Phosphorous-doped bimetallic sulfides embedded in heteroatom-doped carbon nanoarrays for flexible all-solid-state supercapacitors

Shuo Li¹, Minghao Hua¹, Yuan Yang¹, Xiaowen Zheng¹, Wei Huang², Pengchao Si^{1*}, Lijie Ci¹ and Jun Lou³

ABSTRACT Flexible supercapacitors (SCs) have become a popular research topic due to their extra-long service life, foldability, and wearability. Nevertheless, their low energy density restricts their applications. Here, we synthesized phosphorus-doped bimetallic sulfides embedded in heteroatom-doped (N, S, and P) carbon shells (P-ZCS/HC) using a simple approach to create high-performance flexible electrodes. The three-dimensional architecture made by interlaced nanosheets was preserved, and raised nanoparticles appeared on the rough surface during the annealing operation, increasing the specific surface area and potential exposure to the electrolyte. It is noteworthy that the optimal P-ZCS/HC electrode possessed a remarkable capacity of 1080 C g⁻¹ at 1 A g⁻¹ along with superb cycling stability. These extraordinary properties were primarily caused by plentiful redox reactions, enhanced conductivity, and synergic effects of the P-doped metal sulfides and heteroatom-doped carbon shells. Density functional theory simulations confirmed the good function of the P-doped electrodes and their ability to boost conductivity, improve reactive dynamics, and promote OH⁻ adsorption. Notably, the assembled all-solid-state hybrid SC exhibited a maximum energy density of 62.9 W h kg⁻¹ and a power density of 16 kW kg⁻¹, while being able to maintain 92.0% of its initial capacity after 10,000 cycles. This systematic report provides new insight into the design and synthesis of electrodes with complex components and outstanding structures for the flexible energy field.

Keywords: supercapacitors, metal sulfides, phosphorus doping, DFT calculations, nanoarrays

INTRODUCTION

Over the past several decades, flexible devices, such as folding electronic screens, wearable electronics, and portable power tools, have become increasingly attractive [1]. As a consequence, the demands for light weight, high safety, and good flexibility in energy-storage facilities have become high [2]. Flexible supercapacitors (SCs) not only satisfy the above requirements but also possess other desirable characteristics, such as outstanding power density, quick response, and extra-long service life [3,4]. However, their low energy density limits their widespread application and is currently the most pressing issue to be addressed regarding these components [5,6]. An efficient strategy to enhance their energy density is to fabricate flexible hybrid SCs (HSCs) that incorporate battery-type capacitive electrodes to widen the potential window [7–9]. Another method is to increase the specific capacity, which can be accomplished by designing innovative electrode materials. To date, numerous studies have been undertaken with a focus on designing new electrodes for HSCs [10,11]. However, engineering and optimizing low-cost and highly conductive electrodes with controllable constructions for flexible SCs remains a challenge.

Recently, transition metal sulfides (TMSs) have received enormous attention, both academic and industrial, due to their improved electroconductivity and reactivity during electrochemical measurements in comparison with oxides/hydroxides [12–15]. Researchers have confirmed that multi-element TMSs possess better performance than single-element TMSs, which is due to

¹ Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), Research Center for Carbon Nanomaterials, School of Materials Science and Engineering, Shandong University, Jinan 250061, China

² Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

³ Department of Materials Science and NanoEngineering, Rice University, Houston, TX 77005, USA

* Corresponding author (email: pcsi@sdu.edu.cn)

enhanced synergy originating from more abundant redox processes [16]. However, the unsatisfying reaction dynamics and inadequate active sites of TMSs on the nanoscale still hinder their further development in SCs [14,17]. Recently, adjusting the compositions of TMSs has stood out as a feasible method to heighten their electrochemical behavior, such as by doping heteroatoms into their original structures [18]. In particular, doping with phosphorus, which has atomic properties very similar to those of sulfur, into the lattice of TMSs has been found to promote their overall performance [19–21]. This phenomenon can be explained by the fact that the substitution of a few P atoms for S atoms during P doping leads to variations in the initial electronic structure, which can generate more available reactive sites and decrease the strain in the electrochemical process [22]. Despite these intriguing advantages, engineering controllable P-doped mixed-metal sulfides with uniformly distributed compositions is still a great challenge because the doping may cause undesirable disordered interfaces and/or the collapse of the compound architecture [19].

In this respect, metal-organic frameworks (MOFs) possessing high specific surface area (SSA) and porous construction have been extensively researched as profitable sacrificial templates for the subsequent synthesis of electrodes with well-designed architectures and tunable components [23]. Indeed, transforming MOFs into other derivatives is simple and highly efficient [24]. However, many traditional MOF-based electrodes are fabricated as powders, in which case a tedious slurry-coating process is required, during which the binder decreases the rate of charge transport [25]. Fabricating two-dimensional (2D) MOF-based materials directly onto 3D conductive substrates can help to effectively avoid this problem and boost the close connection between the material and substrate at the same time. Many studies have used metallic materials as substrates for growing active materials, such as nickel foam [26], copper foam [27], and titanium foil [28], while their rigidity limits their application to flexible products. Hence, carbon cloth (CC) has emerged as the best choice due to its light weight, 3D architecture, and high flexibility. Therefore, researching MOF-derived multivalent P-doped metal sulfides with fixed nanostructures and controllable compositions that grow on CC as an electrode material is a promising approach for the development of flexible SCs.

Based on this background, we here undertake systematic research on the synthesis strategy, intrinsic features, and electrochemical behavior of P-doped zinc-cobalt sulfide (ZCS) embedded in heteroatom-doped

carbon (HC) shells, which can be denoted as P-ZCS/HC. The developed electrode consisted of multiple anions and cations and was fabricated *via* a simple room-temperature reaction followed by a two-step ion-exchange process. The P-ZCS/HC network, which grew directly on CC, inherited the 3D architecture of the MOF precursor, and the resulting well-ordered leaf-like nanosheets possessed uneven surfaces with newly generated nanoparticles. Through alteration of the phosphating parameters, samples with different P concentrations were obtained, and their properties were investigated. Density functional theory (DFT) simulations were in good agreement with the experimental measurements, demonstrating the enhanced conductivity and positive effects on the reaction kinetics. Overall, the P-ZCS/HC electrode demonstrated outstanding specific capacity and a long cycle life. Impressively, the fabricated P-ZCS/HC/reduced graphene oxide (RGO) HSC was found to also possess a remarkable energy density of 62.9 W h kg^{-1} at 800 W kg^{-1} along with good flexibility and cycling stability. These properties mean the electrode outperforms most previously published phosphide or sulfide electrodes and devices [16,29,30]. This work thus leads to tremendous possibility for synthesizing multivalent, heteroatom-doped metallic sulfides with excellent performance and stable architecture by a universal and low-cost strategy to fulfill the high demands of flexible SCs.

EXPERIMENTAL SECTION

Synthesis of ZnCo MOF on CC

The CC was submerged in concentrated nitric acid at 50°C for 6 h. Afterward, it was rinsed with deionized water (DW) four times and dried under vacuum at 55°C for 9 h. Then, the CC was sputtered with a Co target (99.99% pure) on both sides using a magnetron sputtering system (SKY Company, TRP-450) for 300 s. Finally, it was cut into $2 \text{ cm} \times 2.5 \text{ cm}$ pieces.

Next, 0.179 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.524 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dispersed in 40 mL of DW. In addition, 1.314 g of 2-methylimidazole (2-MIM) was dispersed in 40 mL DW, and both solutions were magnetically stirred for 15 min. Subsequently, one piece of the aforementioned CC was immersed in the first solution, and the organic ligand solution was then slowly decanted into it. After sitting for 4 h at room temperature, the violet CC substrate was removed, rinsed with DW, and dried in a vacuum at 55°C for 8 h. Co-MOF grown on CC was prepared by the same method using 0.699 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ without $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Synthesis of ZnCoS/heteroatom-doped carbon nanosheets on CC

The CC with ZnCo-MOF was placed in a porcelain boat, and 0.32 g of sublimed S was placed in another porcelain boat. The two boats were put into an annealing furnace, with the S situated in the upstream position. Then, the samples were heated at 450°C for 2 h at a 2°C min⁻¹ heating rate in Ar. After being cooled, a sample denoted as ZCS/HC was fabricated. A CoS₂/HC sample was prepared by annealing the Co-MOF on the CC by the same method.

Synthesis of phosphorus- and ZnCoS/heteroatom-doped carbon nanosheet network on CC

To prepare the electrode on the CC, another thermal phosphating process was required. First, the CC with the ZCS/HC network was placed in a porcelain boat, and 0.6 g of NaH₂PO₂ powder was placed in another porcelain boat, which was located at the upstream region in the furnace. Then, the electrode was annealed at 350°C for 2 h at a 2°C min⁻¹ heating rate in argon. After being cooled, the electrode on the CC (denoted as P-ZCS/HC) was fabricated. The average weight of the P-ZCS/HC was determined to be approximately 2.5 mg cm⁻². In addition, the ZCS/HC sample was thermally processed using different NaH₂PO₂ contents as controls (0.3 and 0.9 g) with different P/S ratios (Table S1). The P/S ratios were recorded by an energy-dispersive spectrometer, and the samples were labeled P-ZCS/HC-1 and P-ZCS/HC-3.

Electrochemical evaluations

A CHI 660E electrochemical workstation was used to test the electrochemical behaviors of the active materials. A 6 mol L⁻¹ KOH solution was used as an electrolyte. For the three-electrode measurements, CC with self-supported samples, platinum plates, and calomel electrodes acted as the working, counter, and reference electrodes. The cycle properties were tested through the LAND system. The specific gravimetric capacities (C_g , C g⁻¹) were confirmed by the equation below:

$$C_g = \frac{I \times \Delta t}{m}, \quad (1)$$

where I expresses the current, Δt is the discharging period, and m is the mass of the materials.

Preparation of the all-solid-state hybrid semiconductor device

The HSC device was prepared using P-ZCS/HC and RGO as the positive and negative electrodes, respectively. The fabrication technique for RGO was outlined in detail in

our previous report [31]. The preparation of the RGO slurry was performed by the same method as used previously, and the slurry was coated on CC. The gel electrolyte was synthesized as follows. First, 1 g of polyvinyl alcohol (PVA) was dissolved into 8 mL of DW and constantly stirred at 90°C for 1 h. After the gel cooled down to 60°C, 3 mL of 6 mol L⁻¹ KOH solution was slowly dropped into the gel. After being cooled down, the gel was smeared on the negative and positive CC as well as on the filter paper (separator). Finally, these components were assembled into the HSC device and heated at 60°C for 8 h. In consideration of the charge storage theories regarding the different materials in the HSC, the weights of the load on the electrodes follow the formula below:

$$\frac{m_+}{m_-} = \frac{C_{gc-}}{C_{gc+}}. \quad (2)$$

Here, + represents the positive electrode, and - is the negative one. The energy (E) and power (P) densities follow the equations below, respectively:

$$E = \frac{I \int V dt}{3.6 \times m}, \quad (3)$$

$$P = \frac{E \times 3600}{\Delta t}, \quad (4)$$

where V is the potential range, and m is the mass sum of the positive and negative samples.

DFT calculations

DFT simulations were performed by the Vienna *Ab initio* Simulation Package (VASP) [32]. The exchange-correlation potential was calculated using the Perdew-Burke-Ernzerhof (PBE) scheme [33] with a cutoff energy of 500 eV. The Brillouin zone integrations were performed with 11 × 11 × 11 gamma k-point grids for geometry optimization and 13 × 13 × 13 for electronic structure calculations. All the atoms were fully relaxed until the residual force on each atom was lower than 0.02 eV Å⁻¹, and the energy convergence criterion was set as 10⁻⁵ eV.

The OH⁻ adsorption energy can be calculated as follows:

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{slab}} - E_{\text{OH}^-}, \quad (5)$$

where E_{total} represents the total energy of the ZCS or P-doped ZCS slab with OH⁻ adsorbed on the surface, E_{slab} represents the energy of the supercell, and E_{OH^-} represents the energy of a single OH⁻ anion.

RESULTS AND DISCUSSION

The fabrication method for the 3D self-supporting P-

ZCS/HC construction on CC is schematically presented in Fig. 1. The hierarchical P-doped ZCS was grown on CC by a simple room-temperature reaction followed by a two-step thermal treatment, meaning the electrode could be mass-produced at a low cost. At first, the metal ions reacted with the organic ligands to form the well-aligned ZnCo-MOF precursor nanosheets on the CC substrate at room temperature. Then, during the annealing procedure in the presence of S, the precursors were converted into bimetallic sulfide nanosheets with distributed nanoparticles enveloped by a heteroatom-doped carbon shell. With subsequent thermal treatment, the sulfides were further transformed into P-ZCS/HC in an Ar atmosphere containing P through an ion-exchange reaction.

The morphologies of the fabricated ZnCo-MOF, ZCS/HC, and P-ZCS/HC electrodes are shown in Fig. 2. The 2D leaf-like MOF nanosheets were interlaced with one another, forming a 3D architecture (Fig. 2a) with plentiful voids favorable for the permeation of electrolyte [16,34]. As exhibited in the magnified image shown in Fig. 2b, the precursor possessed a very smooth surface. After the S treatment, the interlinked ZCS/HC (Fig. 2c, d) nanosheets

maintained their 3D architectures containing open spaces. At the same time, the surfaces of the nanosheets became rough with many nanometer-sized spherical particles. This surface evolution was mainly caused by the etching of S^{2-} ions [35], and the metal groups aggregated into nanoparticles during the thermal process, a phenomenon that has also appeared in previous studies [36–39]. The exact composition of the ZCS/HC was measured by energy-dispersive X-ray spectroscopy (EDS) tests, as shown in Fig. S1. The atomic percentages of Zn, Co, and S were found to be 3.1%, 6.4%, and 21.1%, respectively. After the phosphating process, the P-ZCS/HC nanosheets (Fig. 2e–h) still evenly covered the CC surface, and the morphology exhibited almost no change compared with ZCS/HC. In addition, the CoS_2/HC and P-ZCS/HC-1 and -3 electrodes had identical morphologies to ZCS/HC, as shown in Fig. S2, indicating that the P doping at different contents and the introduction of Zn had no effect on the sample morphologies. Such a construction can effectively enlarge the SSA of an electrode, potentially increasing its electrochemical properties [31].

Fig. 3 shows the transmission electron microscopy

Figure 1 Diagrammatic sketch of the fabrication strategy for P-doped ZCS nanoparticles locked in heteroatom-doped carbon nanoarrays.

Figure 2 The scanning electron microscopy (SEM) images of (a, b) ZnCo-MOF, (c, d) ZCS/HC nanosheets, and (e–h) P-ZCS/HC nanosheets.

Figure 3 (a, b) TEM images, (c–f) HRTEM images, and (g) SAED pattern of the P-ZCS nanoparticles encapsulated in heteroatom-doped carbon shells, with (e₁) and (f₁) showing the average distances computed from the corresponding diffraction lattice fringes. (h) Elementary EDS mappings of the P-ZCS/HC nanosheet.

(TEM) images of the P-ZCS/HC sample to further reveal the morphological transformation. As shown in Fig. S3a, the precursor nanosheet possessed a perfectly smooth surface. After the sulfurizing process (Fig. S3b, c), the ZCS/HC nanosheets had newly formed uneven surfaces. As the phosphorization proceeded (Fig. 3a, b), the P-ZCS/HC nanosheets inherited the surface constructions of the ZCS/HC, with an abundance of nanoparticles on the nanosheets, indicating good agreement with the SEM morphologies. The high-resolution TEM (HRTEM) images shown in Fig. 3c, d verify that the irregular P-ZCS/HC nanoparticles were tightly encapsulated in the carbon shell. The amplifying HRTEM images (Fig. 3e, f) show that the calculated average fringe spacings were approximately 0.250 and 0.278 nm, corresponding to the (210) and (200) planes of P-ZCS/HC, respectively. These were slightly larger than those of ZCS/HC due to the P doping (Fig. S3d, e). The well-defined diffraction rings in the selected area electron diffraction (SAED) patterns of P-ZCS/HC (Fig. 3g) and ZCS/HC (Fig. S3f) can be in-

dexed to the (200), (210), (211), (220), and (311) planes of CoS₂, indicating similar polycrystalline properties. Further, the elemental mappings of the uniformly distributed Co, Zn, S, P, C, and N elements in the P-ZCS/HC nanosheet exhibited in Fig. 3h indicate the successful synthesis of the P-doped bimetallic sulfides and the heteroatom-doped carbon shell.

The crystal constructions of the prepared electrodes were characterized using X-ray diffraction (XRD). Fig. S4a shows the XRD results of the ZnCo-MOF grown on CC. Aside from the CC peaks, all the other diffraction peaks can be indexed to the zinc-cobalt zeolitic imidazole frameworks without impurities, implying the successful synthesis of ZnCo-MOF [35]. The XRD patterns of the ZCS/HC and P-ZCS/HC electrodes shown in Fig. 4a indicate that the ZCSs had identical structures before and after the P doping and that both were consistent with CoS₂ (JCPDS No. 41-1471). There was no newly generated phase of metal phosphide after the phosphating treatment, revealing that the P atoms occupied only some

Figure 4 (a) XRD tests and (b) Raman spectra of the P-ZCS/HC and ZCS/HC electrodes. (c) Nitrogen sorption isotherms of the P-ZCS/HC and ZnCo-MOF samples. (d–i) XPS spectra of (d) Zn 2p, (e) Co 2p, (f) S 2p, (g) P 2p, (h) N 1s, and (i) C 1s for the P-ZCS/HC electrode.

of the S atom sites, and the final product was P-doped sulfide rather than phosphide. In addition, due to the presence of Zn and P, the diffraction peaks of P-ZCS/HC had a number of deviations compared with those of CoS₂ [40]. The XRD patterns of CoS₂/HC, P-ZCS/HC-1, and P-ZCS/HC-3 shown in Fig. S4b, c reveal the same CoS₂ crystal structures. This phenomenon indicates that using different P contents for doping did not alter the pristine crystalline structure of the sulfide. The XRD analyses fit well with TEM results, again verifying the success of the P doping strategy.

Raman spectroscopy was used to detect the defects and characteristics of these carbonaceous materials. The two peaks around 1341 and 1544 cm⁻¹ shown in Fig. 4b corresponded to the D and G bands, representing disordered and sp² hybridized carbon, respectively [38]. Further, the intensity ratio (I_D/I_G) of P-ZCS/HC (0.89) exceeded that of ZCS/HC (0.85), indicating that additional defects were generated by the doping treatment. This is considered a good result because defects can lead to more approach-

able surfaces and charge accumulations, making for easier transmission during the charging and discharging processes [41].

The N₂ sorption isotherms of the ZnCo-MOF and P-ZCS/HC nanosheets were tested to thoroughly investigate their inherent properties. The two type-IV patterns with hysteric loops shown in Fig. 4c indicate that these electrodes had numerous mesoporous regions [13]. The P-ZCS/HC sample possessed a 77.1-m² g⁻¹ SSA, which was significantly larger than that of ZnCo-MOF (27.8 m² g⁻¹). During the annealing processes, the lightweight carbon skeleton transformed into a highly mesoporous structure, which led to the large SSA of the prepared materials. The pore-size distributions of the two materials (Fig. S5) obtained from the Barrett-Joyner-Halenda (BJH) analysis reveal that the P-ZCS/HC structure had a greater variety of pores than that of the precursor after the sulfuration and phosphorization treatments. Such a multilevel architecture is conducive not only to the transportation of ions/electrons but also to

decreasing the internal impedance [37].

The chemical environments of the component elements of the electrodes were researched using X-ray photoelectron spectroscopy (XPS). Fig. 4d–i display the Zn 2p, Co 2p, S 2p, P 2p, N 1s, and C 1s spectra of the P-ZCS/HC, respectively, and the corresponding spectra of the ZCS/HC sample are displayed in Fig. S6. The two main peaks in the Zn 2p (Fig. 4d) of P-ZCS/HC at 1022.4 and 1045.5 eV corresponded to the Zn 2p_{3/2} and Zn 2p_{1/2} of Zn²⁺, respectively [42]. For the Co 2p region of the P-ZCS/HC shown in Fig. 4e, the peaks at 778.7 and 793.8 eV, which belong to Co 2p_{3/2} and 2p_{1/2}, respectively, represent the bonding between Co and S or P [43,44]. In addition, the peaks at 781.9 and 798.0 eV indicate the existence of oxidative Co arising from surface oxidation [42]. The other two peaks at 785.9 and 803.0 eV were indexed as satellite peaks (marked as “Sat”). Concerning the Zn 2p and Co 2p regions of the ZCS/HC sample (Fig. S6a, b), the main peaks were located at slightly lower positions in comparison with those of P-ZCS/HC, indicating that the phosphorization process caused the electrode to become more positively charged [44]. Further, the Co–S/Co–P region grew slightly after the P doping, which may have been due to the increased combination of Co–P [45]. As for the S 2p region of P-ZCS/HC shown in Fig. 4f, the peaks at 162.5 and 163.7 eV were indexed to S 2p_{3/2} and S 2p_{1/2} of Co–S bonds, while the peaks at 162.9 and 164.2 eV fit well with S 2p_{3/2} and S 2p_{1/2} of Zn–S bonds [12]. The peaks at 164.8 and 165.6 eV can be ascribed to C–S–C bonds, indicating the combination of S with C atoms [46,47]. The peak at 169.0 eV was caused by S–O bonds [48]. For the P 2p spectrum shown in Fig. 4g, the two peaks at 129.5 and 130.6 eV were indexed to P 2p_{3/2} and P 2p_{1/2}, respectively, representing the bonding of P and metals. The peak at 133.0 eV represents P–C bonds, indicating the combination of P with C atoms [49,50]. The peak at 134.0 eV reflects the existence of phosphate in the superficial position, and this peak has also been present in previously reported P-containing materials [49]. The phosphate peak was relatively strong, indicating phosphate modification on the surface. The P–O species on the surface had a positive effect on reducing the free energy barrier and enhancing the electrochemical activity [51–53]. To verify the primary effect of the P doping on the metal sulfide, it is necessary to investigate the difference in P species between the surface and bulk materials. We performed depth-profiling XPS on the P-ZCS/HC electrode, a detailed explanation of which is presented in Fig. S7. Accordingly, it was found that phosphate modification

existed on the surface, while in the bulk material, the P species mainly consisted of P–C and M–P combinations. Compared with the elemental P (130.2 eV), P 2p_{3/2} moved to a lower-energy position, a phenomenon that also appeared in the S 2p spectrum, demonstrating that P and S were negatively charged. These elements with opposite charges are able to form strong bonds that may modulate the electronic environments of the P-ZCS/HC network, having a positive effect on the electrochemical behavior [44,54]. The N 1s spectrum (Fig. 4h) of the P-ZCS/HC electrode exhibited four N types: pyridinic (398.4 eV), pyrrolic (399.1 eV), graphitic (400.1 eV), and oxidized N (401.2 eV) [36]. According to a previous report [55], the relatively high ratios of pyridinic and pyrrolic N may contribute to better energy storage. The carbon peaks presented in Fig. 4i can be divided into four sections: C–C (284.8 eV), C–N/C–S/C–P (286.2 eV), C=N/C=O (287.0 eV), and O=C–O (288.6 eV) [56,57]. These bonds reflect the N, S, and P heteroatoms codoped into the carbon network. The XPS measurements indicate that this strategy achieved the successful introduction of P atoms into the metal sulfide lattices and the codoping of N, S, P heteroatoms in carbon shells.

The different active materials grown on the CC were applied as the electrodes of SCs to study their electrochemical properties. The CC with sputtered Co coating exhibited negligible capacitance in comparison with the other prepared samples (Fig. S8). Fig. S9 shows the electrochemical performance of the electrodes with different P contents, which was used to investigate the influence of the P doping in detail. The P-ZCS/HC sample possessed a much larger cyclic voltammogram (CV) region and longer discharge period than those of the P-ZCS/HC-1 and -3 samples, indicating it had better properties. Therefore, the ZCS/HC electrode annealed with 0.6 g of NaH₂PO₂ powder was selected as the optimal electrode.

Fig. 5a displays the CV curves of the P-ZCS/HC material with the voltage ranging from –0.2 to 0.7 V. All the curves were similar, even at 40 mV s^{–1}, illustrating the good rate performance of the material [58]. Each curve presented an evident pair of redox peaks, representing battery-type properties. The movements of anodic and cathodic peaks toward the opposite voltages were primarily due to the interior impedance caused by the rising sweep rates [59]. A comparison of the CV plots among the P-ZCS/HC, ZCS/HC, CoS₂/HC, and ZnCo-MOF electrodes is shown in Fig. 5b. Clearly, the P-ZCS/HC exhibited the largest CV area among them, indicating the presence of additional redox processes after the sulfuriz-

Figure 5 (a) CV plots of the P-ZCS/HC electrode tested at various sweep rates. (b) CV plots of the ZnCo-MOF, CoS₂/HC, ZCS/HC, and P-ZCS/HC electrodes at 20 mV s⁻¹. (c) *b* values calculated using the peak currents and scan rates of the P-ZCS/HC electrode. (d) Contribution rates of the two different controlled types of the P-ZCS/HC electrode. (e) GCD plots of the P-ZCS/HC electrode measured at 1 to 20 A g⁻¹. (f) GCD curves at 1 A g⁻¹, (g) specific capacities under diverse current densities, and (h) EIS and the equivalent electric circuit of the ZnCo-MOF, CoS₂/HC, ZCS/HC, and P-ZCS/HC electrodes. (i) Cycle performance of the CoS₂/HC, ZCS/HC and P-ZCS/HC electrodes at 15 A g⁻¹.

ing treatment and P doping. The feasible Faradaic reactions originated from the redox reactions of metal ions in the electrodes [60–62]. The redox reactions of this bimetallic sulfide can be expressed as follows [61]:

Further, this electrode contained N-, S-, and P- co-doped carbon materials. Therefore, some of the redox reactions resulted from heteroatom-doped C and O-containing functional groups. In addition, CV measurements are good tools to further study energy-storage kinetics. Generally, peak currents (*i*) have relations with scanning rates (*v*) [63], as follows:

$$i = av^b, \quad (9)$$

where *a* and *b* are constants. The above formula can be

transformed into: $\log i = b \log v + \log a$. The *b* value reflects whether the redox reaction in the electrochemical process is mainly controlled by the surface (*b* = 1 indicates capacitive behavior) or by diffusion (*b* = 0.5 indicates battery-type behavior) [64]. Based on the relations of $\log i$ and $\log v$ presented in Fig. 5c, it can be inferred that the P-ZCS/HC electrode stores charge mainly through a diffusion-controlled redox process. The respective amounts of the capacitance- (*k*₁*v*) and diffusion-controlled (*k*₂*v*^{1/2}) capacities can be quantified as follows:

$$i = k_1v + k_2v^{1/2}, \quad (10)$$

$$i/v^{1/2} = k_1v^{1/2} + k_2, \quad (11)$$

where *v* is the sweep rate, and *k*₁ and *k*₂ can be estimated via the relationship between *i/v*^{1/2} and *v*^{1/2}. As shown in Fig. 5d, the diffusion-controlled contribution decreased with rising scanning rates, which was caused by the lack of time required for Faradaic reactions at fast scanning

rates. However, at high sweep rates, the diffusion-controlled process still maintained a dominant position in the P-ZCS/HC electrode, demonstrating its battery-type characteristics and delicate construction advantageous for charge transport [65]. The capacity contributions of the ZCS/HC electrode are shown in Fig. S10, in which it can be seen that the capacitance-controlled capacities were lower than those of the P-ZCS/HC. This phenomenon suggests that the P-ZCS/HC possessed more near-surface active sites to achieve rapid electrochemical responses during the charging and discharging processes, promoting the rate capability [66,67].

Fig. 5e presents the galvanostatic charge/discharge (GCD) measurement results of the P-ZCS/HC electrode at $1\text{--}20\text{ A g}^{-1}$ in a range of $0\text{--}0.45\text{ V}$. The nearly symmetric curves indicate good reversible behavior for the charging and discharging processes [59]. Each GCD curve exhibited a voltage plateau, indicating the typical battery-type properties of the P-doped metal sulfide electrode. This phenomenon also fits well with the redox reactions shown in the CV plots. The GCD curves of the P-ZCS/HC, ZCS/HC, CoS_2/HC , and ZnCo-MOF electrodes are shown in Fig. 5f, according to which it is evident that the P-ZCS/HC possessed better energy-storage performance. The specific capacities of the P-ZCS/HC calculated by GCD measurements ranged from $684\text{--}1080\text{ C g}^{-1}$ at current densities of $1\text{--}20\text{ A g}^{-1}$, corresponding to area capacities of $2.68\text{--}1.69\text{ C cm}^{-2}$. In comparison with the capacities of the ZCS/HC, CoS_2/HC , and ZnCo-MOF electrodes (841 , 740 , and 196 C g^{-1} , respectively, at 1 A g^{-1}), the P-ZCS/HC electrode exhibited much higher capacity. The electrochemical measurements of the other three samples are shown in Fig. S11. The coulombic efficiencies of the P-ZCS/HC electrode were less than 100% but remained at relatively high levels (Fig. S12a). Even at a high current density of 20 A g^{-1} , the coulombic efficiency remained at approximately 96.9%. The P-ZCS/HC electrode also exhibited good performance compared with similar materials previously reported (Table S2). The active sites of the electrode materials involved in the redox processes decreased with increasing current densities, and the capacities then decreased, as shown in Fig. 5g [13]. Therefore, the sulfurizing and phosphating treatments of the nanosheet electrodes were able to significantly increase their electrochemical properties, especially their specific capacities.

Electric impedance spectroscopy (EIS) is a good method for researching the reaction dynamics of electrodes in detail. Fig. 5h shows the Nyquist plots of the four electrodes with an equivalent circuit, which were

recorded from $100\text{ kHz--}0.01\text{ Hz}$ at a 0.005-V alternating current (AC) perturbation. The plots of each of these four electrodes exhibited an oblique line and a semicircle, indicating behavior typical of SCs. These four electrodes with steep slopes demonstrate that the nanosheets formed constructions with sufficient open spaces to exhibit fast electrolyte diffusion. The diameter of the semicircle expresses the charge transfer resistance (R_{ct}), and the x -coordinate of the intersection expresses the bulk resistance (R_s) [68]. Clearly, the P-ZCS/HC electrode exhibited lower resistances ($R_{\text{ct}} = 1.33\text{ }\Omega$ and $R_s = 1.30\text{ }\Omega$) than those of the ZCS/HC ($R_{\text{ct}} = 1.68\text{ }\Omega$ and $R_s = 2.23\text{ }\Omega$), CoS_2/HC ($R_{\text{ct}} = 1.93\text{ }\Omega$ and $R_s = 2.87\text{ }\Omega$), and ZnCo-MOF ($R_{\text{ct}} = 3.47\text{ }\Omega$ and $R_s = 3.92\text{ }\Omega$) electrodes. That is, the P-ZCS/HC electrode possessed a higher ion-transfer rate between the electrode and electrolyte and lower inner resistance than the others. These results indicate that the bimetallic sulfide electrode possessed better reaction kinetics after the P doping, helping to improve its conductivity and electrochemical properties.

To appraise the working life of the electrodes, we performed successive GCD measurements on the P-ZCS/HC, ZCS/HC, and CoS_2/HC electrodes at 15 A g^{-1} , as shown in Fig. 5i. Encouragingly, the P-ZCS/HC electrode was able to maintain approximately 93.8% of its capacity after 10,000 cycles, which was much higher than the retentions of ZCS/HC (86.8%) and CoS_2/HC (80.7%). In addition, the coulombic efficiencies of the P-ZCS/HC, ZCS/HC, and CoS_2/HC electrodes after 10,000 cycles at a current density of 15 A g^{-1} were 95.9%, 93.1%, and 91.8%, respectively (Fig. 5i and Fig. S12b–d). Therefore, the cyclic stability and reversible behavior of the ZCS/HC electrode were enhanced after the phosphating treatment. The cycling behavior of the P-ZCS/HC was also better than that of other previously synthesized electrodes (Table S2). Further, the morphology, crystal structure, and EIS results of the P-ZCS/HC electrode after 10,000 cycles are shown in Fig. S13. The networks composed of interlinked nanosheets on the CC were well maintained, while some of the nanosheets had tiny fractures (Fig. S13a–c). There were also many nanoparticles located on the surfaces of the nanosheets, indicating the electrode had unchanged morphology and surface characteristics after 10,000 continuous cycles. The XRD pattern of the P-ZCS/HC sample after the cycling test (Fig. S13d) revealed the remaining crystal structure of the CoS_2 . There were only a few diminutions in the peak values, mainly due to the oxidation in the electrochemical processes [13]. The EIS plot shown in Fig. S13e is similar to the curve measured before the test, exhibiting only a small change, reflecting

the well-maintained capacitive properties and superior charge transfer kinetics after the cycle tests. Overall, our analyses consistently verified the excellent stability of the P-ZCS/HC electrode during the charging and discharging processes.

The remarkable performance of the P-ZCS/HC sample can be principally ascribed to the following factors. First, the two-step thermal approach successfully introduced S and P atoms into the sample and resulted in increased electrical conductivity, enhancing its electrochemical properties. The P-ZCS/HC electrode contained more redox-reactive sites, and its complex composition improved the reaction dynamics compared with monometallic sulfides or phosphides [66]. Second, the synergy caused by the effective combination of P-doped bimetallic sulfides and heteroatom-doped carbon shells increased the electrochemical performance. In addition, the carbon layer was able to efficiently protect and support the metal materials, resulting in excellent cycling stability. Third, the 3D construction consisted of 2D interconnected nanosheets with space among them serving as electrolyte storage rooms and temporary buffers, accelerating the permeation of electrolyte and adapting the volume transformation during the use process [16]. Additionally, the newly generated raised nanoparticles on the surface acted as edge sites to enhance the SSA and exposure to electrolyte [69]. Finally, the self-supporting approach guaranteed tight adhesion between the active materials and CC, establishing a pathway to transmit charges and effectively boosting the cycling stability and reducing the

interior impedance caused by the slurry-coating method [12].

To further demonstrate the possible synergic effects and the great enhancement of electrochemical properties originating from the P doping, we performed calculations on the density of states (DOS). Fig. 6a shows the optimized crystalline structural model of P-ZCS from two viewpoints. This model was derived from the CoS_2 structure containing a number of substitutions of Co and S with Zn and P atoms, respectively, based on the elementary proportions shown in Fig. S14. In addition, the ZCS structure is depicted in Fig. S15. The DOS patterns of ZCS and P-ZCS (Fig. 6b, c, respectively) both exhibited no band gaps at the Fermi level (denoted as E_f), reflecting the metallic features of the two materials [29]. In addition, the P-ZCS delivered a higher DOS at E_f , indicating the higher charge-occupied state and enhanced electron mobility [35]. This result also indicates the more obvious metallic character and the increased conductivity after P doping, which agrees well with the enhanced bonds between the metal ions and anions in the XPS analyses and the decreased bulk resistance in the EIS measurements. The partial DOS (Zn, Co, S, and P) of the P-ZCS shown in Fig. S16 indicates that the outermost 3d orbit of Co contributes largely to the electronic state around E_f . Due to synergic effects, the primary role of Zn atoms is to motivate the electroactivity of Co and accelerate the charge transmission between Co and S or P atoms [16,23,70]. The introduction of Zn in metal compounds can ameliorate the electronic structure, improve con-

Figure 6 (a) Crystalline structure of P-doped ZCS from two perspectives. DOS of (b) ZCS and (c) P-doped ZCS. (d) Diagrammatic sketch of the OH^- adsorption on Co sites of the (200) facet of P-doped ZCS. (e) OH^- adsorption energies of different sites in ZCS and P-doped ZCS.

ductivity, and accelerate electron transport between metal ions and OH^- , which is favorable for the OH^- adsorption and protonation/deprotonation processes [16]. The partial substitution of Zn for Co can also decrease the band gap and enhance the charge density at the Fermi level, which can effectively increase the electroactivity and electrochemical performance [70]. Further, Zn has a strong coordination ability and can easily combine with different metal ions to form stable compounds. The potential synergy from the complex composition of metal compounds can also generate more redox centers [68]. Therefore, bimetallic sulfides possess more plentiful Faradaic reactions in comparison with monometallic sulfides, which can further improve electrochemical performance [68]. Thus, the introduction of Zn is favorable.

We also carried out simulations on the adsorption energies of OH^- on the ZCS and P-ZCS surfaces to further exploit the redox behavior during the electrochemical processes. Based on the XRD and TEM analyses, the (200) facets of ZCS and P-ZCS were selected as the adsorbed surfaces. Fig. S17 and Fig. 6d show the OH^- adsorptions on Co sites of the most stable (200) facets of ZCS and P-ZCS, respectively. The slabs of these two different structures exposed different adsorption sites. In addition to the Co site, the (200) slab of P-ZCS also exposed the Zn site. As shown in Fig. 6e, the adsorption energy of hydroxyl for P-ZCS was -3.30 eV (Co site), which is lower than the energy adsorbed on the Co site of ZCS (-2.95 eV). Further, the Zn site of P-ZCS also exhibited a low OH^- adsorption energy (-3.02 eV). The low adsorption energies of OH^- indicate that P-ZCS has better adsorptive capability and a faster transfer of ions or electrons on the surface between the electrode and electrolyte, facilitating the electrochemical reactions [16]. This simulation result also explains the enhanced contribution of capacitive control to capacity and the decreased charge transfer resistance in the P-ZCS [67]. These results verify that the P doping in mixed-metal sulfides can improve the electronic structure and conductivity, promoting the synergy between different elements and facilitating OH^- adsorption. This ion substitution technique is able to ameliorate the reactive dynamics during the charging and discharging processes and make a great contribution to the electrochemical behavior. It thus has promising potential for application to the design of electrodes in energy-related fields.

All-solid-state flexible HSC devices were also assembled to test the applicability of the electrode in electronic products, following the assembly diagram depicted in Fig. 7a. Fig. S18 shows the electrochemical properties of

RGO. The CV plots (-1 – 0 V) were approximately rectangular, and the GCD curves were linear. These tests reflect the typical double-layer electrical behavior of RGO, which clearly differs from that of battery-type electrodes. The stable working voltages of the positive and negative electrodes indicate that the HSC device can be used in a range of 0 – 1.7 V. The P-ZCS/HC//RGO HSC device was then measured at 20 mV s^{-1} in operating windows from 0 – 1.0 and 0 – 1.8 V. As can be seen in Fig. 7b, the CV areas gradually increased with the rise of working potentials. The oxygen evolution reaction then appeared when the voltage increased beyond 1.6 V. Therefore, the appropriate window was set as 0 – 1.6 V, and Fig. 7c shows the CV tests within this potential range. The shapes of the curves remained consistent at different scanning rates, demonstrating the excellent rate capability. The GCD curves in the corresponding voltage window are depicted in Fig. 7d, and the nonlinear charging and discharging curves illustrate the Faradaic characteristic of the HSC device. As shown in Fig. 7e, the prepared all-solid-state HSC possessed high specific capacity ranging from 283 C g^{-1} at 1 A g^{-1} to 160 C g^{-1} at 20 A g^{-1} , exceeding those obtained in many published studies on SCs [22,23,71]. The inset in the figure also shows that light-emitting diodes (LEDs) could be successfully lit up by the HSC devices using a serial circuit. The electrochemical behavior of this P-ZCS/HC//RGO HSC device at different bending states was also recorded to further study its flexibility, which is an important indicator of its potential use in flexible devices. As displayed in Fig. 7f, g, this device exhibited nearly overlapping CV patterns and almost identical discharge periods at different bending states, indicating perfect mechanical flexibility. Such an outstanding performance suggests that the two-step thermal treatment method could be used in the future as a universal approach for designing wearable electronic products.

Energy and power densities are also vital factors for estimating the practicability of SCs, and these can be expressed clearly through a Ragone plot. Fig. 7h provides a comparison of our prepared P-ZCS/HC//RGO and other reported devices fabricated by similar materials. Notably, the P-ZCS/HC//RGO device exhibited an energy density of 62.9 W h kg^{-1} at 800 W kg^{-1} and was able to maintain a density of 35.6 W h kg^{-1} at 16 kW kg^{-1} . This performance is superior to those of many published devices, such as P-NiCo₂S₄//AC (42.1 W h kg^{-1} at 750 W kg^{-1}) [22], CoS₂//AC (52.1 W h kg^{-1} at 401 W kg^{-1}) [60], NiCo₂S_{2.2}Se_{1.8}//AC (39.6 W h kg^{-1} at 1501 W kg^{-1}) [71], Co₂P//graphene (24 W h kg^{-1} at

Figure 7 (a) Fabrication sketch of the P-ZCS/HC//RGO HSC. (b) CV plots of this device at diverse voltages and 20 mV s^{-1} . (c) CV plots (0–1.6 V) of this device tested at different sweep rates. (d) GCD plots and (e) specific capacities of P-ZCS/HC//RGO under different current densities, with the inset presenting the successful illumination of the LEDs by two HSC devices in series. (f) CVs at 30 mV s^{-1} and (g) GCDs at 1 A g^{-1} of this HSC at different bending angles, with the insets displaying the diagrams of the bending angles. (h) The Ragone plot of the P-ZCS/HC//RGO compared with those from analogous works. (i) The cycling performance and coulombic efficiency of the HSC at a flat, bent, and twisted status at 5 A g^{-1} over 10,000 cycles.

300 W kg^{-1} [72], and NiCo_2S_4 /ordered mesoporous carbon (45.5 W h kg^{-1} at 512 W kg^{-1}) [73], among others (Table S3). The results of a cycling test of the HSC at flat, bent, and twisted status are exhibited in Fig. 7i. After 10,000 GCD measurements at 5 A g^{-1} , approximately 92.0% of the capacity and 97.2% of the coulombic efficiency were maintained, even when the device was bent and twisted. In addition, the last five GCD curves shown in Fig. S19 remained perfectly symmetrical, reflecting superior cycling stability, mechanical flexibility, and reversibility.

CONCLUSIONS

In this study, we propose a two-step thermal treatment approach that completely converts the precursors (ZnCo-MOF) into ZCSs *via* P doping (P-ZCS/HC) to fabricate flexible electrodes with complex components and porous

structures. A 3D architecture with interlaced nanosheets was integrally preserved, and raised nanoparticles appeared on the rough surface during the annealing operations, increasing the SSA and exposure to electrolyte. The optimal P-ZCS/HC electrode possessed a remarkable capacity of 1080 C g^{-1} at 1 A g^{-1} along with superb cycling stability. These extraordinary properties were mainly caused by the plentiful redox reactions, enhanced conductivity, and synergic effects between the P-doped metal sulfides and heteroatom-doped carbon shells. DFT simulations attested to the boosted conductivity, improved reactive dynamics and promoted OH^- adsorption of these P-doped bimetallic sulfides. Further, the prepared HSC device exhibited energy and power densities up to 62.9 W h kg^{-1} and 16 kW kg^{-1} , respectively, with a retention of 92.0% over 10,000 cycles. The report further explored the advantages of P-doped mixed-metal sulfides

by experiments and theoretical simulations, indicating its promising status as a candidate for novel flexible electrodes. Overall, this research presents an applicable methodology for engineering advanced materials with sophisticated compositions and superior electrochemical performance *via* an ion substitution approach, which can be widely used in the energy field.

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

Shuo Li obtained her Bachelor degree in 2016 from the School of Materials Science and Engineering, Shandong University. She is currently a PhD student under the supervision of Prof. Pengchao Si at Shandong University. Her present research interests mostly concentrate on the transition metal sulfides and phosphides for energy storage applications.

Pengchao Si received his PhD degree in 2007 in natural science from Roskilde University, Denmark. Then he worked as a postdoctoral research fellow in the Department of Chemistry, Curtin University. He has been a full professor at the School of Materials Science and Engineering, Shandong University since 2010. His present research interests are mainly on the synthesis of nanomaterials for energy storage, conversion and electrochemical sensors.

嵌入多原子掺杂碳纳米阵列中的磷掺杂双金属硫化物应用于柔性全固态超级电容器

李硕¹, 华明昊¹, 杨媛¹, 郑小雯¹, 黄卫², 司鹏超^{1*}, 慈立杰¹, 楼峻³

摘要 柔性超级电容器具有超长使用寿命、可折叠、可穿戴等特点, 已成为研究热点. 然而, 较低的能量密度限制了其更广泛的应用. 本文采用简单的方法合成了一种嵌入多原子(氮, 硫和磷原子)掺杂碳壳的磷掺杂双金属硫化物(P-ZCS/HC)作为高性能柔性电极. 在退火过程中, 前驱体的三维形貌保持不变, 同时纳米片表面有凸起的纳米球形颗粒形成, 这大大增加了电极的比表面积. 优化后的P-ZCS/HC电极在 1 A g^{-1} 时具有 1080 C g^{-1} 高比电容值, 且循环稳定性出色. 这些优异的性能主要是由于该电极材料可发生丰富的氧化还原反应, 磷化后增强的导电性, 以及磷掺杂金属硫化物和多原子掺杂碳壳之间的协同效应. 密度泛函理论模拟表明, 磷掺杂处理具有提高电导率、改善反应动力学和促进 OH^- 吸附的积极作用. 组装的全固态柔性混合超级电容器最高能量密度可达 62.9 Wh kg^{-1} , 功率密度可达 16 kW kg^{-1} , 循环10,000次后仍能保持初始容量的92.0%. 这一完整和系统的研究为将来设计具有复杂成分和优异结构的柔性电极提供了一种新的思路.