance of NZP@PC and NP@PC electrodes at a current density of 100 mA g^{-1} in the voltage range of 0.01–3.0 V versus Na^+/Na and Fig. 5b shows the corresponding charge-discharge voltage profiles. The NZP@PC electrode exhibits the initial discharge and charge capacities of 701 and 513 mA h g^{-1} at 100 mA g^{-1} , respectively, corresponding to a high Coulombic efficiency of 73.1%. This initial irreversibility may be attributed to the formation of the solid electrolyte interphase (SEI) film and other undesirable side reactions [42]. A high reversible discharge capacity of 436 mA h g^{-1} is achieved in the second cycle, which maintains 249 mA h g^{-1} even after 100 cycles (Fig. 5a), suggesting the good cycling stability of NZP@PC. In contrast, the NP@PC electrode exhibits much inferior cycling performance (an initial Coulombic efficiency of 68.2% and a capacity retention of 35.2% from the second cycle to the 100th). Fig. S5 shows the CV curves of the initial three cycles for NZP@PC electrode at a scan rate of 0.1 mV s^{-1} in the voltage range of 0.01–3.0 V versus Na^+/Na . In the first cathodic sweep, several broad peaks can be ascribed

Figure 5 The electrochemical characterizations of the as-prepared $\text{Ni}_2\text{P-ZnP}_4$ composite (NZP@PC) and Ni_3P (NP@PC) as a half-cell anode in the potential range of 0.01–3.0 V versus Na^+/Na . (a) Cycling performance at the current density of 100 mA g^{-1} . (b) Galvanostatic charge/discharge profiles of selected cycles at 100 mA g^{-1} . (c) Rate performance at various current densities from 50 to 2000 mA g^{-1} . (d) Galvanostatic charge/discharge profiles of NZP@PC at various current densities. (e) Long-term cycling performance and Coulombic efficiency of the NZP@PC electrode at 500 mA g^{-1} for 500 cycles.

to the conversion reaction forming the metal element and Na_3P , the alloying reaction forming the NaZn_{13} , and the formation of SEI film [32,43–45]. As for anodic scan, the peaks can be attributed to the reversible oxidation reaction of the metal element into mixed-metal phosphides [43–46]. The rate capability of the NZP@PC and NP@PC electrodes is compared and the representative charge/discharge voltage profiles at various current densities are provided (Fig. 5d and Fig. S6). As shown in Fig. 5c, the

discharge capacity of the NZP@PC electrode in the second cycle at 50 mA g^{-1} is 595 mA h g^{-1} , much higher than that of NP@PC (417 mA h g^{-1}) in the same cycle. Along with the increase of the current density from 100 mA g^{-1} to 2000 mA g^{-1} , the specific capacity of the NZP@PC electrode decreases from 441 to 133 mA h g^{-1} . The decline of capacity with increasing charge/discharge current density is routinely observable for mass transport limiting process. The specific capacity returns to 339 mA h g^{-1}

when the current density comes back to 100 mA g^{-1} , implying the much superior kinetics of NZP@PC as compared with that of NP@PC. Fig. 5e shows the long-term cycling performance and Coulombic efficiency of the NZP@PC electrode at high current density of 500 mA g^{-1} . The 4th discharge capacity of NZP@PC anode is 262 mA h g^{-1} . After 500 cycles, the electrode can deliver a specific capacity of 175 mA h g^{-1} with a capacity retention of 66.8%.

The Nyquist plots (Fig. S7) show that the charge transfer resistance (R_{ct}) of the NZP@PC electrode after 1st and 5th cycles are 288 and 279Ω , respectively, indicating the fast charge transfer kinetics. In addition, the hierarchical structure can be well maintained without obvious pulverization or size variation after discharge and charge (Fig. S8). The nanoflakes-constructed hierarchical microspheres of NZP@PC with abundant phase boundaries can facilitate the penetration of electrolyte and shorten the diffusion path of ions, thereby achieving fast reaction kinetics. Table S2 gives a list of previously reported transition-metal phosphides as anode materials for SIBs, which indicates the good electrochemical performance of the NZP@PC electrode.

We further investigated the HER activity of NZP@PC and NP@PC for water splitting in 1 mol L^{-1} KOH aqueous solution, with commercial Pt/C electrode for comparison. Fig. 6a shows the polarization curves with iR correction. The NP@PC requires an overpotential of about 166 mV to reach a current density of 10 mA cm^{-2} . In sharp contrast, the NZP@PC exhibits excellent electrocatalytic activity in the HER and delivers a current density of 10 mA cm^{-2} at an overpotential of 62 mV, only 25 mV larger than that of Pt/C electrode. The corresponding Tafel plots based on the LSV curves are presented in Fig. 6b. These linear regions of Tafel plots are fitted to the Tafel equation ($\eta = b \log j + a$, where b is the Tafel slope). The Tafel slope of NZP@PC (53 mV dec^{-1}) is smaller than that of the NP@PC (103 mV dec^{-1}), implying the favorable HER kinetics for NZP@PC hierarchical microspheres. The Tafel slope of NZP@PC composite shows that the hydrogen evolution process of this material might be based on the Volmer-Heyrovsky mechanism [47]. These results indicate the electrocatalytic HER activity of the NZP@PC is better than that of the NP@PC and comparable to those of transition-metal-based phosphides catalysts (Table S3). In addition, the dur-

Figure 6 The electrocatalytic performances of the as-prepared $\text{Ni}_2\text{P-ZnP}_4$ composite (NZP@PC) and Ni_2P (NP@PC). (a) Polarization curves and (b) Tafel plots of bare NZP@PC, NP@PC, and Pt/C for HER in 1 mol L^{-1} KOH. (c) The long-term durability test of NZP@PC at an overpotential of 150 mV. (d) Estimation of C_{dl} by plotting the current density variation against scan rate to fit a linear regression.

ability of catalysts is also critical for practical applications. As shown in Fig. 6c, the electrode was operated at a certain potential to obtain the time-dependent current. It can be seen that the current maintain stability within 18 h of continuous measurement, which demonstrates the good stability of the hierarchical NZP@PC microspheres during the HER process. By the way, a minor current rise in the first hour may be a result of the activation process of catalyst in the alkaline electrolyte [48,49]. At the end of the measurement, the obtained polarization curve is close to the initial one, demonstrating the strong durability of the catalyst (Fig. S9). Besides, SEM images (Fig. S10b–d) indicate that this catalyst electrode still maintains its morphology after durability test. *Ex situ* XRD analysis (Fig. S10a) of this NZP@PC electrode further suggests the excellent phase stability. Furthermore, the double-layer capacitances (C_{dl}) were evaluated by CV (Fig. S11) in a voltage range from 0.3 to 0.4 V to measure the electrochemically active surface area (ECSA) of the material. The larger ECSA represents the more effective utilization of catalytic active sites. The C_{dl} of NZP@PC is determined to be 14.5 mF cm^{-2} (Fig. 6d), higher than that of NP@PC (6.9 mF cm^{-2}), indicating that the $\text{Ni}_2\text{P-ZnP}_4$ composite has higher accessible active surface areas than Ni_2P . The P-doped carbon can greatly enhance the electrical conductivity of the composite (Fig. S12). Compared with NP@PC, the phase boundaries of NZP@PC provide more active sites to achieve higher HER activity. Moreover, the unique hierarchical architecture can expose these active sites and accelerate mass transfer, resulting in the faster kinetics. The integration of advantages from hierarchical architecture, P-doped carbon modification, and compositional manipulation can enhance HER performance remarkably.

CONCLUSIONS

In summary, we have successfully developed a facile strategy for the synthesis of bimetallic phosphides nanocrystals embedded in P-doped carbon hierarchical microspheres *via* sequential pre-decomposition and phosphatization processes of Zn-doped Ni-MOF. Compared with the irregularly bulk particles of monometallic phosphide, the hierarchical porous micro/nano architecture along with P-doped carbon encapsulation of bimetallic phosphides can provide favorable ion and electron transportation, as well as robust structural integrity. The abundant phase boundaries induced by two-phase construction can also expose the electrochemically active sites for Na ions storage and catalytic reaction. As a result, the optimum NZP@PC exhibits good electro-

chemical performance for SIBs and excellent electrocatalytic performance for HER. Such a synergistic integration of compositional manipulation with architectural regulation may also be extended to other functional materials for future applications.

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Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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磷掺杂碳微球封装双金属磷化物在钠离子电池和电催化析氢中的应用

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摘要 过渡金属磷化物由于其独特的物理化学特性, 在钠离子电池和电催化析氢反应领域被广泛研究. 然而, 过渡金属磷化物存在严重团聚和动力学迟缓等问题. 本研究将双金属磷化物($\text{Ni}_2\text{P}/\text{ZnP}_4$)嵌入到P掺杂的碳微球中, 得到的纳米材料具有结构稳定、电荷转移快和活性位点丰富等优势. 结果表明, 结构优化的 $\text{Ni}_2\text{P}/\text{ZnP}_4$ 复合材料作为钠离子电池负极材料具有良好的电化学性能, 包括高比容量、循环稳定和倍率性能佳等. 同时, $\text{Ni}_2\text{P}/\text{ZnP}_4$ 复合材料也表现出良好的电催化析氢性能, 其过电势为62 mV, Tafel斜率为53 mV dec^{-1} , 且稳定性良好.