Amorphous cobalt hydroxysulfide nanosheets with regulated electronic structure for high-performance electrochemical energy storage

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ABSTRACT Pseudocapacitors with high power density, long-term durability, as well as reliable safety, play a key role in energy conversion and storage. Designing electrode materials combining the features of high specific capacitance, excellent rate performance, and outstanding mechanical stability is still a challenge. Herein, a facile partial sulfurization strategy has been developed to modulate the electronic structure and crystalline texture of cobalt hydroxide nanosheets (denoted as $\text{Co}(\text{OH})_2$) at room temperature. The resultant cobalt hydroxysulfide nanosheet (denoted as CoSOH) electrode with abundant low-valence cobalt species and amorphous structure, exhibits a high specific capacitance of 2110 F g^{-1} at 1 A g^{-1} with an excellent capability retention rate of 92.1% at 10 A g^{-1} , which is much larger than that of $\text{Co}(\text{OH})_2$ precursor (916 F g^{-1} at 1 A g^{-1} and 80% retention at 10 A g^{-1}). Furthermore, the fabricated asymmetric supercapacitor device constructed with CoSOH and active carbon displays a considerable high energy density of 44.9 W h kg^{-1} at a power density of 400 W kg^{-1} , and exceptional stability after 8000 cycles.

Keywords: hydroxysulfide, amorphous, supercapacitor, electronic structure, nanosheet

INTRODUCTION

High-efficiency energy storage devices play a vital role in alleviating the global energy crisis and environmental pollution. Supercapacitor with high power density, good operational safety and long lifespan, is particularly desirable for potential applications where a large amount of

energy needs to be either quickly stored or delivered, such as electric vehicles, portable electronic devices, subway systems and so on [1–6]. Generally, supercapacitors can be classified into two types on the basis of energy storage principle: electrochemical double layer capacitors (EDLCs) and pseudocapacitors. The EDLC has high power density and long cycle stability due to the rapid charge transfer during the charge and discharge process, resulting from the physically adsorbed ions on the electrode. However, the low charge storage capacity of EDLC seriously limits the practical application. In the case of pseudocapacitor, the presence of Faradaic redox reaction between the electrode surface and electrolyte as illustrated in battery endows the pseudocapacitor with merits of superior energy density, which makes it have received much more attention than EDLC [7]. To optimize the electrochemical properties of pseudocapacitor, design and fabrication of advanced electrode materials are the key factor. Up to date, a variety of electrode materials, such as metal oxides/hydroxides [8–10], phosphides [11], chalcogenides [12], nitrides [13], borides [14], polymers [15] and heteroatom-doped carbon [16], have been developed for capacitive energy storage. Among the various candidates, $\text{Co}(\text{OH})_2$ has attracted extensive attention due to its high theoretical capacity, low cost and easy complex with other substances [17,18]. For example, $\text{Co}(\text{OH})_2$ nanosheets were synthesized by a facile electrodeposition strategy, which achieved a specific capacitance of 800 F g^{-1} at a current density of 2 A g^{-1} [19]. Such a considerable performance was attributed to the favorably

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perpendicular orientation of CoO_2 planes in $\text{Co}(\text{OH})_2$ platelet [20]. Although lots of achievements have been made, the main obstacles of $\text{Co}(\text{OH})_2$ as supercapacitor electrode materials are the poorly intrinsic electrical conductivity and structural instability in alkaline electrolyte, which result in the poor specific capacitance, unsatisfactory rate capability and limited cycle life, severely restraining the maximization of the $\text{Co}(\text{OH})_2$ for energy storage.

Recently, dual anions-doped metal hydroxides with regulated electronic and crystalline structure exhibit attractive potential for electrochemical applications [21–23]. Specifically, the introduction of S species into metal hydroxides can bring three characteristics: (1) the electronic structure of hydroxysulfides can be optimized by S ion regulation. The lower electronegativity of S than O leads to a decreased valence of the adjacent metal ions, which can significantly improve the charge storage capacity during the redox reaction. (2) The resultant metal hydroxysulfides demonstrate a superior conductivity to hydroxide precursor, which is advantageous for the charge/ion transfer and transportation at high current densities, resulting in excellent rate capability. (3) Hydroxysulfide materials with amorphous structure possess abundant defects and ion diffusion channels, moderate volume changes and strong corrosion resistance in the alkaline electrolyte, which can give rise to considerable long-term durability for supercapacitor [24–27]. Currently, amorphous metal hydroxysulfides have been studied in tailoring the electrocatalysis performance, but very limited attention has been paid to the application for supercapacitor [28–30].

Herein, a facile hydrothermal strategy combined with a post room-temperature sulfurization treatment was successfully performed to synthesize CoSOH nanosheets. The chemistry and electronic structures, and crystalline texture of the CoSOH were manipulated by introducing the S species into cobalt hydroxide, which leads to enhanced electrochemical performance for supercapacitor. The resultant electrode delivers a high specific capacitance of 2110 F g^{-1} at the current density of 1 A g^{-1} with excellent rate capability (capacitance retention rate of 92.1% at 10 A g^{-1}) and outstanding cycling stability over 8000 charge-discharge cycles. In addition, the assembled CoSOH/AC asymmetric supercapacitor (ASC) with an operating voltage window of 1.6 V delivers a considerable energy density of 44.9 W h kg^{-1} at a power density of 400 W kg^{-1} . The strategy and concept reported here can be extended to other mono- or multi-metal hydroxysulfides for energy conversion and storage.

EXPERIMENTAL SECTION

Synthesis of cobalt hydroxysulfide

All chemicals were purchased from Sinopharm group chemical reagent Co. LTD, and were used as received. In a typical procedure, 5 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 20 mmol of urea were dissolved in 10 mL of deionized water and 70 mL of ethylene glycol to form homogenous solution under stirring. Afterwards, the resultant pink solution was transferred into a Teflon-lined stainless-steel autoclave and kept at 120°C for 4 h. The obtained green $\alpha\text{-Co}(\text{OH})_2$ nanosheets were immersed in $1 \text{ mol L}^{-1} \text{ Na}_2\text{S}$ solution for 12 h with vigorous stirring. Ultimately, the black products were collected by centrifugation followed by washing with distilled water several times, and dried at -40°C by freeze-drying for 48 h.

Computational details

All spin-polarized density functional theory (DFT) calculations were performed with proton balance equation (PBE) exchange correlation in the Gaussian and plane waves (GPW) formalism as implemented in the CP2K code [31–33]. Double-zeta valence polarized (DZVP) basis sets in combination with Geodcker-Teter-Hutter (GTH) pseudopotentials were used, and the plane wave density cutoff was set to be 400 Ry [34,35]. For the H, O, S and Co, 1, 6, 6 and 17 valence electrons were taken into account, respectively. DFT-D3 correction was employed to improve the description of van der Waals interaction [36]. According to the previous study, DFT+*U* method, where the *U*-*J* was 3.0 eV, was used for the on-site Coulomb interaction correction of the Co 3d states [37]. The optimized unit cell lengths of $\alpha\text{-Co}(\text{OH})_2$ were 3.22, 3.22 and $4.55 \text{ \AA}$, respectively, consistent with experimental results. The Brillouin Zone was represented by the Γ point in calculating the $c(4 \times 3)$ $\alpha\text{-Co}(\text{OH})_2$ (110) surface, which was composed by five atomic layers, and the bottom two layers were fixed.

Characterization

The morphology and microstructure of the as-obtained materials were characterized using field emission scanning electron microscope (FESEM, Hitachi, SU-70), and high-resolution transmission electron microscope (HRTEM, Hitachi, JEM-F200). The crystalline features were investigated using X-ray diffraction (XRD, Bruker D8). The chemical composition and states of the material surface were collected through X-ray photoelectron spectroscopy (XPS, K-Alpha+, Thermo fisher Scientific). The specific surface area was measured by the N_2 ad-

sorption/desorption isotherms and calculated using the Brunauer-Emmett-Teller (BET) method.

Electrochemical measurement

The working electrode was constructed by mixing the as-obtained materials, acetylene black and polytetrafluoroethylene (PTFE) with a mass ratio of 8:1:1 in a certain amount of ethanol to form the slurry by ultrasonic. The dispersive mixture was then coated on a piece of nickel foam with a size of 1 cm × 1 cm and dried in vacuum at 80°C for 12 h. The current collector was pressed to be a thin foil with the thickness of 0.11 mm under 10 MPa. The mass loading of electroactive materials was about 2.0 mg cm⁻². The electrochemical tests of all electrodes were conducted in a three-electrode system with a Pt counter-electrode and an Hg/HgO reference electrode in 6 mol L⁻¹ KOH solution on the electrochemical working station (CHI 760E, Shanghai, China). The electrochemical alternative-current impedance measurements were carried out to assess the electrical properties at the open circuit voltage with frequency from 0.01 Hz to 100 kHz and an amplitude of 5 mV. The specific capacitance of the electrodes was calculated from the corresponding galvanostatic charge-discharge (GCD) curves by the following Equation (1):

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

where C_s is the specific capacitance of the capacitor (F g⁻¹); I is the current of the charge/discharge process; Δt is the discharging time in seconds for the potential change ΔV , in volts; m is the mass loading of the electroactive material.

The asymmetric supercapacitor was fabricated by using the electroactive material as cathode and active carbon (AC) as anode, respectively. The weight ratio of positive and negative electrodes is calculated by the following Equation (2):

$$m_+ \times C_+ = m_- \times C_-, \quad (2)$$

The specific energy density (E , W h kg⁻¹) and power density (P , W kg⁻¹) of the as-fabricated ASC device were determined based on the Equations (3, 4) presented below:

$$E = \frac{1}{2} \times \frac{C \times V^2}{3.6}, \quad (3)$$

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

where C is the specific capacitance (F g⁻¹); V is the cell voltage (V); Δt is the discharge time (s).

RESULTS AND DISCUSSION

The preparation of amorphous cobalt hydroxysulfide nanosheets is illustrated in Fig. 1. Briefly, green cobalt hydroxide precursor was synthesized by a hydrothermal method at 120°C for 4 h. Subsequently, the crystalline hydroxide was immersed in 1 mol L⁻¹ Na₂S solution at room temperature for 12 h. Thanks to the huge difference of solubility between the metal hydroxide and its corresponding metal sulfide, the S species continuously replaced the hydroxy in the solid phase and the CoSOH converted from Co(OH)₂ were obtained [26].

The morphology, crystalline nature and microstructure of the as-prepared materials were studied by using SEM, XRD, HRTEM, and the corresponding selected area electron diffraction (SAED) pattern. Fig. 2a shows the morphology of the Co(OH)₂ precursor composed of uniform and freestanding nanosheets with several micrometers in size. In Fig. 2b, the nanosheets demonstrate a smooth surface. After a partial sulfurization treatment, the 2D morphology of nanosheets is well preserved and the obtained CoSOH nanosheets possess an average thickness of 20 nm and a lateral length of several hundred nanometers (Fig. 2c, d). However, it is clearly observed that the sulfurization process leads to a curly surface for the nanosheets, which can contribute to the contact be-

Figure 1 Schematic illustration of the design of two-dimensional (2D) cobalt hydroxysulfide nanosheets.

Figure 2 FESEM images of (a, b) Co(OH)_2 and (c, d) CoSOH at different magnifications.

tween the electrode surface and electrolyte.

As presented in Fig. 3a, the characteristic peaks in the XRD profile of the precursor are assigned to (006), (012), and (110) peaks of the lamellar $\alpha\text{-Co(OH)}_2$, which is in consistence with the previous literatures [38,39]. Such a crystalline structure disappears after the sulfurization treatment at room temperature, which indicates the abundant local structural distortion in amorphous CoSOH nanosheet caused by the partial substitution of hydroxyl by sulfur species in the $\alpha\text{-Co(OH)}_2$. The TEM image in Fig. 3b exhibits the 2D structure of CoSOH with

almost transparent nature, suggesting the ultrathin feature originating from the Co(OH)_2 (Fig. S1a). The HRTEM image (Fig. 3c) demonstrates that CoSOH nanosheet is homogeneous and has no clear lattice fringe. As a contrast, the HRTEM image of the precursor nanosheet presents the distinct lattice fringes of about 0.266 and 0.159 nm that correspond to the (012) and (110) of crystal $\alpha\text{-Co(OH)}_2$ phase, respectively (Fig. S1b). In addition, the amorphous nature of CoSOH was further confirmed by the broad and diffused halo ring in the corresponding SAED pattern (Fig. 3d), matching well with the XRD results, while the distinguishable diffraction rings in the SAED pattern of $\alpha\text{-Co(OH)}_2$ precursor show the well crystallinity (Fig. S1c). Furthermore, energy-dispersive X-ray spectroscopy (EDX) element mapping reveals the uniform and homogenous dispersion of Co, S and O (Fig. 3e). In contrast, there are only Co and O species in the $\alpha\text{-Co(OH)}_2$ nanosheets (Fig. S1d). The long-range disorders, abundant defects and extensive active sites induced by S incorporation in the amorphous CoSOH nanosheets will facilitate the redox reaction and release the volume change of electrode during the charge-discharge process, which are beneficial for improving capacitance and stability [40]. The N_2 adsorption/desorption isotherms of CoSOH and Co(OH)_2 nanosheets are displayed in Fig. S2. According to the BET method, the specific surface area of CoSOH is about $105 \text{ m}^2 \text{ g}^{-1}$, which is much higher than that of the Co(OH)_2 nanosheets

Figure 3 (a) XRD pattern (b) TEM image, (c) HRTEM image, (d) SAED pattern and (e) EDX mapping of the CoSOH nanosheets.

(about $10 \text{ m}^2 \text{ g}^{-1}$). In addition, the pore features of these two samples were analyzed by the desorption branch of the isotherms through the Barrette-Joynere-Halenda (BJH) method. As illustrated in insets of Fig. S2, the obtained CoSOH nanosheets demonstrate abundant mesopores with an average pore size of 3.6 nm, while the pristine $\text{Co}(\text{OH})_2$ nanosheets deliver a relatively broad pore size distribution between 1 and 50 nm. Furthermore, the total pore volume of CoSOH nanosheets is $0.26 \text{ m}^3 \text{ g}^{-1}$, much higher than that of $\text{Co}(\text{OH})_2$ nanosheets ($0.03 \text{ m}^3 \text{ g}^{-1}$). The large surface and abundant pores of the as-prepared CoSOH will favor the interaction between the electrolyte and electrode, resulting in promising electrochemical capacitive properties.

The chemical state and electronic structure of the materials were investigated by XPS. In Fig. 4a, the Co 2p_{1/2} and Co 2p_{3/2} peaks of $\text{Co}(\text{OH})_2$ locate at 794.33 and 778.79 eV, respectively, similar to previous study [41]. In comparison to $\text{Co}(\text{OH})_2$, there is an evident shift ($\sim 2 \text{ eV}$) for these two peaks in CoSOH towards higher binding energy, suggesting rich electrons around the Co species caused by S-doping. In addition, CoSOH shows distinguishable satellite peaks at 802.53 and 786.05 eV, confirming a decreased valence of Co species. This can be attributed to the lower electronegativity of S in comparison to O, which endows a higher electron density to Co species. The abundant metal species with a low valence have been expected to yield higher specific capacitance of supercapacitors [8,42]. Furthermore, The XPS spectrum of S was also collected and shown in Fig. 4b. The peaks of 168.27 and 162.63 eV are ascribed to S 2p and S-O, respectively, indicating successful doping of sulfur. Furthermore, DFT calculation was also performed to shed light on the effect of S doping. The (110) surface of the $\alpha\text{-Co}(\text{OH})_2$ is considered, and four of OH groups are replaced by S atoms to model the S doping (Fig. 5a, b).

According to the Mulliken population analysis, the average depletion of the surface Co atoms binding with S atoms significantly decreases from 0.80 e to 0.50 e, compared with the surface Co atoms in the pristine $\alpha\text{-Co}(\text{OH})_2$ (110). Thus, the S-doping reduces the oxidation state of Co, which agrees with our experimental results. Meanwhile, the density of states (DOSs) of the surface Co atoms in the pristine $\alpha\text{-Co}(\text{OH})_2$ (110) are not continuous near Fermi level. After S doping, it presents metallic characters, indicating the improved electrical conductivity (Fig. 5c).

The electrochemical performance of the amorphous CoSOH nanosheets was evaluated in a three-electrode system by using 6 mol L^{-1} KOH as the electrolyte. Fig. 6a shows the typical cyclic voltammetry (CV) curve of CoSOH electrode between 0 and 0.6 V (vs. Hg/HgO) at a scan rate of 5 mV s^{-1} . The CV profile of the pristine $\alpha\text{-Co}(\text{OH})_2$ was also obtained for comparison. Both CV curves show typical pseudocapacitive feature with a pair of well-defined redox peaks. The larger CV closed area of CoSOH than that of $\alpha\text{-Co}(\text{OH})_2$ indicates a higher capacitive behavior for CoSOH. There is an increased number of anodic peaks accompanied with a significant negative shift in the peak position for CoSOH, which verifies the abundant low-valent cobalt species in CoSOH. Furthermore, the CoSOH electrode shows a negligible shape deformation in CV curves and a slight shift of the redox peaks with the increasing scan rates, which demonstrates a superior reversibility and rate capability to the $\text{Co}(\text{OH})_2$ electrode (Fig. S3a, b).

The GCD plots at various current densities from 1 to 20 A g^{-1} for the as-obtained electrodes were measured by chronopotentiometry (CP), as shown in Fig. S3c, d. The presence of platforms during GCD curves with symmetric shape indicates a distinct pseudocapacitive behavior. In Fig. 6b, the GCD curves of these electrodes at 1 A g^{-1}

Figure 4 (a) The Co 2p XPS spectra of $\text{Co}(\text{OH})_2$ and CoSOH nanosheets. (b) The S 2p spectrum of CoSOH nanosheets.

Figure 5 Top view (a) and side view (b) of S-doped α -Co(OH)₂ (110) surface. The white, red, yellow and blue balls are H, O, S and Co atoms, respectively. (c) DOSs of the surface Co atoms in α -Co(OH)₂ (110) and CoSOH (110). The Fermi level was set to 0.00 eV.

clearly show that the CoSOH electrode has a longer discharge time than Co(OH)₂, indicating a higher capacitive performance. The specific capacitances of these electrodes at various current densities have been calculated and the results are presented in Fig. 6c. Notably, the amorphous CoSOH electrode exhibits a high specific capacitance of 2110 F g⁻¹ at the current density of 1 A g⁻¹, which is 3.2 times higher than that of the Co(OH)₂ electrode. The outstanding electrochemical capacitive property of CoSOH can be attributed to the low-valent Co species and amorphous texture, which is consistent with the CV results. Meanwhile, the impressive capacitance of the amorphous CoSOH is also much higher than those of many reported cobalt-based materials, such as organic-Co(OH)₂ nanotubes (502 F g⁻¹@2 A g⁻¹) [18], Co(OH)₂ electrode (800 F g⁻¹@2 A g⁻¹) [19], β -Co(OH)₂ (1066 F g⁻¹@2 A g⁻¹) [38], β -Co(OH)₂ nanosheets (604 F g⁻¹@1 A g⁻¹) [43], 3D Co(OH)₂/CNFs (1186 F g⁻¹@1 A g⁻¹) [44], α -Co(OH)₂ (885 F g⁻¹@1 A g⁻¹) [45], ultrathin α -Co(OH)₂ nanosheets (981.7 F g⁻¹@1 A g⁻¹) [46], mesoporous Co(OH)₂ nanocubes (420 F g⁻¹@1 A g⁻¹) [47] and α -(Ni/Co)(OH)₂/graphene (1668 F g⁻¹@0.5 A g⁻¹) [48]. More importantly, the amorphous CoSOH electrode can maintain a specific capacitance of 1943 and 1857 F g⁻¹ at the current density of 10 and 20 A g⁻¹, respectively, demonstrating excep-

tional capacitance retention rates of 92% and 88% with respect to the value at the current density of 1 A g⁻¹. In contrast, the Co(OH)₂ electrode only maintains retention rates of 80% and 71% at the same current densities. The considerable rate capability of the amorphous CoSOH at high current density is also superior to most reported cobalt hydroxide-based electrodes (Table S1), which can be attributed to two reasons. i) The amorphous nature can enhance the electrical conductivity of the CoSOH, and therefore promote fast redox reactions. ii) The amorphous CoSOH has amounts of structural defects, and abundant grain boundaries, which are beneficial to the ion diffusion and charge transfer, resulting in improved rate capability.

The kinetics of charge transfer process was also evaluated by electrochemical impedance spectroscopy (EIS), as shown in Fig. 6d. The sloped line of CoSOH is steeper than that of the pristine α -Co(OH)₂ in the low frequency region, indicating a favorable ion diffusion process. The magnification in the high frequency region is presented in the built-in image. Apparently, the equivalent series resistance (R_s , the value of the intercept at x axis) and the charge transfer resistance (R_{ct} , the diameter of the semi-circle) of the amorphous CoSOH are about 0.36 and 0.20 Ω , respectively, which are smaller than those of the α -Co(OH)₂ electrode (0.42 and 0.45 Ω , respectively), demonstrating the faster charge transfer process. The EIS results obviously manifest the superiority of the amorphous hydroxysulfide for high-performance supercapacitor. In addition, the long-term durability of the obtained electrodes was evaluated by GCD measurement at the current density of 5 A g⁻¹ in a three-electrode configuration (Fig. 6e). Evidently, the amorphous CoSOH electrode exhibits a pristine capacitance retention of 97.2% after 8000 charge-discharge cycles, while the retention value of Co(OH)₂ is 78.1% after 5000 cycles. The considerable durability performance of CoSOH is ascribed to the amorphous feature of the electrode with strong chemical resistance and stability in alkaline, which mildly releases the structural tension generated during the charging-discharging process [49]. Furthermore, the higher electronegativity of OH⁻ confined in CoSOH promotes the electron transfer from antibonding orbital of Co-S bonds to Co-OH bonds, which endows the stronger bond energy and interaction between Co and S, resulting in outstanding stability for long-term test [50]. The α -Co(OH)₂ is metastable phase and transfers to stable and thick β -Co(OH)₂ in the alkaline solution, and consequently bring the α -Co(OH)₂ relatively poor durability performance.

Figure 6 (a) CV curves, (b) GCD curves, (c) specific capacitances and (d) the Nyquist plots of Co(OH)_2 and CoSOH nanosheets. (e) Cycle stability of Co(OH)_2 and CoSOH at the current density of 5 A g^{-1} .

To evaluate the practical application of the amorphous cobalt hydroxysulfide nanosheets for energy storage, an ASC was assembled by using the CoSOH nanosheets and AC as positive and negative electrodes, respectively. The electrochemical performance of AC was assessed by a three-electrode system in 6 mol L^{-1} KOH electrolyte. As expected, the CV curves with an analogous rectangular exhibit promising double layer capacity in the potential range of -1 to 0 V (Fig. S4a). Meanwhile, the AC electrode delivers a specific capacitance of 255.2 F g^{-1} at the current density of 1 A g^{-1} and retains 232.2 F g^{-1} when the current density increases to 20 A g^{-1} (Fig. S4b, c). In order to determine the optimized voltage window for the

ASC device, the CV curves with a series of potential ranges at a scan rate of 5 mV s^{-1} were performed. As shown in Fig. 7a, there is no apparent polarization when the voltage extends up to 1.6 V. Hence, we chose a potential range of 0 – 1.6 V as the operating voltage for the ASC device. The CV curves of the CoSOH/AC ASC at various scan rates from 5 – 100 mV s^{-1} are shown in Fig. S5. The well-maintained patterns without obvious distortion in all scan rates demonstrate that the device has superior charge-discharge behaviors. Fig. 7b shows the GCD profiles at different current densities with nearly symmetric shape and voltage platform, indicating the high capacitance and remarkable reversibility of the Co-

Figure 7 Electrochemical properties of the CoSOH//AC ASC device. (a) CV curves at different scan rates. (b) GCD curves at different current densities. (c) The specific capacitances at different current densities. (d) The Ragone plot compared with cobalt-based ASC cells in previous reports. (e) The durability of CoSOH//AC ASC device over 8000 cycles at 2 A g⁻¹.

SOH//AC full cell. Furthermore, the Coulombic efficiencies of the ASC device at 0.5–20 A g⁻¹ are all higher than 97% (Fig. S6). The capacitances at various current densities are calculated by the corresponding GCD curves, and the results are presented in Fig. 7c. Meaningfully, the specific capacitances of 119, 92, and 79 F g⁻¹ are achieved at the current densities of 1, 10 and 20 A g⁻¹, respectively. It is noted that the ASC cell presents a capacitance retention rate of 77.3% and 66.4% even when the current density is increased to 10 and 20 A g⁻¹, respectively. In addition, the relationship of energy density

and power density (Ragone plot) is an important parameter for ASC. The Ragone plot of the CoSOH//AC device based on the GCD curves is shown in Fig. 7d. Surprisingly, the ASC cell possesses maximum energy density of 44.9 W h kg⁻¹ at a power density of 400 W kg⁻¹, and still retains 33.8 and 28 W h kg⁻¹ at 6400 and 12,000 W kg⁻¹, respectively. The impressive electrochemical properties are superior to those of the reported state-of-the-art cobalt-based ASCs, such as Co(OH)₂//AC [19], Co(OH)₂//AC [51], CNTF@Co(OH)₂//CNTF [52], NiCoP/NiCo-OH//porous carbon [53], Co₃O₄/NHCS//

AC [54], Co₉S₈-NSA//AC [55], NiCo₂S₄@graphene//porous carbon [56], CoNi-MOF//AC [57], and CoSe₂//N-doped carbon [58]. Furthermore, the stability of the ASC device was assessed by CP measurement at the current density of 2 A g⁻¹. As shown in Fig. 7e, the specific capacitance can retain 96% after 8000 cycles compared with the initial capability. The exceptional durability of the full capacitive devices can be ascribed to the amorphous feature and improved electrical conductivity of CoSOH, which might meet the demands for the future energy storage applications.

CONCLUSIONS

Amorphous CoSOH nanosheets were fabricated by S doping of Co(OH)₂ at room temperature. The obtained CoSOH nanosheets possess abundant low-valence Co species and exhibit significantly improved conductivity, resulting in superior specific capacitance and rate capability. Meanwhile, the unique amorphous nature provides favorable mass transport, buffers the volumetric expansion, and maintains the structure stability during the charge-discharge process. The synergistic effect of the modulated electronic structure and amorphous feature endows the CoSOH with remarkable energy storage capacity, as well as outstanding energy and power density for the CoSOH//AC ASC. This work definitely contributes to the development of the advanced electrode materials for promising capacitive energy storage.

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具有可调电子结构的无定型羟基硫化钴纳米片用于高性能电化学储能

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摘要 赝电容超级电容器具有高功率密度、超长寿命以及可靠的安全性,使其在能源转化和存储中扮演着重要角色。但是,设计具有高容量、优异倍率性能以及出色的机械稳定性的电极材料依旧是一个挑战。本工作中,我们采用室温部分硫化策略来调节氢氧化钴纳米片的电子结构和晶态。得到的羟基硫化钴具有无定形结构,同时还有丰富的低价钴离子。三电极体系下,该电极在电流密度为 1 A g^{-1} 时的比电容达 2110 F g^{-1} ,当电流密度增大至 10 A g^{-1} 时容量仍有 92.1% 的保留,容量和倍率性能都远高于氢氧化钴前驱体 (916 F g^{-1} @ 1 A g^{-1} , 10 A g^{-1} 的比电容保留率为 80%)。此外,利用该电极与商业活性炭组成的不对称电容器具有 44.9 W h kg^{-1} 的高能量密度以及优异的稳定性(8000 次循环后仅衰减 4%)。