In situ construction of heterostructured bimetallic sulfide/phosphide with rich interfaces for high-performance aqueous Zn-ion batteries

Fang Yang¹, Yuenian Shen², Ze Cen¹, Jie Wan¹, Shijie Li^{3*}, Guanjie He⁴, Junqing Hu^{2,5} and Kaibing Xu^{2*}

ABSTRACT It is still challenging to develop suitable cathode structures for high-rate and stable aqueous Zn-ion batteries. Herein, a phosphating-assisted interfacial engineering strategy is designed for the controllable conversion of NiCo₂S₄ nanosheets into heterostructured NiCoP/NiCo₂S₄ as the cathodes in aqueous Zn-ion batteries. The multicomponent heterostructures with rich interfaces can not only improve the electrical conductivity but also enhance the diffusion pathways for Zn-ion storage. As expected, the NiCoP/NiCo₂S₄ electrode has high performance with a large specific capacity of 251.1 mA h g⁻¹ at a high current density of 10 A g⁻¹ and excellent rate capability (retaining about 76% even at 50 A g⁻¹). Accordingly, the Zn-ion battery using NiCoP/NiCo₂S₄ as the cathode delivers a high specific capacity (265.1 mA h g⁻¹ at 5 A g⁻¹), a long-term cycling stability (96.9% retention after 5000 cycles), and a competitive energy density (444.7 W h kg⁻¹ at the power density of 8.4 kW kg⁻¹). This work therefore provides a simple phosphating-assisted interfacial engineering strategy to construct heterostructured electrode materials with rich interfaces for the development of high-performance energy storage devices in the future.

Keywords: phosphating, heterostructure, NiCoP/NiCo₂S₄, Zn-ion batteries, high capacity

INTRODUCTION

To alleviate the excessive consumption of traditional fossil fuels and increasing environmental pollution issues, it is particularly urgent and important to develop high-efficiency and clean energy storage devices. Typically, lithium (Li)-ion batteries have been widely used in a variety of energy storage systems, such as portable electronics, electric vehicles, and grid-scale energy-storage systems [1]. However, the large-scale application of Li-ion batteries is still a huge challenge because of limited lithium resources and toxic organic electrolytes [2–5]. Recently, researchers have focused on the exploration of high-performance aqueous rechargeable batteries with low cost and reliable safety [6–10]. Among various rechargeable batteries, aqueous Zn-ion batteries are emerging as one of the most competitive candidates to replace Li-ion batteries by virtue of the high the-

oretical capacity of the zinc anode (820 mA h g⁻¹), high working voltage (~1.8 V), as well as its low cost and low toxicity [11–20]. However, the unsatisfactory energy/power density and poor cycling stability severely limit their practical application. Designing and constructing highly active cathode materials has been demonstrated as a promising strategy to improve the performance of Zn-ion batteries.

Transition metal sulfides have been extensively investigated as electrode materials due to their higher electronic conductivity and better reversible electrochemical properties than those of their oxide counterparts [21–24]. Especially, NiCo₂S₄ electrode materials have been proved to have better electronic conductivities of about 100 times higher than that of NiCo₂O₄ [21,25]. In addition, compared with its corresponding single-component sulphides (NiS_x and CoS_x), NiCo₂S₄ has significantly richer redox reactions because of multiple available oxidation states and faster electron transfer properties [26,27]. For instance, Han *et al.* [28] developed sulfur-deficient NiCo₂S_{4-x} nanotube arrays on carbon cloth as an effective cathode material for flexible Zn batteries, which delivered a high capacity of 298.3 mA h g⁻¹ at 0.5 A g⁻¹ and superior rate capability. On the other hand, transition metal phosphides have attracted extensive research interest due to their unique electronic structure and high thermal/chemical stability, which show high electrocatalytic activity/durability and good conductivity [29–33]. For example, Zhang *et al.* [34] developed ultrafine and highly active bimetallic Co_xNi_{1-x}P nanoparticles loaded on carbon nanofibers, exhibiting an extraordinary specific capacitance of 3514 F g⁻¹ at 5 A g⁻¹. Therefore, the *in-situ* construction of metal phosphides based on metal sulfides can effectively realize the coupling of their respective advantages. Furthermore, constructing novel multicomponent heterostructures with metal sulfides and phosphides is emerging as an effective strategy to generate abundant interfaces for fast charge transfer and to improve the number of highly exposed active sites for redox reactions, showing great application potential.

In this study, we developed a controllable route to fabricate heterostructured NiCoP/NiCo₂S₄ nanosheet arrays on carbon cloth as electrode, which showed the strong synergistic effect and rich interfaces between NiCoP and NiCo₂S₄, and delivered a high specific capacity of 251.1 mA h g⁻¹ at a high current density

¹ School of Mechanical and Automotive Engineering, Shanghai University of Engineering Science, Shanghai 201620, China

² State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Research Center for Analysis and Measurement & College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

³ Institute of Innovation & Application, National Engineering Research Center for Marine Aquaculture, Zhejiang Ocean University, Zhoushan 316022, China

⁴ School of Chemistry, University of Lincoln, Brayford Pool, Lincoln LN6 7TS, UK

⁵ College of Health Science and Environmental Engineering, Shenzhen Technology University, Shenzhen 518118, China

* Corresponding authors (emails: lishijie@zjou.edu.cn (Li S); xukaibing@dhu.edu.cn (Xu K))

of 10 A g^{-1} and excellent rate capability. The aqueous Zn-ion battery based on NiCoP/NiCo₂S₄ (NiCoP/NiCo₂S₄//Zn battery) delivered a high specific capacity of $265.1 \text{ mA h g}^{-1}$ at 5 A g^{-1} and good cycling stability (capacity retention of 96.9% after 5000 cycles). Moreover, this battery possessed a high energy density of $444.7 \text{ W h kg}^{-1}$ at the power density of 8.4 kW kg^{-1} . This study verifies that establishing transition metal sulfides and phosphides heterostructured materials for enhancing the energy storage performance of aqueous Zn-ion batteries is efficient.

EXPERIMENTAL SECTION

Synthesis of NiCo₂S₄ nanosheet arrays

Ni(NO₃)₂·6H₂O (1 mmol), Co(NO₃)₂·6H₂O (2 mmol), and hexamethylenetetramine (5.7 mmol) were dissolved in deionized water (25 mL) and ethanol (25 mL) under vigorous stirring. The resulting pink solution was then transferred into a 60-mL stainless steel autoclave with a piece of pretreated carbon cloth (1 cm × 4 cm) and sealed at 95°C for 8 h. Subsequently, the obtained precursor on carbon cloth was annealed in air at 350°C for 2 h, to obtain NiCo₂O₄. Finally, the above carbon cloth was immersed in 50 mL of deionized water with 1 g of Na₂S·9H₂O, and maintained at 100°C for 24 h to obtain NiCo₂S₄ samples.

Synthesis of NiCoP/NiCo₂S₄ nanosheet arrays

To fabricate the NiCoP/NiCo₂S₄ nanosheet arrays, the NiCo₂S₄ nanosheet arrays on carbon cloth were annealed under N₂ atmosphere with the presence of NaH₂PO₂ (0.25–1 g) at 350–450°C for 1–4 h. The mass loadings of NiCo₂S₄ and NiCoP/NiCo₂S₄ materials were 0.60 and 0.63 mg cm⁻², respectively. For comparison, the NiCo₂O₄ nanosheet arrays were prepared at 400°C for 2 h with 0.5 g of NaH₂PO₂ to obtain NiCoP nanosheet arrays.

Materials characterization

The as-obtained materials were investigated by scanning electron microscopy (SEM; Hitachi, S-4800), transmission electron microscopy (TEM; JEOL, JEM-2100F), X-ray diffractometer (XRD; Rigaku, D/max-2550 PC), X-ray photoelectron spectroscopy (XPS; Thermo Fisher, Escalab 250Xi), and Brunauer-Emmett-Teller analyzer (BET; Quantachrome, Autosorb-iQ).

Electrochemical measurement

The electrochemical measurements were carried out on an electrochemical workstation (Metrohm Autolab PGSTAT302N,

the Netherlands). A three-electrode system was assembled for the evaluation of electrochemical properties of individual electrodes in 1 mol L⁻¹ KOH aqueous solution. The NiCoP/NiCo₂S₄ nanosheet arrays on carbon cloth were used directly as the working electrode, with the saturated calomel electrode as a reference and a platinum plate as the counter electrode. The aqueous Zn-ion battery was assembled using NiCoP/NiCo₂S₄ materials as the cathode and a piece of commercial Zn plate as the anode with the mixed solution of 1 mol L⁻¹ KOH and 0.01 mol L⁻¹ Zn(CH₃COO)₂ as the electrolyte, and the two-electrode configuration was constructed to assess the electrochemical performance of the as-fabricated batteries.

RESULTS AND DISCUSSION

Fig. 1 schematically illustrates the entire preparation procedure of heterostructured NiCoP/NiCo₂S₄ nanosheet arrays on carbon cloth. First, NiCo₂O₄ nanosheets are directly grown on the bare carbon cloth through a facile hydrothermal reaction, and calcined under air atmosphere to improve their crystallinity. After that, hydrothermal reaction is again employed to realize the phase transformation between NiCo₂O₄ and NiCo₂S₄ by using Na₂S·9H₂O as the sulfur source, where all the O²⁻ is exchanged into S²⁻ via the Kirkendall effect. Finally, to accomplish the interfacial engineering of NiCo₂S₄, phosphate treatment is conducted with NaH₂PO₂ as the phosphorus source. During this process, newly formed NiCoP nanoparticles are embedded into NiCo₂S₄ nanosheets, generating an updated heterostructured nanostructure with rich interfaces due to the higher electronegativity of P than those of Ni and Co [35]. The NiCoP/NiCo₂S₄ electrode prepared at 400°C for 2 h with 0.5 g of NaH₂PO₂ is discussed in the following sections, unless otherwise stated, as it shows the highest specific capacities.

The micromorphology of the NiCo₂S₄ nanosheets on carbon cloth was preliminarily investigated by SEM and TEM (Fig. 2). The SEM images (Fig. 2a, b) show that the NiCo₂S₄ nanosheets derived from NiCo₂O₄ nanosheets (Fig. S1) remain uniformly supported on the carbon cloth, and these nanosheets are interconnected to each other. In Fig. 2c, the TEM image of the NiCo₂S₄ nanosheet shows numerous small pores uniformly distributed throughout the surface. The high-resolution TEM image (HRTEM) characterization clearly displays the lattice fringe with an interplanar distance of 0.332 nm, well corresponding to the (220) plane of NiCo₂S₄ (Fig. 2d). Furthermore, the energy dispersive X-ray spectroscopy (EDS) element mapping images (Fig. 2e) show the even distribution of Ni, Co and S

Figure 1 Schematic illustration of the heterostructured NiCoP/NiCo₂S₄ nanosheet arrays supported on carbon cloth.

Figure 2 (a, b) SEM, (c) TEM, (d) HRTEM, and (e) elemental mapping images of the NiCo_2S_4 nanosheets.

Figure 3 (a, b) SEM, (c) TEM, (d) HRTEM, and (e) the corresponding elemental mapping images of the $\text{NiCoP/NiCo}_2\text{S}_4$ nanosheets.

elements in the NiCo_2S_4 nanosheet.

According to the SEM images of Fig. 3a, b, the densely packed and highly ordered $\text{NiCoP/NiCo}_2\text{S}_4$ nanosheet arrays are uniformly grown on the carbon cloth surface, and these nanosheets are interconnected to each other with plenty of spaces, which are beneficial to the charge transportation and ion diffusion, thus enhancing the specific capacity. Compared with NiCo_2S_4 nanosheets, the surface of the $\text{NiCoP/NiCo}_2\text{S}_4$ nanosheets becomes much rougher after phosphating treatment due to the

formation of NiCoP nanoparticles. Moreover, the effects of phosphating conditions on the morphology of the $\text{NiCoP/NiCo}_2\text{S}_4$ materials were also systematically investigated by adjusting the treatment temperature, the reaction time and the mass of NaH_2PO_2 . As shown in Fig. S2, with the increase of temperature, time and amount of the P source, more NiCoP nanoparticles are generated on the NiCo_2S_4 nanosheets. Additionally, the BET surface areas were also tested (Fig. S3). The specific area of $\text{NiCoP/NiCo}_2\text{S}_4$ is $26.2 \text{ m}^2 \text{ g}^{-1}$, while that of NiCo_2S_4 is $27.3 \text{ m}^2 \text{ g}^{-1}$. The decrease in specific surface area may be caused by the newly formed NiCoP nanoparticles plugging the pores in the NiCo_2S_4 nanosheets. The formation of heterostructured $\text{NiCoP/NiCo}_2\text{S}_4$ nanosheets was further confirmed by TEM. As shown in Fig. 3c, NiCoP nanoparticles are distributed on the surface of the NiCo_2S_4 nanosheets, which is consistent with the result from SEM analysis. Fig. 3d shows the HRTEM of the $\text{NiCoP/NiCo}_2\text{S}_4$ nanosheet, and the obvious lattice fringes spaced at 0.332 and 0.335 nm, correspond well to the (220) plane of NiCo_2S_4 and (001) plane of NiCoP . The EDS mapping images (Fig. 3e) further confirm that the Ni, Co, S and P elements are uniformly distributed throughout the $\text{NiCoP/NiCo}_2\text{S}_4$ nanosheet.

The phase of the as-prepared materials was firstly acquired through the analysis of XRD data. As shown in Fig. 4a, the XRD pattern of $\text{NiCoP/NiCo}_2\text{S}_4$ displays well-defined diffraction peaks, which well match with the standard XRD patterns of NiCo_2S_4 (JCPDS No. 73-1704) and NiCoP (JCPDS No. 71-2336), confirming the coexistence of NiCoP and NiCo_2S_4 after phosphating treatment without any residues or contaminants. Moreover, XPS was further performed to investigate the elemental compositions and valence states of $\text{NiCoP/NiCo}_2\text{S}_4$. As shown in Fig. S4a, there is an extra P signal in the $\text{NiCoP/NiCo}_2\text{S}_4$ sample compared with the original NiCo_2S_4 sample. In the Ni 2p region (Fig. 4b), the spin orbitals located at 875.4 and 857.4 eV indicate the presence of Ni^{3+} , while the other two peaks centered at 871.1 and 853.8 eV prove the existence of Ni^{2+} [36,37]. In the case of the Co 2p spectrum (Fig. 4c), two strong peaks located at the binding energy of 798.5 and 782.6 eV confirm the presence of Co^{2+} , and the other two peaks at 794.0 and 779.1 eV prove the existence of Co^{3+} [38,39]. Therefore, the chemical composition of the as-prepared materials contain the cations of Ni^{2+} , Ni^{3+} , Co^{2+} and Co^{3+} . As for the S 2p spectrum (Fig. 4d), apart from the shake-up satellite peak at 169.3 eV, two peaks are located at 163.0 eV for S 2p_{1/2} and 161.8 eV for S 2p_{3/2}, corresponding to the metal-sulfur (M-S) bonds in the samples [40,41]. In the P 2p region (Fig. 4e), the dominant peak located at 134.3 eV indicates that P exists mainly in the form of phosphate ions. And two peaks at 130.6 and 129.4 eV correspond to P 2p_{1/2} and P 2p_{3/2} spin orbitals [42,43], corresponding to metal phosphides. On the other hand, there is no signal in the P 2p region for pure NiCo_2S_4 sample. These results suggest that the heterostructured $\text{NiCoP/NiCo}_2\text{S}_4$ electrodes have been successfully prepared through the phosphate treatment with the NaH_2PO_2 as the phosphorus source.

The electrochemical performances of the as-prepared samples were evaluated on the three-electrode system with 1 mol L^{-1} KOH as the electrolyte. Fig. 5a shows the comparison cyclic voltammetry (CV) curves of the NiCo_2O_4 , NiCo_2S_4 , NiCoP and $\text{NiCoP/NiCo}_2\text{S}_4$ electrodes at the same scan rate of 10 mV s^{-1} . The current density and integral area of $\text{NiCoP/NiCo}_2\text{S}_4$ are much higher than that of the NiCo_2O_4 , NiCo_2S_4 , and NiCoP

Figure 4 (a) XRD patterns of NiCo₂O₄, NiCo₂S₄ and NiCoP/NiCo₂S₄. (b) Ni 2p, (c) Co 2p, (d) S 2p and (e) P 2p core-level XPS spectra of NiCo₂S₄ and NiCoP/NiCo₂S₄.

Figure 5 Comparison of (a) CV and (d) discharge curves of the NiCo₂O₄, NiCo₂S₄, NiCoP and NiCoP/NiCo₂S₄ electrodes. (b) CV and (e) discharge curves of the NiCoP/NiCo₂S₄ electrode. (c) Variation in the redox peak currents with the square root of the scan rates of the NiCoP/NiCo₂S₄ electrode. (f) Specific capacities versus current densities of the NiCo₂O₄, NiCo₂S₄, NiCoP and NiCoP/NiCo₂S₄ electrodes. Specific capacities of the NiCoP/NiCo₂S₄ electrodes as a function of (g) phosphating temperature, (h) reaction time and (i) mass of NaH₂PO₂.

electrodes, suggesting the enhanced specific capacity and faster redox reaction kinetics. As the scan rate increases from 10 to 30 mV s^{-1} , the CV curves of NiCoP/NiCo₂S₄ electrode remain symmetric redox peaks (Fig. 5b), indicating the great reversibility of redox reactions. As shown in Fig. 5c, there is a near linear relationship between peak currents and the square root of scan rates, demonstrating that the redox reactions for the NiCoP/NiCo₂S₄ electrode are diffusion-controlled [3,36]. The improved specific capacity can also be achieved by analyzing the discharge curves, as depicted in Fig. 5d, where the discharge plateau of the NiCoP/NiCo₂S₄ electrode is much longer than others at the same current density of 10 A g^{-1} . Additionally, in contrast to the NiCo₂O₄, NiCo₂S₄, and NiCoP electrodes, the discharge curves of the heterostructured NiCoP/NiCo₂S₄ remain steady discharge plateau as the current densities increase from 10 to 50 A g^{-1} , indicating the good rate performance (Fig. 5e and Fig. S5). The highest specific capacity obtained for the NiCoP/NiCo₂S₄ electrode is $251.1 \text{ mA h g}^{-1}$ at a high current density of 10 A g^{-1} (Fig. 5f), which is higher than that of NiCo₂O₄ (76.9 mA h g^{-1}), NiCo₂S₄ ($154.2 \text{ mA h g}^{-1}$) and NiCoP ($180.0 \text{ mA h g}^{-1}$). Importantly, the NiCoP/NiCo₂S₄ electrode exhibits exceptional capacitive retention at a high current density. Even after increasing the current density to 50 A g^{-1} , the NiCoP/NiCo₂S₄ electrode shows a capacity of $190.3 \text{ mA h g}^{-1}$, which is about 76% retention of that at 10 A g^{-1} . The specific capacity of NiCoP/NiCo₂S₄ is close or even superior to many similar materials, such as Co₃S₄ ($234.0 \text{ mA h g}^{-1}$ at 8 A g^{-1}) [8], R-Co₃O₄ ($212.6 \text{ mA h g}^{-1}$ at 2 mA cm^{-2}) [18], Ni₃S₂@PANI ($247.6 \text{ mA h g}^{-1}$ at 11.4 A g^{-1}) [44], and NiCo₂O₄ ($183.1 \text{ mA h g}^{-1}$ at 1.6 A g^{-1}) [45]. Fig. 5g–i, Figs S6 and S7 show the electrochemical performances of the NiCoP/NiCo₂S₄ electrode under different phosphating conditions. It is clear that the optimal condition for the NiCoP/NiCo₂S₄ electrode is 400°C for 2 h with 0.5 g of NaH_2PO_2 , which presents the highest specific capacity.

The outstanding specific capacity and high rate capability of the heterostructured NiCoP/NiCo₂S₄ electrode render it a great potential as the cathode in aqueous Zn-ion battery. An aqueous

Zn-ion battery was assembled by using the NiCoP/NiCo₂S₄ electrode as the cathode and Zn plate as the anode with the mixed solution of 1 mol L^{-1} KOH and 0.01 mol L^{-1} $\text{Zn}(\text{CH}_3\text{-COO})_2$ as the electrolyte. The NiCoP/NiCo₂S₄ reacts with OH^- on the cathode, while reversible $\text{Zn}(\text{OH})_2^{2-}/\text{Zn}^0$ stripping/plating occurs on the anode (Fig. 6a). Fig. 6b displays the CV curves of the NiCoP/NiCo₂S₄//Zn battery at various scan rates. Well-defined symmetric redox peaks can still be observed even at a high scan rate of 60 mV s^{-1} , revealing the highly reversible redox reaction. As shown in the charge-discharge curves of Fig. 6c, the discharge plateau of the NiCoP/NiCo₂S₄//Zn battery is approximately at 1.7 V . Additionally, the NiCoP/NiCo₂S₄//Zn battery shows better performances than the NiCo₂S₄//Zn battery (Fig. S8). Particularly, the NiCoP/NiCo₂S₄//Zn battery exhibits much higher specific capacity than the NiCo₂S₄//Zn battery, which is clearly demonstrated by comparing the CV and discharge curves (Fig. S9). Notably, the NiCoP/NiCo₂S₄//Zn battery yields an incredibly high specific capacity of $265.1 \text{ mA h g}^{-1}$ at a high current density of 5 A g^{-1} (Fig. 6d), which is substantially higher than that of the NiCo₂S₄//Zn battery ($144.3 \text{ mA h g}^{-1}$) and most reported Zn-ion batteries, such as Ni(OH)₂/CNFs//Zn (184 mA h g^{-1} at 5 mA cm^{-2}) [46], Co₃O₄//Zn (162 mA h g^{-1} at 1 A g^{-1}) [47], Ni₃S₂//Zn (148 mA h g^{-1} at 0.2 A g^{-1}) [48], NiO//ZnO (203 mA h g^{-1} at 0.5 mA cm^{-2}) [14], NiCo₂O₄//Zn ($183.1 \text{ mA h g}^{-1}$ at 1.6 A g^{-1}) [45], Zn//R-Co₃O₄ ($240.8 \text{ mA h g}^{-1}$ at 2 mA cm^{-2}) [18]. The NiCoP/NiCo₂S₄//Zn battery possesses a specific capacity of $139.7 \text{ mA h g}^{-1}$ with ~53% capacity retention at 10 A g^{-1} , indicating its excellent rate capability. The high rate capability of the NiCoP/NiCo₂S₄//Zn battery was further demonstrated in Fig. 6e, where the current density increased from 5 to 10 A g^{-1} and returned to 5 A g^{-1} . The NiCoP/NiCo₂S₄//Zn battery delivers an average capacity of 264.9, 242.1, 206.2, 175.8, 155.2, and $139.7 \text{ mA h g}^{-1}$ at 5, 6, 7, 8, 9, 10 A g^{-1} , respectively. When the current density is reduced back to 5 A g^{-1} after 50 cycles, the average capacity of $274.4 \text{ mA h g}^{-1}$ is recovered, revealing excellent rate performance. Fig. 6f shows the long-term cycling performance of the NiCoP/NiCo₂S₄//Zn bat-

Figure 6 (a) Schematic diagram of the reaction mechanism of the NiCoP/NiCo₂S₄//Zn battery. (b) CV and (c) charge-discharge curves of the NiCoP/NiCo₂S₄//Zn battery. (d) Specific capacities versus current densities and (e) rate performances of the NiCo₂S₄//Zn and NiCoP/NiCo₂S₄//Zn batteries. (f) Cycling test of the NiCoP/NiCo₂S₄//Zn battery and the SEM image of the NiCoP/NiCo₂S₄ cathode after 5000 cycles (inset).

Figure 7 Ragone plots of the NiCo₂S₄//Zn battery and NiCoP/NiCo₂S₄//Zn battery compared with other similar studies. The inset is the digital photo of heart-shaped LEDs powered by two as-fabricated NiCoP/NiCo₂S₄//Zn batteries in series.

tery collected at a high scan rate of 100 mV s⁻¹. The NiCoP/NiCo₂S₄//Zn battery maintains 96.9% of the initial capacity after 5000 cycles. The NiCoP/NiCo₂S₄ nanosheet arrays are well-reserved (inset in Fig. 6f), further demonstrating the excellent cycling performance.

Energy density and power density are two important parameters to estimate the practicability of energy storage devices. Fig. 7 shows the Ragone plots of the as-assembled NiCo₂S₄//Zn battery and NiCoP/NiCo₂S₄//Zn battery. It can be observed that the NiCoP/NiCo₂S₄//Zn battery delivers a maximum energy density of 444.7 Wh kg⁻¹ at the power density of 8.4 kW kg⁻¹. When the power density is increased to 16.3 kW kg⁻¹, the energy density still remains 228.2 Wh kg⁻¹. While the NiCo₂S₄//Zn battery only delivers a maximum energy density of 240.5 Wh kg⁻¹ at the power density of 8.3 kW kg⁻¹. The energy density of the obtained NiCoP/NiCo₂S₄//Zn battery is close to or even higher than those of some aqueous Zn-ion batteries reported previously, such as NiO//ZnO (355.7 Wh kg⁻¹ at 17.9 kW kg⁻¹) [14], Ni₂P//Zn (318.0 Wh kg⁻¹ at 1.4 kW kg⁻¹) [49], Ni₃S₂//Zn (419.6 Wh kg⁻¹ at 1.8 kW kg⁻¹) [48], Ni₃S₂@PANI//Zn (386.7 Wh kg⁻¹ at 3.9 kW kg⁻¹) [44], Co₃O₄//Zn (241.0 Wh kg⁻¹ at 1.5 kW kg⁻¹) [47], Co₃O₄@NiO//Zn (215.5 Wh kg⁻¹ at 3.5 kW kg⁻¹) [50], NiCo₂O₄//Zn (210.7 Wh kg⁻¹ at 19.5 kW kg⁻¹) [45], and Co-Ni(OH)₂//Zn (138.0 Wh kg⁻¹ at 1.7 kW kg⁻¹) [51]. The inset of Fig. 7 shows that two as-fabricated batteries connected in series can effectively power heart-shaped light-emitting diodes (LEDs) indicators, demonstrating the great promise for potential practical utilization.

CONCLUSION

In summary, we report the synthesis of heterostructured NiCoP/NiCo₂S₄ nanosheet arrays on carbon cloth through treating NiCo₂S₄ nanosheet arrays in the presence of P source, and demonstrate its excellent property as the electrode material in aqueous Zn-ion batteries. The high electrochemical activity between NiCoP and NiCo₂S₄ enables fast electron transport and rapid ion diffusion. As a result, the NiCoP/NiCo₂S₄ electrode shows a large specific capacity of 251.1 mA h g⁻¹ at a high current density of 10 A g⁻¹ and satisfactory rate capability (retaining

about 76% even at 50 A g⁻¹). Furthermore, the assembled NiCoP/NiCo₂S₄//Zn battery delivers a high specific capacity of 265.1 mA h g⁻¹ at 5 A g⁻¹, excellent cycling stability with 96.9% retention after 5000 cycles, as well as a competitive energy density of 444.7 Wh kg⁻¹ at the power density of 8.4 kW kg⁻¹. The successful construction of aqueous Zn-ion batteries by interfacial engineering of electrode materials sheds light on the exploration of high-performance energy storage devices in the future.

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Conflict of interest The authors declare that they have no conflict of interest.

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

Fang Yang received her PhD degree from Donghua University in 2015. Currently, she works at the School of Mechanical and Automotive Engineering at Shanghai University of Engineering Science. Her research focuses on rational design and synthesis of nanocomposite materials for energy storage devices.

Shijie Li received his PhD degree in environmental engineering from Donghua University in 2014. He is currently an associate professor at the National Engineering Research Center for Marine Aquaculture, Zhejiang Ocean University. His research interests focus on the development of functional nanomaterials and their applications in electrochemical energy storage and conversion, and environmental remediation.

Kaibing Xu received his PhD degree from Donghua University in 2015. Currently, he works at the Research Center for Analysis and Measurement, Donghua University. His research focuses on rational design and synthesis of nanocomposite materials for applications in electrochemical energy storage and conversion such as supercapacitors, alkaline rechargeable batteries and lithium ion batteries.

原位构筑富异质界面的双金属硫/磷化合物提升水系锌电池性能

杨方¹, 沈越年², 岑泽¹, 万杰¹, 李世杰^{3*}, 何冠杰⁴, 胡俊青^{2,5}, 徐开兵^{2*}

摘要 目前开发高倍率和稳定的水系锌离子电池电极材料仍然是一个挑战. 本研究提出了一种磷化辅助界面工程策略, 将 NiCo_2S_4 纳米片可控转化为 $\text{NiCoP}/\text{NiCo}_2\text{S}_4$ 异质结构作为水系锌离子电池电极材料. 具有丰富界面的多组分异质结构不仅提高了电极材料的电导率, 而且增强了锌离子的扩散路径. 和预期结果一样, $\text{NiCoP}/\text{NiCo}_2\text{S}_4$ 电极材料在 10 A g^{-1} 的电流密度下其容量高达 251.1 mA h g^{-1} , 且具有优异的倍率性能(电流密度高达 50 A g^{-1} 时, 其容量保持约为76%). 此外, 以 $\text{NiCoP}/\text{NiCo}_2\text{S}_4$ 为正极组装的锌离子电池也展现了优异的比容量(在 5 A g^{-1} 的电流密度下高达 265.1 mA h g^{-1}), 长循环稳定性(经过5000圈循环后比容量保持率为96.9%)和高能量密度(在 8.4 kW kg^{-1} 的功率密度下高达 444.7 W h kg^{-1}). 因此, 本研究为构建具有丰富界面的异质结电极材料提供了一种简单的磷化辅助界面工程策略, 为未来开发高性能储能器件提供了理论基础.