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Construction of morphologically differentiated phosphorus-doped zinc oxide
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Abstract

As a key component of supercapacitors, electrode materials serve as an important indicator for evaluating the performance of supercapacitors. ZnO, a transition metal oxide, has attracted extensive attention due to its high theoretical specific capacitance, low cost, and other advantages. However, the inherent drawbacks of ZnO, such as poor intrinsic electrical conductivity and easy pulverization during cycling, limit its further development. In this work, non-metal phosphorus doping was employed to address the issues of low electrical conductivity and poor structural stability of ZnO, and the influence of phosphorus doping concentration on the structure and performance of ZnO materials was systematically investigated. By adjusting the phosphorus doping concentration, the microstructure of ZNR-P and ZNS-P was successfully regulated. The introduction of phosphorus caused lattice distortion in ZNR-P and ZNS-P, which effectively optimized the electronic structure of the materials, and the improvement in conductivity was more significant for ZNR-P. The mass specific capacitances of ZNR-P2 and ZNS-P2 at $0.5 \text{ A} \cdot \text{g}^{-1}$ were $513 \text{ F} \cdot \text{g}^{-1}$ and $470 \text{ F} \cdot \text{g}^{-1}$, respectively. After 10,000

cycles at $1 \text{ A}\cdot\text{g}^{-1}$, their capacitance retention rates were 57.89% and 46%, respectively.

When assembled into an asymmetric supercapacitor with a voltage window of 1.5 V, ZNR-P2 exhibited a power density of $375 \text{ W}\cdot\text{kg}^{-1}$ and an energy density of $15.9 \text{ Wh}\cdot\text{kg}^{-1}$. The results show that one-dimensional rod-like structures have intrinsic advantages in improving charge storage and structural stability.

Keywords: ZnO; morphology control; non-metal phosphorus doping; electrochemical performance

Introduction

With the intensification of the global energy crisis and the advancement of the dual carbon strategy, renewable energy storage technologies and new electrochemical energy storage devices have developed rapidly[1, 2]. Supercapacitors, due to their high power density, fast charging and discharging speed, long cycle life, and safety and environmental friendliness, have been widely applied in new energy vehicles, smart grids, portable electronic devices, and other fields[3]. Electrode materials are the core factor determining the energy storage performance of supercapacitors, and developing electrode materials with high specific capacity, high stability, and high conductivity has become a research hotspot[4-6].

Metal oxides, due to their high theoretical specific capacity and rich redox activity, are important research targets for supercapacitor electrode materials[7, 8]. Among them, zinc oxide, with characteristics such as simple preparation process, low cost, environmental friendliness, and rich nano-morphologies, has attracted extensive attention from researchers[9-11].

However, pure ZnO has many defects in practical applications: first, its low electrical conductivity leads to slow charge transfer rates and high charge transfer resistance, seriously affecting the device's power density and charge-discharge efficiency; second, its crystal structure stability is poor, and during long-term charge-discharge cycles, it is prone to phenomena such as grain agglomeration and structural collapse, resulting in the loss of active sites and shortened cycle life; third, it has few surface active sites, and the actual specific capacitance is far lower than the theoretical value, with the energy storage performance needing further improvement. These defects greatly limit the application of ZnO-based electrode materials in high-performance supercapacitors. Therefore, modifying ZnO to enhance its electrochemical performance has become the focus of current research.

To overcome these shortcomings, researchers have attempted various modification strategies, including nanostructuring of the material (such as nanorods, nanosheets, and nanoparticles)[12-15], composites with highly conductive carbon materials (such as graphene and carbon nanotubes)[16, 17], and doping with metal or non-metallic elements[18-20].

The nanostructured design of materials can effectively reduce electron loss during charge transport, inhibit material agglomeration and stacking, thereby exposing more active sites. At the same time, it can optimize electron migration rate and ion diffusion kinetics, alleviate structural changes during charging and discharging, thereby reducing volume changes and improving the cycle stability and reversible capacitance of supercapacitors[15].

The doping of non-metallic elements can significantly enhance the electron conduction rate of the material, solving the problem of poor conductivity of pure ZnO, while also improving the cycling stability of the electrode material and extending its service life[21]. Non-metallic element doping induces lattice distortion in ZnO, generating more defect sites and pore structures[22]. On the one hand, this increases the contact area with the electrolyte, providing more active sites for redox reactions and enhancing the pseudocapacitive effect; on the other hand, it shortens the ion transmission path and accelerates the charge migration rate.

In this experiment, ZnO nanorods (ZNR) and ZnO nanosheets (ZNS) with different phosphorus doping amounts were synthesized via a hydrothermal method, and the effects of phosphorus doping on the material's structure, morphology, conductivity, and electrochemical performance were systematically investigated. The synergistic effects of ZNR, ZNS and $\text{Zn}(\text{OH})_2\text{PO}_4$ and their enhancing effects on charge transport and cycling stability were mainly discussed. Finally, combined with the assembly and testing results of asymmetric supercapacitors, the practical application potential of phosphorus-doped ZnO-based materials was evaluated.

2. Experimental Section

2.1 Materials

Urea and $(\text{CH}_3\text{COO})_2\text{Zn}$ were purchased from Shanghai Reagent General Factory. ZnCl_2 was obtained from Hengxing Chemical Reagent Co., Ltd. polyethylene glycol (PEG 10000) and N-Methylpyrrolidone were obtained from Tianjin Fine Chemical Research Institute. CTAB was purchased from Tianjin Shuangqi Chemical Reagent Factory. Sodium dihydrogen phosphate was purchased from Tianjin North Chemical

Reagent Co., Ltd. Acetylene black, Diaphragm and Polyvinylidene fluoride (PVDF) were obtained from Bolike Electrochemical Energy Materials Network. All analytical-grade chemicals and solvents required no further purification. Deionized water was utilized consistently throughout the whole experimental procedure.

2.2 Material Synthesis

2.2.1 Preparation of Phosphorus-Doped Zinc Oxide Nanorods

The ZNR-P electrode materials were prepared via the solvothermal method. Firstly, $\text{CO}(\text{NH}_2)_2$ (0.3 g), ZnCl_2 (0.087 g), PEG10000 (0.33 g) and Sodium dihydrogen phosphate were weighed, respectively, and added to 40 mL Deionized water solvent while stirring continuously for thirty minutes until the particles were completely dissolved. The mixed solutions and Pre-treated nickel foam were then transferred to a PTFE liner, placed in a high-pressure reactor and then followed by oven reaction at 120 °C for 12 h. Once the reaction was complete, the in situ-grown ZNR-P electrode material was cooled to room temperature and repeatedly washed with deionized water, before being placed in a vacuum oven at 60 °C to dry. The samples were designated ZNR-P1, ZNR-P2, ZNR-P3 and ZNR-P4 according to their respective phosphorus doping masses (0.001 g, 0.002 g, 0.003 g and 0.004 g). For comparison, undoped ZnO nanorods were also prepared and named ZNR-C120.

2.2.2 Preparation of Phosphorus-Doped Zinc Oxide Nanosheets

The ZNS-P electrode material was prepared by the hydrothermal method. Firstly, 0.3 g of urea ($\text{CO}(\text{NH}_2)_2$) was weighed and added to 0.14 g of zinc acetate and 0.437 g of CTAB. Then, different amounts of sodium dihydrogen phosphate were prepared and mixed with 40 mL of deionized water. The mixture was thoroughly stirred for 30 min.

The pre-treated foam nickel was then placed into the stirred solution and transferred to the hydrothermal reactor. The reaction was carried out at 110 °C for 12 h. The subsequent processing was the same as above. The samples were designated ZNS-P1, ZNS-P2, ZNS-P3 and ZNS-P4 according to their respective phosphorus doping masses (0.001 g, 0.002 g, 0.003 g and 0.004 g). For comparison, undoped ZnO nanorods were also prepared and named ZNS-C110.

2.3 characterization

Using a D7ADVANCE X-ray diffractometer (XRD) to investigate the crystal structure and phase composition of materials. X-ray photoelectron spectroscopy (XPS) was measured on K-alpha device to analysis surface chemistry and bonding states of the prepared materials. The surface morphology and microstructural characteristics of the materials were analyzed using a SU5000 scanning electron microscope, and X-ray (EDX) analysis was performed. Fourier transform infrared spectroscopy (FT-IR) was employed to analyze changes in the functional group structure and bonding characteristics of the prepared materials.

2.4 Electrochemical measurements

2.4.1 Electrode preparation

The nickel foam (NF) substrate was pre-treated by ultrasonic cleaning with ethanol and hydrochloric acid solutions in sequence, followed by repeated rinsing with deionised water to remove surface impurities; it was then dried and set aside for later use. Weighing the prepared active material, acetylene black and PVDF in a mass ratio of (8:1:1), mix them thoroughly using a magnetic stirrer, then add an appropriate amount of N-methylpyrrolidone solution dropwise to form a slurry mixture. The

prepared slurry was evenly coated onto a nickel foam surface measuring $1 \times 1 \text{ cm}^2$, followed by drying in a vacuum environment at $60 \text{ }^\circ\text{C}$ for 12 h; the resulting dried electrode sheet was then cold-pressed for 50 seconds under a constant pressure of 40 MPa, yielding a standardised test electrode with a dense structure and good interfacial contact.

2.4.2 Electrochemical performance test

Using the three-electrode system of the CHI760E electrochemical workstation, with a platinum sheet as the counter electrode and a Hg/HgO electrode as the reference electrode, the electrochemical properties of the samples were investigated by CV, GCD and EIS.

The specific capacitance (C_m) in $\text{F}\cdot\text{g}^{-1}$ for the three-electrode system were calculated from the GCD profile by the following the equation

$$C_m = \frac{I \times t}{m \times V} \quad (1)$$

Where I (mA), t (s), m (mg), and V (V) are the current, discharge time, active material mass, and potential window for a GCD profile, respectively.

2.4.3 Asymmetric supercapacitor

The charge stored across the electrodes (positive and negative) was balanced ($Q_+ = Q_-$) according to eq 2

$$\frac{m_+}{m_-} = \frac{C_{m-} \times E_-}{C_{m+} \times E_+} \quad (2)$$

where m_+ , m_- , C_{m-} , C_{m+} , E_- , and E_+ represent the respective mass loading, specific capacitance, and operating potential window for the positive and negative. For the ASC device, C_m was calculated using eq 1, where “ m ” represents the total mass of both positive and negative electrodes.

Energy density (E) and power density (P) of the supercapacitor were measured by

eq 3 and 4:

$$E = \frac{C \times V^2}{7.2} \quad (3)$$

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

where C ($\text{F} \cdot \text{g}^{-1}$), V (V), and t (s) are the specific capacitance, active potential window, and GCD curve discharge time, respectively, for the device.

3. Results and discussion

3.1 Characterization and Analysis of ZNR-P and ZNS-P

XRD was used to perform a qualitative analysis of the phase composition of the synthesized ZNR-P2 and ZNS-P2 composites, as shown in Figure 1. In the XRD patterns of the composites prepared with different sodium dihydrogen phosphate loadings, distinct diffraction peaks at $2\theta = 30.2^\circ$, 33.9° , 35.4° , 50.1° , 58.2° , and 59° were observed which matched well with the peak positions in PDF#51-1647, corresponding to the (100), (002), (101), (102), (110), and (103) crystal planes. In addition to the characteristic peaks of $\text{Zn}(\text{OH})_2\text{PO}_4$ [23], there are also impurity peaks of $\text{Zn}(\text{OH})_2$. This is due to the presence of a large number of hydroxyl groups during the hydrothermal process, inadequate heat treatment resulted in Zn^{2+} not being completely dehydrated and oxidized[24]. Comparison reveals that the overall characteristic peaks of ZNR-P2 are slightly stronger than those of ZNS-P2. This is because the rod-like structure has higher crystallinity and tends to grow preferentially along the (002) crystal plane[25]. Phosphorus doping helps maintain good crystallinity, significantly enhancing the diffraction peaks of the crystal planes. In contrast, the ZNS flake-like structure suffers from severe stacking, which leads to lattice defects, resulting in reduced crystallinity and weaker diffraction peaks.

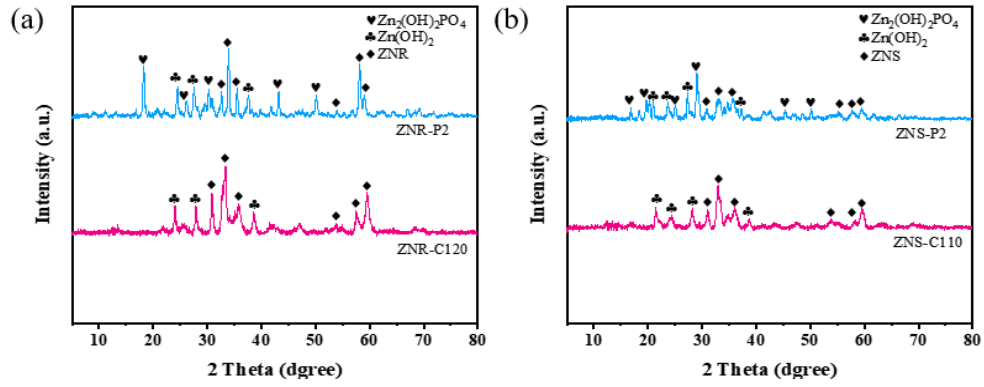


Figure 1. (a) XRD patterns of ZNR-C120 and ZNR-P2; (b) XRD patterns of ZNS-C110 and ZNS-P2

The surface chemical states and compositions of ZNR-P2 samples were analyzed using XPS. As shown in the XPS full spectrum in Figure 2(a), the presence of C, O, Zn and P elements in the sample indicates that phosphorus has been successfully doped into the ZNR-P2 sample. The deconvolution results of the high-resolution O 1s spectrum for sample ZNR-P2 are shown in Figure 2(b); the characteristic peaks at 529.6 eV and 531.7 eV are attributed to Zn-O and C=O. Figure 2(c) shows two characteristic peaks in the Zn 2p spectrum at 1019.7 eV and 1042.5 eV, attributed to Zn 2p_{3/2} and Zn 2p_{1/2}. In Figure 2(d), the characteristic peaks at 131.7 eV, 133.9 eV and 139 eV are attributed to P-P/Zn-P, P-O-P and P-O-Zn, respectively. The characteristic peaks at P-P and Zn-P indicate that P atoms are doped into the interstitial sites of the ZNR lattice, introducing lattice defects and increasing the carrier concentration in the material, thereby enhancing electrical conductivity and improving cycling stability[26, 27]. The characteristic P-O-P peak arises because phosphorus replaces oxygen atoms in the ZNR lattice, forming phosphate-like oxides on the material's surface. This process fills the oxygen vacancies in the ZNR, suppressing structural collapse during charging and discharging, ensuring efficient electron transport, and thereby improving its electrochemical performance. The formation of the characteristic P-O-Zn peak accompanies the doping of phosphorus[28].

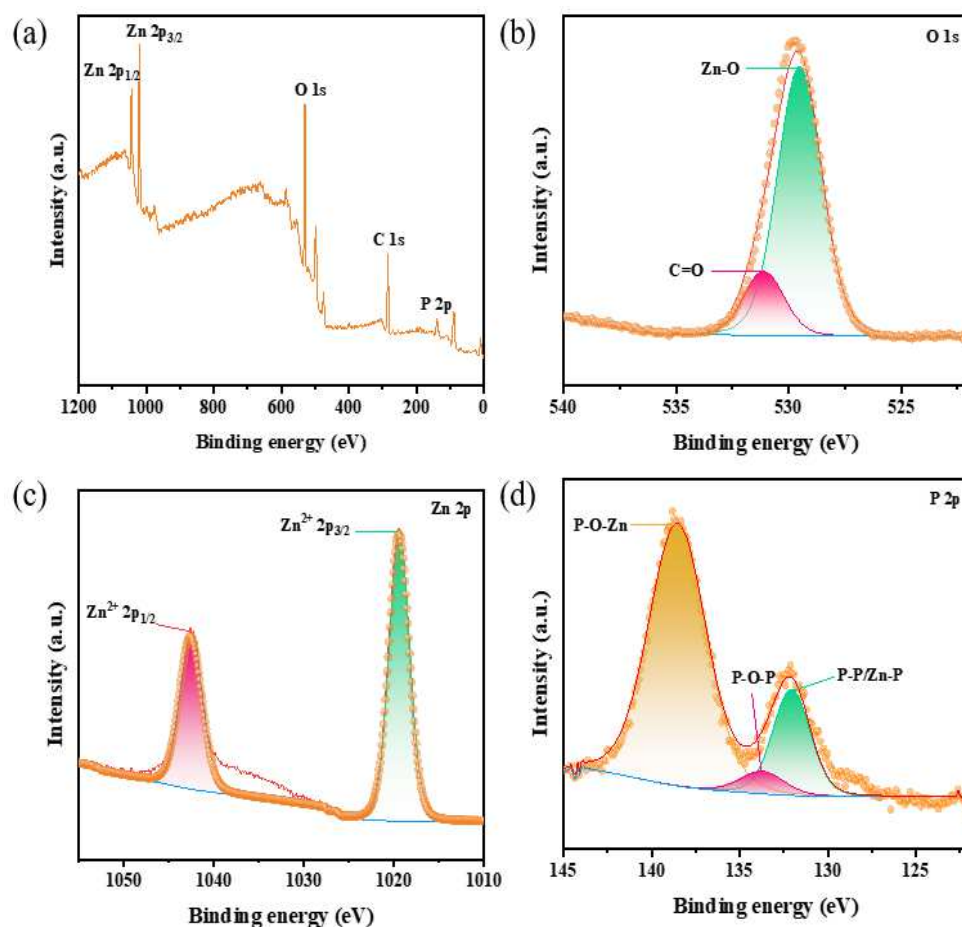


Figure 2. XPS spectra of ZNR-P2: (a) Survey spectrum of ZNR-P2;(b-d) High-resolution XPS spectra of O 1s, Zn 2p and P 2p for ZNR-P2

Figure 3(a) illustrates the XPS measurement spectra of ZNS-P2, which confirmed the existence of C, O, Zn and P elements in all samples. The deconvolution results of the high-resolution O 1s spectrum of the ZNS-P2 sample are shown in Figure 3(b). The characteristic peaks at 528.5 eV and 531 eV are attributed to Zn-O and C=O, respectively. The shift in the characteristic peaks at Zn-O and C=O compared to ZNR-P2 is due to an increase in surface defects following phosphorus doping, which leads to greater lattice distortion in the nanosheets, exacerbating changes in bond energy and resulting in a slight shift. Figure 3(c) shows two characteristic peaks in the Zn 2p spectrum at 1018.9 eV and 1043.4 eV, attributed to Zn 2p_{3/2} and Zn 2p_{1/2}. The characteristic peaks showing at Figure 3(d) at 131.3 eV, 133.2 eV and 138.7 eV are

attributed to P-P/Zn-P, P-O-P and P-O-Zn bonds

The peak intensity of the ZNS-P2 sample at the P-P/Zn-P site is significantly higher than that of the ZNR-P2 sample. This is because the doping process for ZNS-P2 was less effective than that for ZNR-P2; a large number of P atoms remained on the surface rather than entering the lattice, resulting in the formation of a large number of P-P/Zn-P bonds solely at the surface. The P-O-P characteristic peak arises from phosphorus replacing oxygen atoms in the ZNS lattice, resulting in the formation of phosphate oxides on the material's surface. These oxides fill the oxygen vacancies in the ZNS lattice, thereby suppressing structural collapse during charging and discharging. The intensity of the characteristic peak at the P-O-Zn site in the ZNS-P2 sample is significantly lower than that in the ZNR-P2 sample because the crystallinity of the flake-like structure is weaker than that of the rod-like structure, resulting in structural instability; P atoms enter the lattice to form a small number of P-O-Zn bonds, leading to a marked decrease in peak intensity[29].

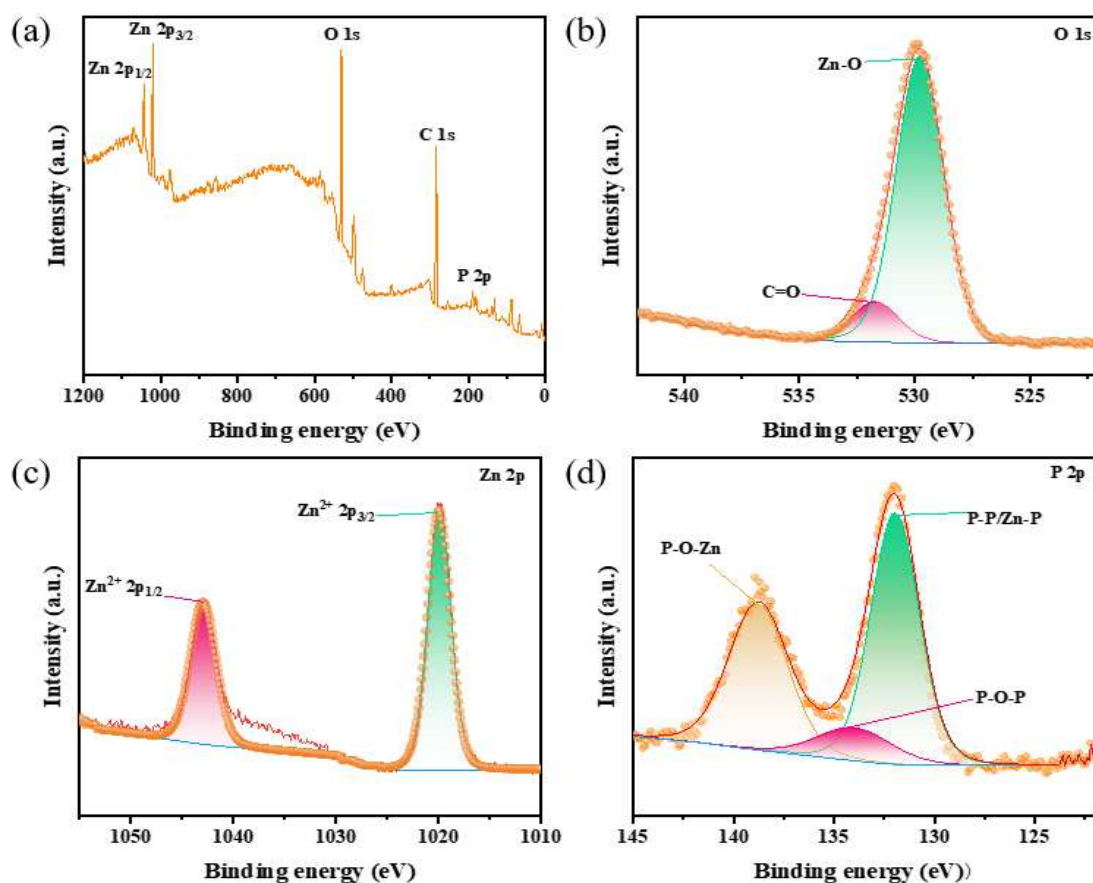


Figure 3. XPS spectra of ZNS-P2: (a) Survey spectrum of ZNS-P; (b-d) High-resolution XPS spectra of O 1s, Zn 2p and P 2p for ZNS-P2

Figure 4 displays SEM images of ZNR-P. As shown in Figure 4(a) and Figure S1(a-b), when the phosphorus doping concentration set at a low level, the material retains the one-dimensional linear structure characteristic of ZNRs and exhibits excellent crystallinity. The doping process did not have a significant effect on its original morphology. As can be seen from Figure 4(b), a moderate increase in the amount of phosphorus source causes the ZNR-P units to bind more tightly together, thereby optimising the charge transport pathways within the lattice and enhancing the structural stability, which results in a significant improvement in cycling stability[30]. As shown in Figure 4(d-e), when an excessive amount of phosphorus is added, the aspect ratio of ZNRs decreases significantly and severe agglomeration occurs, resulting in a reduction in the number of active sites in the electrode material and ultimately

leading to a decrease in specific capacitance. The EDS spectrum shown in Figure 4(f) indicates that Zn, O and P are uniformly distributed within ZNR-P2.

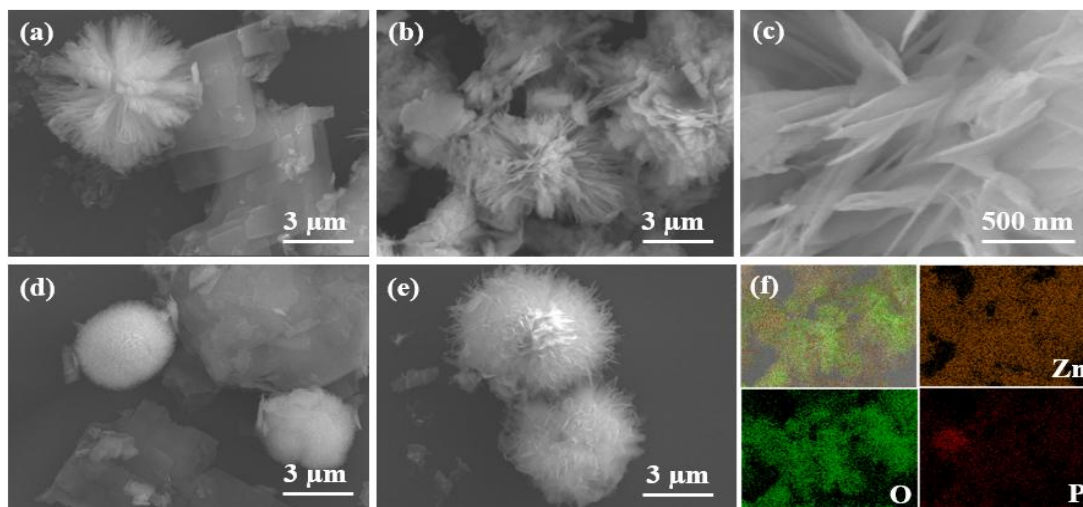


Figure 4. SEM images of ZNR-P: (a) ZNR-P1; (b-c) ZNR-P2 and its high-magnification image; (d) ZNR-P3; (e) ZNR-P4; (f) EDS image of ZNR-P2

Figure 5 displays SEM images of ZNS-P. As shown in Figure 5(a) and Figure S1(c-d), when the amount of phosphorus source added is small, the material retains the inherent flake-like structure of ZNS and has a smooth surface. It can be seen from Figure 5(b-e) that, as the amount of phosphorus source is gradually increased, the nanosheets become slightly rougher, and a layered structure forms between the layers through the action of the phosphorus source. However, excessive addition causes the lateral growth rate of ZNS to far exceed the vertical growth rate, leading to the gradual coalescence of small-sized nanosheets through epitaxial growth, ultimately forming a large-area, well-ordered bulk structure. The EDS spectrum shown in Figure 5(f) indicates that Zn, O and P elements are uniformly distributed within ZNS-P2.

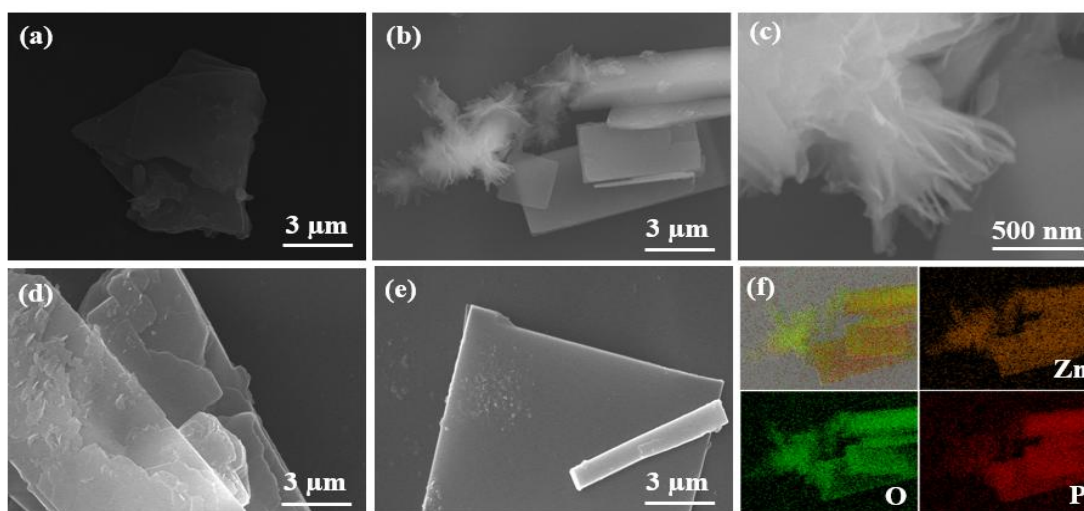


Figure 5. SEM images of ZNS-P: (a) ZNS-P1; (b-c) ZNS-P2 and its high-magnification image; (d) ZNS-P3; (e) ZNS-P4; (f) EDS image of ZNS-P2

The infrared spectra shown in Figure 6 clearly illustrate the changes in the functional group structures and bonding characteristics of the ZNR-P2 and ZNS-P2 materials. The characteristic absorption peaks at 3458 cm^{-1} , 3382 cm^{-1} , 3282 cm^{-1} and 1014 cm^{-1} in Figure 6(a) are attributed to the stretching vibrations of the O-H bonds in crystalline water. The distinct disappearance of the characteristic peak at 3382 cm^{-1} in ZNR-P2 is attributed to the formation of additional active sites on the ZNR surface following phosphorus-source composite modification. These sites effectively adsorb water molecules from the air to form hydroxyl groups; this structural feature significantly enhances the material's surface wettability and the number of electrochemical active sites, playing a crucial role in optimising its electrochemical performance. The absorption peak at 2920 cm^{-1} is caused by the stretching vibration of the C-H bond. The characteristic peak at 1500 cm^{-1} corresponds to the vibration of the C=C bond, this is because the surfactant has not completely decomposed. The Zn-O bond appears at 1390 cm^{-1} , and the characteristic absorption peaks of Zn-OH are observed at 950 cm^{-1} and 830 cm^{-1} [31]. The significant shift in the characteristic Zn-OH peak at 830 cm^{-1} following phosphorus doping is attributed to the doping of

phosphorus into the lattice, which passivates the active Zn^{2+} sites on the surface, thereby preventing the adsorption of H_2O and its subsequent decomposition into hydroxyl groups. The peak at 600 cm^{-1} corresponds to the characteristic Zn-O-P bond. As phosphorus atoms are doped into the lattice, they gradually replace hydroxyl groups to form Zn-O-P bonds. The formation of these bonds enhances structural stability, reduces structural collapse, increases the number of active sites, and improves the material's electrochemical performance. As shown in Figure 6(b), the doping of P results in a significant enhancement of the P-O peaks at 126 cm^{-1} and 945 cm^{-1} , indicating a pronounced electronic modulation effect, which reduces the diffusion resistance and improves the material's electrical conductivity. The peak at 1031 cm^{-1} corresponds to the characteristic C-O-C bond, whilst the peak at 650 cm^{-1} corresponds to $\gamma\text{-OH}$, this is due to new hydroxyl groups formed at high temperatures when CO_2 in the air reacts with the numerous weakly adsorbed water molecules on the ZNS surface. A characteristic peak corresponding to the Zn-O-P stretching vibration appears at 523 cm^{-1} , and the peak intensity is significantly enhanced, indicating that a stable chemical bond has formed between phosphorus and ZNS-C110.

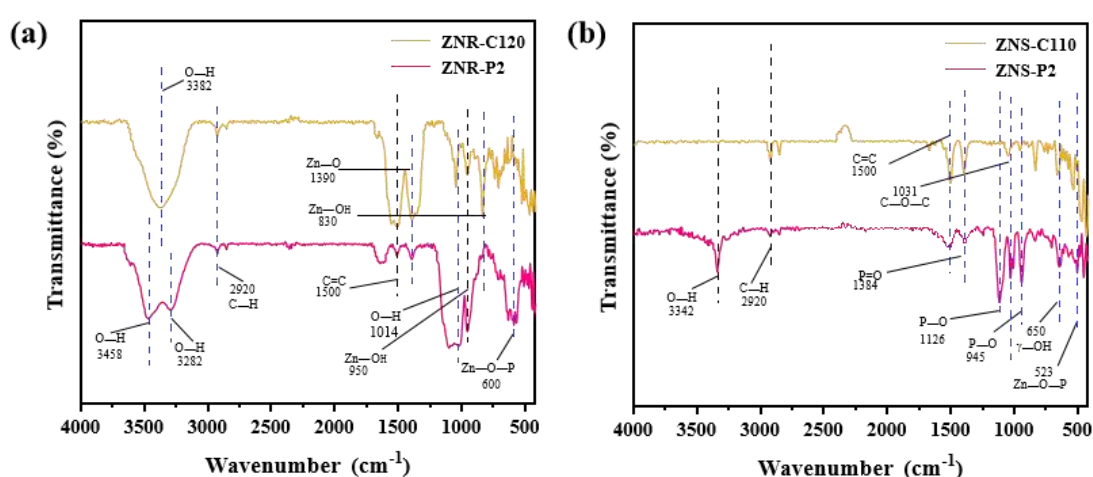


Figure 6. (a) FT-IR spectra of ZNR-C120 and ZNR-P2; (b) FT-IR spectra of ZNS-C110 and ZNR-P2

3.2 Electrochemical Performance of ZNR-P and ZNS-P

To investigate the effect of phosphorus doping on the electrochemical properties of zinc oxide, the CV curve of the electrode material at $5 \text{ mV}\cdot\text{s}^{-1}$ were shown in Figure 7 and Figure S2. It is clear from Figure 7(a) that the area under the CV curve for ZNR-P2 is the largest, indicating that it has the highest specific capacitance. Excessive doping reduces the number of charges participating in the electrochemical reaction, causing a shift in the position of the redox peak[32]. In Figure 7(b), the ZNS-P2 exhibits the largest area under the CV curve and the highest specific capacity, indicating a strong charge storage capability. Compared with ZNR-P2, the ZNS-P2 exhibits a larger area under the CV curve. This is attributed to the successful doping of phosphorus, which results in stronger P-O-Zn bond peaks in ZNR-P2, effectively modulating the electronic structure of the material, enhancing its stability, and ensuring that the rod-like structure does not collapse easily during charging and discharging, allowing active sites to react fully. In contrast, the flake-like structure suffers from severe stacking, which reduces the number of active sites and prevents sufficient redox reactions, resulting in a smaller area under the CV curve.

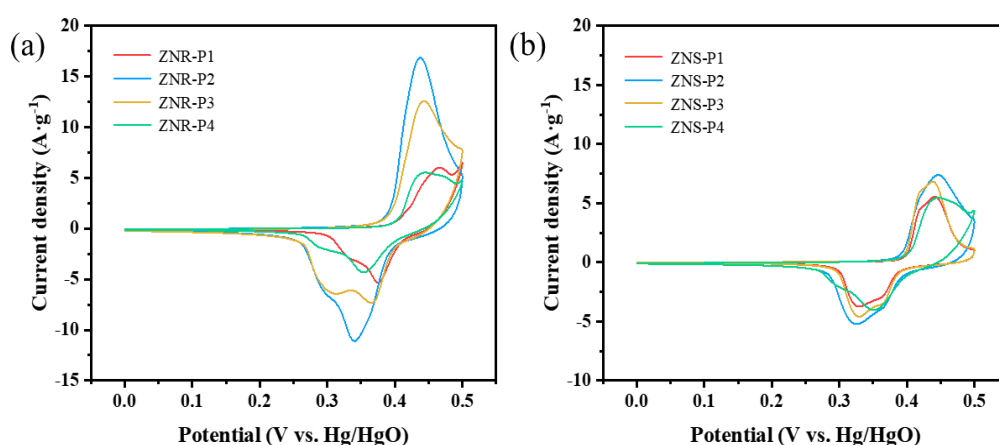


Figure 7. (a-b) CV curves of ZNR-P and ZNS-P

Figure 8 and Figure S3 compares the GCD curves and rate performance of ZNR-P, ZNS-P, ZNR-C120 and ZNS-C110 at a current density of $0.5 \text{ A}\cdot\text{g}^{-1}$. In Figure 8(a),

the specific capacitances of ZNR-P1, ZNR-P2, ZNR-P3 and ZNR-P3 have specific capacitances of $298 \text{ F}\cdot\text{g}^{-1}$, $513 \text{ F}\cdot\text{g}^{-1}$, $492 \text{ F}\cdot\text{g}^{-1}$ and $229 \text{ F}\cdot\text{g}^{-1}$ respectively. It can be seen that ZNR-P2 exhibits the most outstanding charge-discharge performance, with a specific capacitance reaching as high as $513 \text{ F}\cdot\text{g}^{-1}$. This is attributable to the fact that doping with P improves the intrinsic electron mobility of ZNR-C120, enabling charge carriers to undergo complete redox reactions during charging and discharging, thereby enhancing its charge storage capacity[33]. In Figure 8(b), the specific capacitance of ZNS-P1, ZNS-P2, ZNS-P3 and ZNS-P3 have specific capacitances of $199 \text{ F}\cdot\text{g}^{-1}$, $470 \text{ F}\cdot\text{g}^{-1}$, $321 \text{ F}\cdot\text{g}^{-1}$ and $229 \text{ F}\cdot\text{g}^{-1}$ respectively. It can be seen that ZNS-P2 possesses a higher specific capacitance of $470 \text{ F}\cdot\text{g}^{-1}$ and exhibits superior electrochemical performance compared to the other samples. The specific capacitance of ZNR-P2 is superior to that of ZNS-P2 due to the doping of P, which reduces the interfacial charge transfer resistance of ZNR-P2. In contrast, ZNS-P2 tends to form large, block-like structures when stacked, resulting in a reduction in active sites and an increase in charge transfer resistance, which is detrimental to electron transport. As can be inferred from Figures 8(c–d), the ZNR-P2 and ZNS-P2 exhibit poor high-rate performance. This is attributed to significant charge accumulation during high-rate charging and discharging, which leads to a polarization effect. As a result, active sites are not fully utilized, making the cells prone to rapid capacity decay[34].

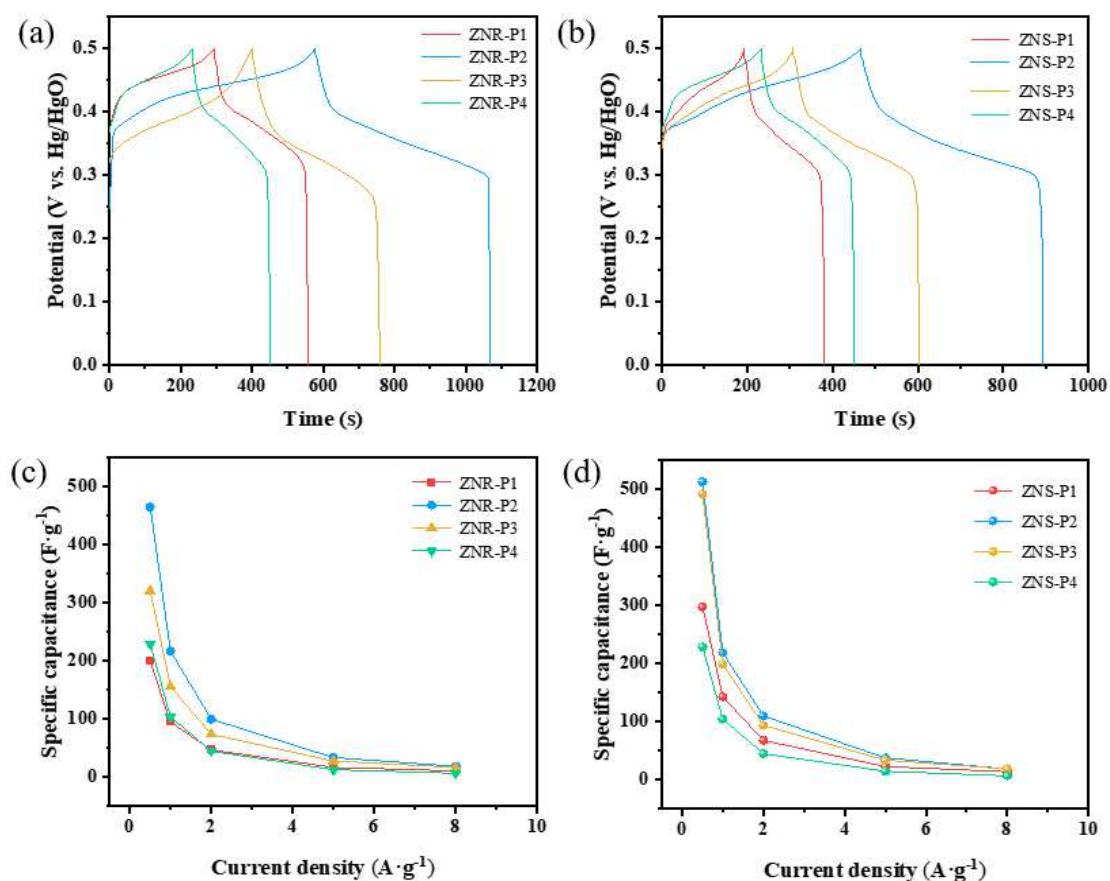


Figure 8. (a-b) GCD curves of ZNR-P and ZNS-P at a current density of 0.5 A·g⁻¹; (c-d) Rate performance curves of ZNR-P and ZNS-P

EIS tests were conducted to investigate the changes in ionic conductivity of ZNR-P, ZNS-P, ZNR-C120 and ZNS-C110, as shown in Figure 9 and Figure S4. As observed in Figure 9(a) and Figure S4(a), the ZNR-P2 sample exhibits a steeper slope compared to ZNR-P1, ZNR-P3, ZNR-P4 and ZNR-C120, indicating lower impedance. Phosphorus doping accelerates charge transfer and widens the ion diffusion channels, thereby optimising the crystal structure and improving the impedance performance. As demonstrated in Figure 9(b) and Figure S4(b), the slope of the ZNS-P2 sample is superior to that of the ZNS-P1, ZNS-P3, ZNS-P4 and ZNS-C110. An appropriate amount of phosphorus doping optimises the internal defect structure, allowing electrons to move more freely between the layers, which facilitates the diffusion of resistance. Consequently, the ZNS-P2 sample exhibits the lowest resistance and the steepest slope.

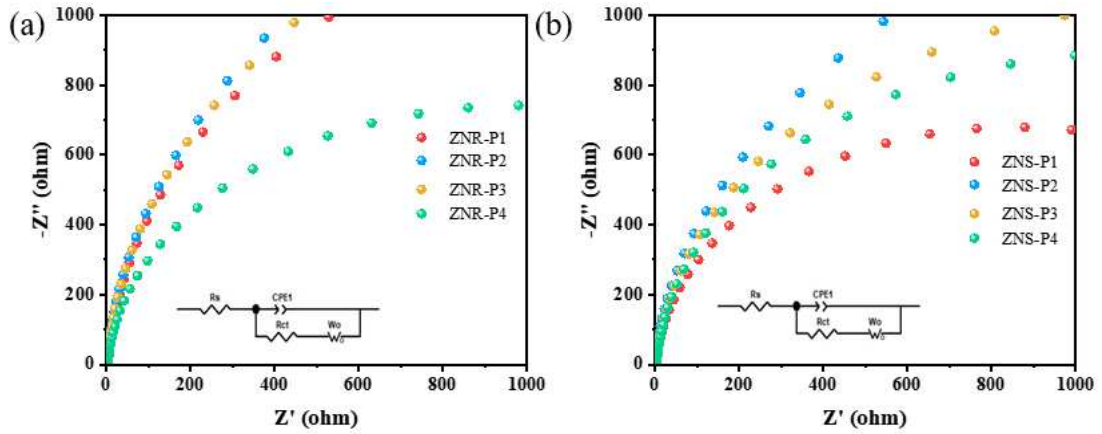


Figure 9. (a-b) Nyquist plots of ZNR-P and ZNS-P

After 10,000 charge-discharge cycles at a current density of $1 \text{ A} \cdot \text{g}^{-1}$, the ZNR-C120, ZNS-C110, ZNR-P2 and ZNS-P2 exhibited capacitance retention rates of approximately 30%, 19.5%, 57.89% and 46%, respectively shown in Figure 10. The ZNR-P2 exhibits excellent cycling stability thanks to P-doping, which enhances its conductivity, creates a more continuous conductive pathway within the rod-like structure, improves the efficient transport of charge, and reduces the increase in impedance during cycling. Furthermore, P-doping mitigates the flaking phenomenon in the ZNR-P2, minimising the shedding of active material and structural damage, thereby enhancing its stability.

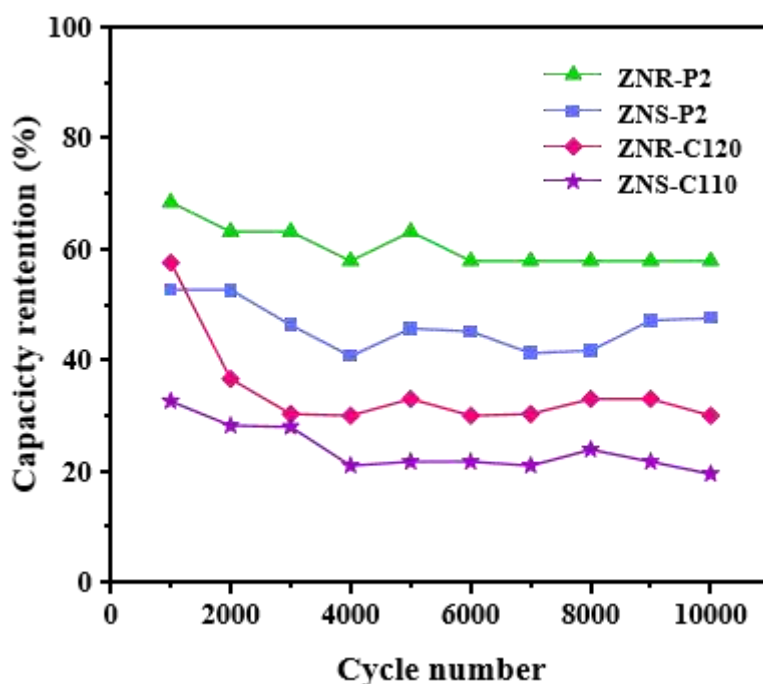


Figure 10. Cycling stability curves of ZNR-C120, ZNS-C110, ZNR-P2 and ZNS-P.

3.3 Electrochemical performance of asymmetric supercapacitor

An asymmetric supercapacitor has been fabricated by leveraging the synergistic energy storage properties of the ZNR-P2 cathode and activated carbon (AC) anode, based on the excellent electrochemical performance of ZNR-P2. The CV scan curves for the ZNR-P2 and AC electrode alone in the voltage windows of 0-0.5 V and -1-0 V are shown in Figure 11(a). By combining the synergistic effects of the battery-type electrode and the double-layer electrode, the voltage window has been extended to 0-1.5 V. As shown in Figure 11(b), as the scan rate increases, the CV curve exhibits characteristics of redox peaks and a rectangular shape, indicating the synergistic effects of multiple mechanisms during the energy storage process[35]. The constant-current charge-discharge curves at different current densities are shown in Figure 11(c). The GCD curves display distinct charge-discharge platform and exhibit symmetry, indicating excellent reversibility[36]. Based on the GCD test results, the specific capacitance of the ZNR-P2//AC at a current density of $0.5 \text{ A} \cdot \text{g}^{-1}$ is $102 \text{ F} \cdot \text{g}^{-1}$. As presented in Figure 11(d), the Nyquist plot is used to analyse ion diffusion behaviour in

capacitors; the assembled capacitor exhibits a steep slope, indicating excellent ion diffusion performance[37]. Figure 11(e) shows that the device delivers a maximum energy density of $15.9 \text{ Wh} \cdot \text{kg}^{-1}$ at a power density of $375 \text{ W} \cdot \text{kg}^{-1}$. As shown in Figure 11(f), a current density of $1 \text{ A} \cdot \text{g}^{-1}$ exhibits a capacity retention of 20% after 10,000 cycle tests.

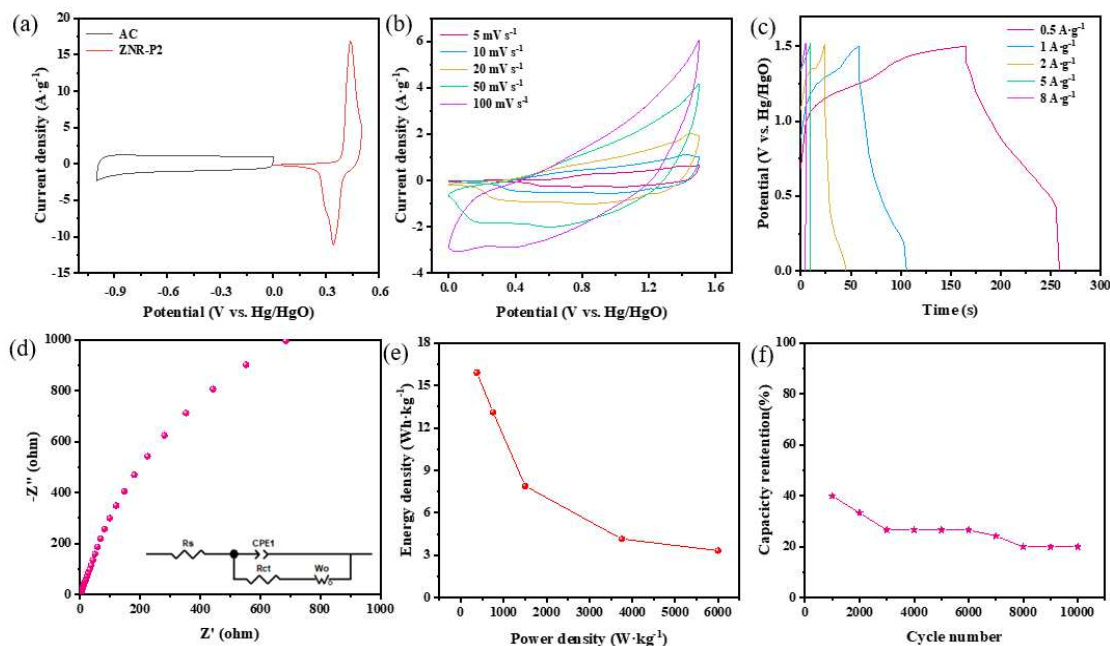


Figure 11. (a) CV curves of ZNR-P2 and AC, respectively; (b) CV curves of the capacitor at different scan rates; (c) GCD curves at current densities of $0.5\text{--}8 \text{ A} \cdot \text{g}^{-1}$; (d) Nyquist plots with the equivalent circuit shown in the inset; (e) galvanostatic charge-discharge curves

Conclusions

In this experiment, using the hydrothermal method and adjusting the phosphorus doping level, electrode materials ZNR-P and ZNS-P with excellent electrochemical performance were prepared. A systematic study was conducted on the relationship between the phosphorus doping level and the crystal structure, microstructure, and electrochemical performance of the ZnO-based materials. At an appropriate phosphorus doping concentration, the P–Zn–O bond energy in ZNR-P2 is higher than that in ZNS P2. Phosphorus doping effectively optimises the electronic structure of the material,

promotes efficient electron transport, and makes full use of active sites for redox reactions, thereby enabling ZNR-P2 to exhibit superior electrochemical performance. At a current density of $0.5 \text{ A} \cdot \text{g}^{-1}$, the specific capacitance of ZNR-P2 reaches $513 \text{ F} \cdot \text{g}^{-1}$, which is higher than the $470 \text{ F} \cdot \text{g}^{-1}$ of ZNS P2. After 10,000 charge-discharge cycles, the capacitance retention rate of the ZNR-P2 capacitor was 57.89%, which was higher than that of other ZnO-based electrode materials. The results show that phosphorus doping can effectively regulate the electronic structure of ZnO, significantly improve the structural stability, and prevent the electrode structure from collapsing during charging and discharging. Compared with ZNS-P2, ZNR-P2 demonstrates superior long-term cycling stability due to its robust one-dimensional structural framework, further demonstrating the advantage of the one-dimensional rod structure in improving the cycling performance of electrode materials.

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Appendix A. Supplementary data

Supplementary data to this article can be found online.

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