Novel bouquet-like cobalt phosphate as an ultrahigh-rate and durable battery-type cathode material for hybrid supercapacitors

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ABSTRACT Red phosphorus (RP) is beneficial to industrialization due to its rich resources, chemical stability and environmental friendliness. However, the low electronic conductivity and large volume expansion limit its application for energy storage. Herein, we first used RP to prepare a novel bouquet-like $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ by the hydrothermal approach as cathode materials for hybrid supercapacitors (HSC), which delivered a large specific capacity ($119.2 \text{ mA h g}^{-1}$ at 1 A g^{-1}), a superb rate capability (83.6 mA h g^{-1} at 100 A g^{-1}) and a splendid electrochemical stability (92% capacity retention after 5000 cycles at 10 A g^{-1}). Furthermore, a novel HSC device assembled with $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ as the cathode, porous carbon (PC) as the anode showed a high energy density of 44.6 W h kg^{-1} and a remarkable power density of 33.75 kW kg^{-1} , along with an exceptional cyclic performance (91.8% capacity retention after 10,000 cycles at 3 A g^{-1}). This study not only develops a novel type of high-performance battery-type cathode material, but also provides a new idea for the industrial application of RP.

Keywords: red phosphorus, novel bouquet-like $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$, hybrid supercapacitors, ultrahigh rate performance, ultrahigh power density

INTRODUCTION

With the excessive consumption of fossil fuels and the increasing environmental pollution problems, a new round of energy revolution featured by the large-scale development and utilization of renewable energy and the rapid development of new energy vehicles have flourished. However, both the use of renewable energy and the development of new energy vehicles are inseparable from electrochemical energy storage technologies. As a novel type of energy storage device, supercapacitors (SCs) have received enormous concern on account of their eminent power density, wonderful rate performance as well as outstanding cyclic stability [1–4]. But the low energy density limits their further development [5]. The hybrid supercapacitors (HSCs) exhibit enhanced electrochemical properties owing to the combination of the features of capacitive materials (excellent rate and cycling performance) and battery materials (high capacity), which have attracted wide attention from researchers. The performance of electrode material is a main factor that determines the performance of SCs [6]. Among the electrode materials, the research on cathode materials is relatively scarce compared with that of anode materials, so it is very meaningful

to carry out further research on cathode materials. Nowadays, the study on cathode materials mainly focuses on the design and development of new electrode materials with low cost and high performance.

Red phosphorus (RP), as an allotrope of elemental phosphorus that is rich-resource, possesses the advantages of being easily available, chemically stable and non-toxic to the environment, which is more conducive to industrialization. Nevertheless, the low electrical conductivity and great volume expansion limit the application of RP in energy storage fields [7,8]. In order to overcome these difficulties, researchers have developed various methods to improve its electrochemical performance, such as compounding, improving structure, and synthesizing metal phosphides [9–11]. However, these methods have their own disadvantages such as complicated processes, high temperature conditions. Therefore, it is of great significance to develop novel methods to enhance the electrochemical properties of RP.

Among cobalt-based materials, Co_3O_4 has a great theoretical capacity ($\sim 3560 \text{ F g}^{-1}$), but its low electronic conductivity hinders the full utilization of its theoretical capacity. Whereas cobalt phosphide has good electronic conductivity and high electrochemical activity, its cycle stability needs to be improved. Note that transition metal phosphates have attracted rising concern due to their excellent electrochemical performance and high chemical stability combined with the advantages of transition metal oxides and transition metal phosphides. Cobalt phosphate can be used as a zeolite-type porous material with a structure that is composed of CoO_x and PO_4 polyhedrons, and is anticipated to be a cathode material for rechargeable ion batteries and SCs. However, its cycle stability in alkaline electrolyte still needs to be improved. Previous reports have shown that the stability of cobalt phosphite in alkaline aqueous KOH electrolyte could be boosted due to the existence of $-\text{OH}$ groups in its structure [12].

Based on the above considerations, in this article, we first utilized RP to synthesize a new type of bouquet-like $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ via the hydrothermal method as cathode materials for HSCs, and the resultant bouquet-like $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ exhibited a large specific capacity ($119.2 \text{ mA h g}^{-1}$ at 1 A g^{-1}), an ultrahigh rate capability (83.6 mA h g^{-1} at 100 A g^{-1}) and an outstanding cycling life (92% capacity retention after 5000 cycles at 10 A g^{-1}). Then, the HSC device was assembled using the bouquet-like $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ as the cathode and porous carbon (PC) as the anode, revealing a high energy density (44.6 W h kg^{-1}), an ultrahigh power density (33.75 kW kg^{-1}) as well as an excellent cycle stability (91.8%

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capacity retention after 10,000 cycles at 3 A g⁻¹). The remarkable electrochemical performance of the Co₃(HPO₄)₂(OH)₂ electrode is attributed to its good chemical composition and hierarchical porous structure with rich mesopores and macropores, which can efficiently boost the electronic conductivity, ion/electron transport capacity as well as chemical stability. This study not only synthesizes a new battery-type cathode material but also affords a new pathway and approach for the commercial application of RP.

EXPERIMENTAL SECTION

Preparation of the bouquet-like Co₃(HPO₄)₂(OH)₂

In a typical synthetic procedure, 389.98 mg of Co(NO₃)₂·6H₂O and 103.75 mg of RP were mixed in 50 mL of distilled water with magnetic agitation for half an hour to obtain a deep-red solution. Next, NH₃·H₂O was added dropwise to the above solution and adjusted the pH to 8. The final solution was transferred into a hydrothermal autoclave and remained at 180°C for 12 h. After naturally cooling to ambient temperature, the resultant precipitated product was adequately centrifugated to remove any unreacted residues, and dried overnight at 50°C to acquire the Co₃(HPO₄)₂(OH)₂ product.

Physical characterization

X-ray diffractometry (XRD) pattern was obtained on a Rigaku D/max 2550 VB⁺. X-ray photoelectron spectroscopy (XPS) test was performed on a Thermo Scientific Escalab 250Xi spectrometer. The N₂ adsorption and desorption characterization was executed on a Micromeritics ASAP 2020. The morphology and structure of the material were investigated by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Energy-dispersive X-ray spectrum (EDS) and elemental mappings were detected *via* FESEM.

Electrochemical measurements

The electrochemical tests of single electrode and HSC device were implemented on a CHI 760E electrochemical workstation

by using 2 mol L⁻¹ KOH, Hg/HgO and platinum foil as the electrolyte, reference electrode and counter electrode, respectively. The working electrode was obtained *via* the subsequent process. Co₃(HPO₄)₂(OH)₂ with acetylene black (AB) and polyvinylidene fluoride (PVDF) were added to the *N*-methyl-2-pyrrolidone (NMP) solution in the mass ratio of 7:2:1. After fully stirring, the slurry was uniformly coated on treated nickel foam (NF) substrate and subsequently dried at 50°C. Ultimately, the working electrode was acquired by pressing the NF at 10 MPa. PC was selected as the anode material to assemble the HSC device with matching Co₃(HPO₄)₂(OH)₂ cathode and an NKK (Nippon Kodoshi Corp.) acted as the separator. For balancing the charges of cathode and anode materials in HSC device, the mass ratio of cathode and anode is obtained from the formula: $m_+/m_- = (C_- \times \Delta V_-)/(C_+ \times \Delta V_+)$, in which + and - represent the cathode and anode, and *C* and ΔV reflect the capacity and voltage window, respectively. The typical loadings of Co₃(HPO₄)₂(OH)₂ and PC are about 1 mg cm⁻².

RESULTS AND DISCUSSION

The synthetic procedure of the Co₃(HPO₄)₂(OH)₂ sample is displayed in Fig. 1. The Co₃(HPO₄)₂(OH)₂ sample was prepared *via* the hydrothermal approach. First, the metal cobalt salts, RP and NH₃·H₂O were mixed adequately and then subjected to hydrothermal reaction at 180°C for 12 h. Lastly, the bouquet-like Co₃(HPO₄)₂(OH)₂ can be acquired by centrifugation and drying. The synthetic process of the Co₃(HPO₄)₂(OH)₂ product is expected to be as follows:

XRD analysis was implemented to identify the crystal structure of the Co₃(HPO₄)₂(OH)₂ sample (Fig. 2a). It is clear that the diffraction peaks of the Co₃(HPO₄)₂(OH)₂ sample appear at 13.3°, 17.8°, 26°, 26.9°, 27.4°, 34°, 38.4°, 42.4°, 48.4°, 53.4°, 55.3°, 56.4° and 70.8°, which are assigned to the (-101), (-111),

Figure 1 Synthetic process of the Co₃(HPO₄)₂(OH)₂ sample.

Figure 2 (a) XRD pattern, (b–e) XPS spectra, and (f) N_2 adsorption-desorption isotherm and pore size distribution curve (inset) of the $Co_3(HPO_4)_2(OH)_2$ sample.

(-112), (111), (021), (121), (031), (-313), (-402), (-224), (222), (042) and (-442) planes of a $Co_3(HPO_4)_2(OH)_2$ crystal (JCPDS No. 80-1996). Further, no additional diffraction peaks are observed, suggesting the formation of pure $Co_3(HPO_4)_2(OH)_2$.

The surface chemical compositions and valence states of the $Co_3(HPO_4)_2(OH)_2$ sample were investigated *via* XPS measurement. The survey spectrum of the $Co_3(HPO_4)_2(OH)_2$ sample verifies the co-existence of Co, P, O, and C elements in the sample (Fig. 2b). For the Co 2p spectrum (Fig. 2c), it is made up of four peaks: Co 2p_{3/2}, Co 2p_{1/2} and two shake-up satellite peaks (marked as “Sat”). The two distinctive peaks at 781.58 and 797.51 eV can match with Co 2p_{3/2} and Co 2p_{1/2}, respectively, conforming well to the electronic state of Co²⁺ species [13]. For the P 2p spectrum (Fig. 2d), the peaks appearing at 133.27 and

134.18 eV match with the distinctive P 2p_{3/2} and P 2p_{1/2} peaks, respectively. The peak at 133.27 eV is a featured peak of phosphate species, indicating that the P species in the form of (PO₄)^{3−} exist on the surface of $Co_3(HPO_4)_2(OH)_2$, which may be helpful in enhancing the surface reactivity [13]. The O 1s spectrum is composed of two peaks (Fig. 2e). The binding energies of 531.14 and 532.67 eV are respectively indexed to the lattice oxygen (O^{2−}) and hydroxyl group (OH), which are consistent with the composition of $Co_3(HPO_4)_2(OH)_2$ [12].

The more structural characterizations of the $Co_3(HPO_4)_2(OH)_2$ sample were investigated through N_2 adsorption/desorption isotherm (Fig. 2f). It is apparent that the $Co_3(HPO_4)_2(OH)_2$ sample demonstrates the type IV isotherm with apparent hysteresis loop between adsorption and desorption isotherms,

demonstrating the presence of mesopores [14]. Further, the fast increase in N_2 adsorption under high relative pressure ($P/P_0 > 0.9$) illustrates the existence of macropores, which originates from the stacking of the $Co_3(HPO_4)_2(OH)_2$ sample [15]. Besides, the $Co_3(HPO_4)_2(OH)_2$ sample owns a great Brunauer-Emmett-Teller (BET) specific surface area of $31.5 \text{ m}^2 \text{ g}^{-1}$. As shown in the inset of Fig. 2f, the pores of the $Co_3(HPO_4)_2(OH)_2$ sample were analyzed *via* the Barrett-Joyner-Halenda (BJH) method, demonstrating that the pore size distribution further reveals the hierarchical porous structure of the $Co_3(HPO_4)_2(OH)_2$ sample with mainly $\sim 4 \text{ nm}$ mesopores and a few macropores. This distinctive pore structure may be advantageous to the electrochemical energy storage of the $Co_3(HPO_4)_2(OH)_2$ sample, because abundant mesopores/macropores are conducive to

promoting mass transfer/ion diffusion.

FESEM was performed to check the microstructure and morphology of the $Co_3(HPO_4)_2(OH)_2$ sample. FESEM images displayed in Fig. 3a, b show that the morphology of the $Co_3(HPO_4)_2(OH)_2$ sample appears as homogeneous bouquets with a height of about $1.5 \mu\text{m}$, which are composed of nano-needles with the widths of $50\text{--}100 \text{ nm}$. As shown in Fig. 3c, the TEM image further confirms this unique bouquet-like morphology. This unique morphology is conducive to exposing more electroactive sites and alleviating the structural change during the electrochemical reaction, effectively improving the electrochemical performance. Fig. 3d displays a high-resolution TEM (HRTEM) image of the bouquet, showing the atomic lattice fringe spacing of 0.643 nm that can be well assigned to the

Figure 3 (a, b) FESEM, (c) TEM, (d) HRTEM, (e) EDS and (f) element mapping images of the $Co_3(HPO_4)_2(OH)_2$ sample.

(-101) plane of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ sample. The EDS image manifests the peaks of Co, P and O elements (Fig. 3e), demonstrating that the resultant $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ sample consists of Co, P and O elements, and the atomic percentage of Co, P and O is 15.11%, 10.61% and 74.28%, respectively. The element mapping images of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ sample reveal that the elements Co, P, and O are evenly distributed within the structure (Fig. 3f) [16].

A three-electrode configuration was used to test the super-

capacitive performance of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode in 2 mol L^{-1} KOH electrolyte, and the results are presented in Fig. 4. Fig. 4a exhibits the galvanostatic charge-discharge (GCD) profiles of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode at diverse current densities of $1\text{--}100 \text{ A g}^{-1}$ from 0 to 0.55 V. All GCD profiles display good symmetry, revealing excellent reversibility and high coulombic efficiency during charging and discharging processes. In addition, all GCD profiles possess obvious voltage plateaus, which illustrate the typical Faraday battery-type behavior char-

Figure 4 (a) GCD profiles, (b) rate property, (c) cycling stability, (d) CV profiles, (e) I_p - $v^{1/2}$, (f) $\log(I_p, \text{A})$ - $\log(v, \text{mV s}^{-1})$, (g) charge contributions at 10 mV s^{-1} , (h) charge contribution at diverse sweep rates, (i) Nyquist plot and the inset showing the equivalent circuit, (j) Bode plot, (k) real capacitance vs. frequency plot and (l) linear diffusion of Z' and $\omega^{-1/2}$ of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode.

acteristics of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode [17]. The prolonged discharge time of the GCD profiles illustrates the high specific capacity of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode. The specific capacity of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode is 119.2, 118.6, 116.8, 114.3, 110.6, 104.9, 99.2, 90.9 and 83.6 mA h g^{-1} at diverse current densities of 1, 2, 3, 5, 10, 20, 30, 50 and 100 A g^{-1} , respectively (Fig. 4b). Importantly, the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode shows an outstanding rate property with 70.1% initial capacity retention at 100 A g^{-1} , revealing its advantage as an ultrahigh-rate Faraday cathode material for energy storage systems. The cycle life is also a vital parameter to verify the supercapacitive performance of electrode materials. Therefore, the repeated charging/discharging process is applied to test the cycling stability of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode at 10 A g^{-1} after 5000 cycles. As presented in Fig. 4c, due to the gradual activation of the electrode, the capacity of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode increases during the first 1300 cycles, then gradually decreases and remains stable at about 3900 cycles, and this phenomenon is consistent with many previous reports [18,19]. After 5000 cycles, the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode can maintain 92% of its initial capacity, showing good cycle performance. Besides, the coulombic efficiency of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode is close to 100%. The electrochemical performance of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode is higher than those of most other reported cobalt-based metal oxides, phosphides and phosphates (Table S1).

Fig. 4d manifests the cyclic voltammetry (CV) profiles of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode at the sweep rates of 2–200 mV s^{-1} . All CV profiles present the similar shape and the area becomes larger as the scanning speed increases, revealing the excellent reversibility and rate performance of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode [20]. Furthermore, each CV profile shows a couple of evident redox peaks that are different from the CV shape of the conventional electrical double-layer capacitors (EDLCs), which signifies the presence of the Faraday battery-type redox reaction during the electrochemical process [21]. The redox reaction could be depicted as the following equations:

In addition, the oxidation peak and the reduction peak respectively move to a higher and lower potential as the scanning speed increases, which mainly result from the polarization effect [22]. Note that the potential difference moved from 2 to 200 mV s^{-1} is small, implying the low polarization, which means the low resistance and good electrochemical kinetics. Besides, we can observe that the peak currents of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode do not show obvious deformation even at a particularly high sweep rate of 200 mV s^{-1} , which indicates that the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode presents rapid charge/discharge characteristic [23]. The OH^- diffusion rate (D) is quantitatively determined according to the equation below [24]:

$$I_p = 2.69 \times 10^5 \times n^{3/2} \times A \times D^{1/2} \times C_{\text{OH}^-} \times v^{1/2}, \quad (6)$$

where n , A , D and C_{OH^-} denote the transferred electron number, electrode area (cm^2), diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$) and OH^- concentration (mol L^{-1}), respectively. The D value can be obtained from the slope of I_p - $v^{1/2}$ (Fig. 4e). The slope values are

18.4 and -19.1 , and the calculated D values are 0.134×10^{-11} and $0.144 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, respectively. Thus, the average D value is about $0.139 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, manifesting that the OH^- intercalation/deintercalation is fast during the charge/discharge process.

The CV test was applied to further study the electrochemical behavior of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode through electrochemical kinetic analysis. A semi-quantitative analysis was carried out based on the relation between the peak current (I_p) and sweep rate (v), as exhibited in the following formula [25]:

$$I = av^b, \quad (7)$$

in which the b value is obtained from the slope of $\log(I_p)$ - $\log(v)$ graph, as shown in Fig. 4f. In general, the value of $b = 0.5$ represents the ideal battery behavior (diffusion-controlled process), and the value of $b = 1$ represents the ideal capacitive feature (surface capacitive process). Here, the b value of $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ is 0.82, indicating the dominant surface capacitive behavior, which implies that it has superior electrochemical kinetics [26]. Besides, the result was further supported via the quantitative calculation of the charge contributions, as demonstrated in the following equation [27]:

$$i(V) = k_1v + k_2v^{1/2}, \quad (8)$$

where k_1v and $k_2v^{1/2}$ respectively denote the contributions of surface capacitive process and diffusion-controlled process. The fitted line of the $i/v^{1/2}$ to $v^{1/2}$ of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode was executed. The values of slope and intercept are constants of k_1 and k_2 , respectively. Fig. 4g shows the CV curve of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode at 10 mV s^{-1} , and the surface capacitive contribution is about 76.4% of the total capacity. It is clear that the capacitive contributions of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode to the total capacity with the increasing sweep rates from 2 to 100 mV s^{-1} are shown in Fig. 4h and Fig. S1. It is worth noting that the contribution of the diffusion-controlled process decreases rapidly as the sweep rate increases while the contribution of the surface capacitive process rises rapidly and reaches high up to 94.8% at 100 mV s^{-1} , indicating the rapid electrochemical kinetics.

Electrochemical impedance spectroscopy (EIS) test was performed to further estimate the electrochemical kinetics of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode. The Nyquist plot of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode is exhibited in Fig. 4i. It can be obviously observed that the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode displays a tiny real axis intercept and inappreciable semicircle in the high-frequency region, verifying an ultra-low internal resistance ($R_s = 0.74 \Omega$) and charge transfer resistance ($R_{ct} = 0.21 \Omega$), which can elucidate that the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode displays superior rate performance. Additionally, the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode presents nearly vertical lines in the low-frequency region, suggesting that OH^- can easily diffuse into the active material, which further illustrates the excellent electrochemical kinetics of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode [28]. To further confirm the electrochemical behavior, a Bode plot of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode is shown in Fig. 4j, revealing good frequency response and short relaxation time. The phase angle is near -90° at low frequencies, confirming the capacitive behavior [29]. Considering the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrode as a whole by utilizing the impedance data, Fig. 4k displays the imaginary part of the capacitance change (C'') versus frequency. The C'' curve shows a peak at frequency f_0 , matching with the dielectric

relaxation time constant of $\tau = 1/f_0 = 1 \text{ s}$ [30]. The diffusion coefficient of OH^- is determined according to the following equation [31]:

$$|Z| = R_{\text{ct}} + R_s + \sigma\omega^{-1/2}, \quad (9)$$

$$D = R^2 T^2 / (2A^2 n^4 F^4 C^2 \sigma^2), \quad (10)$$

where D , R , T , A , n , F , C , σ and ω stand for the diffusion coefficient of OH^- , gas constant, absolute temperature, specific surface area, number of electrons, Faraday's constant, OH^- concentration, Warburg factor and angular frequency, respectively. As depicted by Fig. 4l, the σ value is 2.8, and the calculated D value is $0.22 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, further confirming the superior electrochemical kinetics.

In order to reveal the potential applications of the bouquet-like $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ in energy storage devices, an HSC device was fabricated by employing $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ as the cathode, PC as the anode and 2 mol L^{-1} KOH as the electrolyte with a piece of separator (denoted as $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$). The PC anode shows superior electric double layer (EDL) behavior with a nearly rectangular CV profile from -1 to 0 V (Fig. S2). Fig. 5a shows the schematic diagram of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC

device. The CV measurements of the PC and $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrodes at 10 mV s^{-1} in 2 mol L^{-1} KOH electrolyte were used to investigate the total voltage of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device (Fig. 5b). As seen from the CV profiles, the potential window of the PC and $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrodes is respectively in the range of -1.0 – 0 V and 0 – 0.6 V . The CV profiles of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device at sweep rates varying from 2 to 100 mV s^{-1} in the voltage window of 0 – 1.5 V present rectangular shape accompanied by obvious redox peaks, and the profiles nearly retain the same shapes, indicating the preminent rate performance (Fig. 5c) [32]. The GCD profiles at diverse current densities of 2 – 100 A g^{-1} were performed to further investigate the supercapacitive characteristics of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device. The practically symmetric GCD profiles of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device (Fig. 5d) show an excellent electrochemical reversibility [33]. The $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device shows a high specific capacitance of 142.8 F g^{-1} at 2 A g^{-1} , and still retains 40.8 F g^{-1} even at 100 A g^{-1} (Fig. 5e), demonstrating the good rate property, which originates from the superior chemical composition, unique hierarchical porous structure and exceptional electrical conductivity of the bouquet-like $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$.

Figure 5 (a) Schematic diagram of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device. (b) CV profiles of the PC and $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ electrodes at 10 mV s^{-1} . (c) CV profiles of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device. (d) GCD profiles of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device. (e) The corresponding specific capacitance. (f) Ragone plots of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device. (g) Cycle property and coulombic efficiency of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device after 10,000 cycles at 3 A g^{-1} , and the inset displays the first/last five GCD profiles. (h) An LED display is lighted up, and (i) a fan is driven by two HSC devices.

Fig. 5f shows the Ragone plot of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device. The energy density (E) and power density (P) are obtained by the following equations [34]:

$$E = \frac{1}{2}CV^2, \quad (11)$$

$$P = E/t, \quad (12)$$

where C , t and V represent the specific capacitance, discharge time and voltage window of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device, respectively. The GCD tests demonstrate that the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device possesses an energy density of 44.6 W h kg^{-1} at a power density of 675 W kg^{-1} , and still retains a reasonable value of 12.7 W h kg^{-1} at an ultrahigh power density of 33.75 kW kg^{-1} . The energy density of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device is larger compared with those of previously reported cobalt-phosphide- and phosphate-based HSC devices, including $\text{Co}_3(\text{PO}_4)_2/\text{AC}$ ($26.66 \text{ W h kg}^{-1}$ at 750 W kg^{-1}) [35], $\text{Co}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}/\text{GF}/\text{C-FP}$ (24 W h kg^{-1} at 468 W kg^{-1}) [36], $\text{NH}_4\text{CoPO}_4 \cdot \text{H}_2\text{O}/\text{AC}$ (10.4 W h kg^{-1} at 141.3 W kg^{-1}) [37], $\text{Co}_2\text{P}/\text{HNF}/\text{AC}$ (30.5 W h kg^{-1} at 850 W kg^{-1}) [38], $\text{Co}_2\text{P}/\text{graphene}$ (24 W h kg^{-1} at 300 W kg^{-1}) [39], $\text{Co}(\text{P,S})/\text{CC}/\text{PCP}/\text{rGO}$ (39 W h kg^{-1} at 800 W kg^{-1}) [26], and $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}/\text{AC}$ ($29.29 \text{ W h kg}^{-1}$ at 468.75 W kg^{-1}) [40]. A cycle test was used to explore the cycle stability of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device. After 10,000 cycles, the capacity retention of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device is as high as 91.8% at 3 A g^{-1} , and the coulombic efficiency is near 100%, showing an excellent cycling performance (Fig. 5g), which is verified *via* the almost invariable shapes of the first/last five charge/discharge cycles of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device obtained from the inset of Fig. 4g. To further verify the practicability of the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device, a pair of HSC devices were connected in series to light up a light emitting diode (LED) display and drive a small fan, as shown in Fig. 5h, i. Therefore, the $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device is promising candidate for practical applications.

The excellent electrochemical performance of the as-obtained bouquet-like $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ is due to the following reasons. (1) The $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ combines the advantages of cobalt oxide and cobalt phosphide, effectively improving the electronic conductivity and thus leading to the enhanced rate property. In addition, the presence of hydroxide groups effectively improves the chemical stability. (2) The hierarchical porous structure with abundant mesopores and macropores in the bouquet-like $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ can accelerate ion transport/diffusion and prevent structural collapse during the charging/discharging process, thereby boosting the rate capability and cycling stability of the electrode. (3) The bouquet-like $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ with microscale framework and nanoscale structure can give great exposure of electrochemically active sites and relieve the structural change in the electrochemical process, resulting in enhanced energy storage performance and cyclic stability.

CONCLUSIONS

In this study, the uniform bouquet-like $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ was successfully synthesized using RP as phosphorus source *via* the hydrothermal method, and the synthetic method is very simple and low-consumption. The electrochemical property of the resultant $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ as a new battery-like cathode was investigated through a traditional three-electrode configuration and an HSC device. Impressively, the resultant electrode displays a high specific capacity ($119.2 \text{ mA h g}^{-1}$ at 1 A g^{-1}), an ultrahigh

rate performance (83.6 mA h g^{-1} at 100 A g^{-1}) and an eminent cycling stability (92% capacity retention at 10 A g^{-1} for 5000 cycles). Further, the assembled $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2/\text{PC}$ HSC device shows a maximum energy density (44.6 W h kg^{-1}) and a maximum power density (33.75 kW kg^{-1}). Also, the HSC device displays an outstanding cycle performance of 91.8% capacity retention after 10,000 cycles at 3 A g^{-1} . This current work not only prepares a novel high-performance battery-type cathode material, but also offers a new thought for the industrial application of RP.

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

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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新型花束状磷酸钴作为超高倍率和稳定的混合超级电容器电池型正极材料

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摘要 红磷由于资源丰富、化学稳定性好、环境友好等优点有利于工业化。然而, 低的电子导电性和大的体积膨胀限制了其在储能方面的应用。本工作首次以红磷作为磷源, 利用一步水热法制备了一种新型的花束状 $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$, 将其作为混合超级电容器的正极材料时展现出大的比容量(在 1 A g^{-1} 时的比容量为 119.2 mA h g^{-1})、极好的倍率性能(在 100 A g^{-1} 时的比容量为 83.6 mA h g^{-1})和出色的电化学稳定性(在 10 A g^{-1} 下5000次循环后的容量保持率为92%)。此外, 以 $\text{Co}_3(\text{HPO}_4)_2(\text{OH})_2$ 作为正极和多孔碳作为负极组装出的新型混合超级电容器表现出高达 44.6 W h kg^{-1} 的能量密度和高达 33.75 kW kg^{-1} 的功率密度, 以及出色的循环性能(在 3 A g^{-1} 下10,000次循环后的容量保持率为91.8%)。该研究不仅开发了一种新型高性能的电池型正极材料, 而且为红磷在储能领域的商业化应用提供了新的思路。