Molecule-assisted modulation of the high-valence Co^{3+} in 3D honeycomb-like Co_xS_y networks for high-performance solid-state asymmetric supercapacitors

Haiyan Wang^{1†}, Ying Yang^{1†}, Qinghao Li^{1†}, Wen Lu¹, Jiqiang Ning², Yijun Zhong¹, Ziyang Zhang² and Yong Hu^{1*}

ABSTRACT Modulating the oxidation states of transition metal species has been regarded as a promising strategy to tune the redox activity and achieve more active sites in electrode materials. In this work, a unique three-dimensional (3D) honeycomb-like cobalt sulfide (Co_xS_y) network organized by cross-linked nanosheets (Co_xS_y -T NSs) was prepared *via* a simple triethanolamine (TEOA)-assisted self-templating strategy. Interestingly, it has been found for the first time that the introduction of TEOA in the reaction effectively increases the ratio of high-valence Co^{3+} in the final product. Benefiting from the synergetic effect of the tailored high-valence Co^{3+} with the 3D network structure, the Co_xS_y -T NS electrode exhibits a maximum specific capacity of 351 mA h g^{-1} (2635 F g^{-1}) at 5 A g^{-1} as well as excellent cycling stability. Furthermore, with the solid-state asymmetric supercapacitor (ASC) constructed based on the Co_xS_y -T NSs and activated carbon (AC) electrodes, a high energy density up to $81.62 \text{ W h kg}^{-1}$ has been achieved at the power density of 0.81 kW kg^{-1} and 96.2% capacitance is preserved after 7000 cycles, indicating robust cycling stability. This result highlights the simple approach of simultaneously tailoring high-valence metal species and constructing 3D network structure toward high-performance electrode materials for energy storage and conversion.

Keywords: Co_xS_y , triethanolamine-assisted self-templating strategy, high-valence Co^{3+} , 3D network, solid-state asymmetric supercapacitors

INTRODUCTION

The ever-increasing demand on compact and portable modern electronics has greatly stimulated the research on highly efficient energy storage devices [1–3]. Solid-state supercapacitors (SCs), as newly developed energy storage systems, have attracted considerable attention due to their fast charge/discharge capability, high power density, long life-span, excellent safety and light weight [4–6]. Yet, the low energy density seriously impeded their wide applications [7,8]. In this regard, solid-state asymmetric SCs (ASCs) consisting of a battery-type cathode and a capacitor-type anode have sprung up, which are recognized as a superior structure to effectively enhance the energy density by both widening the voltage window and increasing the specific capacitance [9].

Generally, the battery-type cathode plays a key role in the electrochemical performance of the whole ASC device [10]. Transitional metal sulfides (TMSs) with rich redox sites, high specific capacity and good electrical conductivity have demonstrated great potential as battery-type cathode materials [10,11]. In particular, cobalt sulfides (Co_xS_y) have been investigated vastly and deemed as the promising candidates for energy storage due to their low cost, high theoretical specific capacitance, various stoichiometric compositions and easy synthesis [12]. The charge storage property of Co_xS_y immensely relies on the redox reactions between Co ions of different valences [13]. Sluggish ion diffusion and large volumetric expan-

¹ Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Department of Chemistry, Zhejiang Normal University, Jinhua 321004, China

² Vacuum Interconnected Nanotech Workstation, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China

[†] These authors contributed equally to this work.

* Corresponding author (email: yonghu@zjnu.edu.cn or yonghuzjnu@163.com)

sion during the cycling process are still the major constraints, resulting in the poor rate performance and inferior cycling stability [10,14]. Actually, the electrochemical performance of transitional metal-based electrode materials is closely linked to the nature of the outer d states of the metal elements. Regulating the electronic structures of transitional metal cations was well recognized as an effective route to boost the reaction rate and charge capacity [15,16]. Recently, high-valence transition metal species have been found beneficial for the Faradaic redox reactions [17–19]. For example, Li *et al.* [17] monitored the irreversible phase transition from NiCo carbonate hydroxide nanowires to NiCo layered double hydroxide nanosheets during the cycling, and attributed the tremendously enhanced electrochemical performance to the increased Co oxidation state in the NiCo carbonate hydroxide-Ni(OH)₂ electrode. Tang *et al.* [18] also found that high Co³⁺/Co²⁺ ratio in the Co_xO_ySe_z@C/CC is the key reason for the good battery performance. Despite these great achievements, studies on oxidation state-engineering strategies for improving the performance of SCs are still rare.

Meanwhile, the construction of three-dimensional (3D) porous structures is an effective strategy to accelerate the reaction kinetics and improve the energy storage performance of electrode materials [20]. In particular, those 3D cross-linked nanosheet arrays grown on current collectors can not only shorten the ion diffusion paths, but also reduce the charge-transfer resistance, provide abundant active sites and enough holes to accommodate the volume expansion, which together benefit the rate and cycling performance [21–24]. However, the rational construction of 3D structures with cross-linked nanosheet arrays is still a challenge. Among the numerous strategies proposed, metal-organic framework (MOF) self-templating method has been emerged as an especially fascinating approach. MOFs are a combination of metal ions and organic ligands with ordered tunnels [22,25], and the MOF-derived materials can maintain the architectures of pristine MOFs, achieving well-organized and customizable structures, adjustable pores and large specific surface areas [26]. In addition, the metal ions can be effectively confined by the organic frameworks, which can be further transformed to transition metal-based derivatives [12]. Thus, it is imperative to develop a strategy for controllable conversion of MOFs into highly active and stable electrode materials.

Based on the above considerations, a high-performance battery-type electrode based on a unique 3D honeycomb-like Co_xS_y network assembled with cross-linked

nanosheets (Co_xS_y-T NSs) on the Ni foam (NF) substrate was designed and synthesized *via* a simple triethanolamine (TEOA)-assisted MOF self-templating strategy. Interestingly, it is found for the first time that the introduction of TEOA in the reaction can effectively increase the ratio of high-valence Co³⁺ in the final product. Owing to the synergetic effect of the tailored high-valence Co³⁺ and the unique 3D network structure, the as-prepared Co_xS_y-T NSs exhibit a higher specific capacity of 351 mA h g⁻¹ (2635 F g⁻¹) and better cycling stability compared with Co_xS_y nanosheet arrays (Co_xS_y NSs) obtained without the addition of TEOA. Furthermore, solid-state ASCs were assembled with the Co_xS_y-T NSs and activated carbon (AC) electrodes, and a maximum energy density of 81.62 W h kg⁻¹ at the power density of 0.81 kW kg⁻¹ and a long-term cyclic life with 96.2% capacitance retention after 7000 cycles were achieved. The superior electrochemical performance of Co_xS_y-T NSs provides a good prospect for future energy storage applications.

EXPERIMENTAL SECTION

Synthesis of CCO NWAs

All the reagents were of analytical grade and used without further purification. Co(CO₃)_{0.5}(OH) nanowire arrays (CCO NWAs) on the NF substrate were prepared by a simple hydrothermal method. Typically, a piece of NF (2 cm × 4 cm) was first washed with distilled water and ethanol. 2.5 mmol of Co(NO₃)₂·6H₂O and 15 mmol of urea were dissolved in 30 mL distilled water to obtain a homogeneous solution. The precleaned NF was immersed in the solution and further sonicated for 10 min. Then, the mixture containing the NF was transferred into a 40-mL Teflon-lined stainless steel autoclave and maintained at 90°C for 12 h. Finally, CCO NWAs were repeatedly washed with distilled water and ethanol before drying at 60°C for 12 h.

Synthesis of CCO@ZIF-T

In a typical synthesis, 75 mmol of 2-methylimidazole (2-MI) was dissolved in 28 mL distilled water/TEOA mixture (v/v=6:1) to acquire a homogeneous solution. The obtained solution was then transferred into a 50-mL Teflon-lined stainless steel autoclave and the above-prepared CCO NWAs/NF was immersed into the solution. Then, the autoclave was placed into an oven and maintained at 50°C for 10 h (3, 6 or 15 h). Finally, the product was obtained by washing with distilled water and ethanol for several times and drying at 60°C for 12 h, which was

denoted as TEOA-assisted CCO@TEOA-zeolitic imidazolate framework (CCO@ZIF-T). Unless otherwise specified, CCO@ZIF-T is referred to the product obtained from 10-h hydrothermal reaction. For comparison, the CCO@ZIF was prepared *via* the similar approach to CCO@ZIF-T without the addition of TEOA.

Syntheses of Co_xS_y -T NSs, Co_xS_y NWAs and Co_xS_y NSs

To obtain the Co_xS_y -T NSs, the CCO@ZIF-T/NF was immersed into 30 mL Na_2S aqueous solution (40 mmol L^{-1}). Then the mixture was transferred into a 50-mL Teflon-lined stainless steel autoclave and maintained at 100°C for 6 h. After that, the NF coated with Co_xS_y -T NSs was washed with distilled water and ethanol for several times and dried at 60°C for 12 h. For comparison, Co_xS_y NWAs and Co_xS_y NSs were synthesized after sulfidation of CCO NWAs and CCO@ZIF with the same procedure, respectively. The mass loading of the as-prepared samples on NF was about 2 mg cm^{-2} .

Characterization

Powder X-ray diffraction (XRD) measurements were performed on Bruker D8 Advance with the detector of LynxEye XE using a Cu K α radiation source. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 scanning electron micro-analyzer with an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) measurements were conducted on a JEM-2100F field emission TEM at 200 kV. X-ray photoelectron spectroscopy (XPS) characterization was performed with an ESCALab MKII X-ray photoelectron spectrometer with Al K α X-ray as the excitation source. Raman spectra were recorded with a Renishaw RM 1000 system with a 532 nm excitation laser.

Electrochemical measurements

The electrochemical performances of the electrode materials were investigated with three-electrode and two-electrode configurations on a CHI 660E electrochemical workstation (China). For the three-electrode configuration, the as-prepared samples were used as the working electrode, Pt foil and Hg/HgO as the counter electrode and the reference electrode, respectively, and 6 mol L^{-1} KOH was used as the electrolyte. For the two-electrode configuration, the sample and AC were used as the two working electrodes and KOH/polyvinyl alcohol (KOH/PVA) was used as the solid-state electrolyte. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 10 mHz to

100 kHz with a 5-mV amplitude at open circuit potential.

Assembly of solid-state ASCs

The solid-state ASCs were assembled by using Co_xS_y -T NSs and AC as the positive and negative electrodes, respectively. KOH/PVA gel was used as the electrolyte. In a typical process, a certain amount of the uniform mixture of AC (80 wt%), carbon black (10 wt%), and poly(tetrafluoroethylene) (10 wt%) with several drops of *N*-methyl-2-pyrrolidone was dripped on NF and dried in a vacuum oven at 80°C for 12 h to obtain the AC electrode. To prepare the gel electrolyte, 3 g of PVA was dissolved in 20 mL distilled water with stirring at 90°C for 2 h. Then the KOH solution (10 mL , 0.3 g mL^{-1}) was added dropwise into the viscous solution and stirred for 1 h to obtain the KOH/PVA gel electrolyte. Subsequently, the positive electrode and negative electrode were assembled face to face, which were separated with a piece of cellulose film. According to the charge balance principle, the mass ratio of the Co_xS_y -T NSs and AC was optimized and fixed at 1:5.

Calculations

The specific capacity (C_s , mA h g^{-1}) and specific capacitance (C_{sp} , F g^{-1}) of the as-prepared electrodes were calculated according to Equations (1) and (2), respectively:

$$C_s = \frac{2i \int V dt}{m \Delta V}, \quad (1)$$

$$C_{sp} = \frac{i \Delta t}{m \Delta V}, \quad (2)$$

where i is the current (A), $\int V dt$ is the integral area under the discharge curve, Δt is the discharge time (s), m is the mass of the active materials (g), and ΔV is the potential window (V).

The charge balance was obtained by adjusting the mass of the active materials according to Equation (3):

$$\frac{m_+}{m_-} = \frac{C_- \Delta V_-}{C_+ \Delta V_+}, \quad (3)$$

where m is the mass loading of the active material (g), C is the specific capacity (mA h g^{-1}) and specific capacitance (F g^{-1}), and ΔV is the potential (V) window range for the positive electrode and negative electrode, respectively.

The coulombic efficiency was calculated by the following equation:

$$\eta = \frac{t_d}{t_c}, \quad (4)$$

where t_d and t_c are the discharging and charging time, respectively.

The energy density E (W h kg^{-1}) and power density P

(W kg^{-1}) of the ASCs were calculated based on Equations (5) and (6), respectively:

$$E = 0.5 \times CV^2, \quad (5)$$

$$P = \frac{E}{t} \times 3600, \quad (6)$$

where C is the specific capacitance (F g^{-1}), V is the potential window (V), and t is the discharge time (s) of the device.

RESULTS AND DISCUSSION

The schematic illustration of the formation of 3D honeycomb-like Co_xS_y -T NSs is displayed in Fig. 1. First, using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as the Co precursor, uniform CCO NWAs were first grown on NF through a simple hydrothermal method. Then, CCO NWAs can be converted into CCO@ZIF-T hybrids by reacting in a mixed solution of 2-MI, TEOA and distilled water at 50°C . Finally, Co_xS_y -T NSs were obtained after a sulfidation treatment with Na_2S at 100°C for 6 h.

SEM was first employed to monitor the morphologies of the as-prepared samples. As shown in Fig. 2a, b, nanowire arrays with uniform sizes and smooth surfaces can be observed, which are vertically and firmly grown on the surface of the NF substrate. After reaction with 2-MI and TEOA, some nanowires are transformed into the polyhedra (Fig. 2c), and as the reaction goes on, the amount of nanowire arrays decreases gradually, and more polyhedra are formed on the surface (Fig. S1). A close-up SEM image (Fig. 2d) depicts a hedgehog-like hierarchical microstructure of CCO@ZIF-T hybrid with ZIF polyhedra skewered on CCO nanowires. In the evolution of the hedgehog-like structure, the CCO NWAs serve as the Co-precursor to coordinate with the 2-MI and TEOA, which not only helps the structural retention of nanowire arrays, but also develops the growth of ZIF polyhedra. After sulfidation, the as-prepared Co_xS_y -T NSs exhibit a unique 3D honeycomb-like network structure constructed with cross-linked nanosheets (Fig. 2e). A magnified SEM image (Fig. 2f) clearly demonstrates the 3D honeycomb-like networks with large voids as a result of the etching effect of S^{2-} . The CCO@ZIF-T intermediates serve as a self-template for the development of the honeycomb-like morphology. Specifically, during the sulfidation process, S^{2-} ions react with the outflowing Co^{2+} ions to form a thin layer of Co_xS_y on CCO@ZIF-T . Due to the different diffusion rates of S^{2-} and Co^{2+} ions, the outward diffusion of Co^{2+} ions dominates the inward diffusion of S^{2-} ions, resulting in a honeycomb-like morphology. The unique 3D honeycomb-like networks

Figure 1 Schematic illustration of the formation of the Co_xS_y -T NSs.

Figure 2 SEM images of the as-prepared (a, b) CCO NWAs, (c, d) CCO@ZIF-T after 10 h reaction and (e, f) Co_xS_y -T NSs.

with large voids can act as the electrolyte buffers to facilitate the ion diffusion and expose more active sites to electrolytes, and provide enough space to accommodate the volume expansion, which endows the electrode materials with excellent electrochemical activity and stability. For comparison, in the absence of TEOA, the CCO@ZIF intermediate exhibits a mass of polyhedra on the surface (Fig. S2a, b), whereas it is converted to the honeycomb-like Co_xS_y NSs with cross-linked nanosheets after sulfidation treatment (Fig. S2c, d). This result indicates that the TEOA molecule has no obvious influence on the morphology of the final product. For CCO@ZIF-T intermediates obtained with different hydrothermal times, the corresponding sulfurized products have an obvious difference, as demonstrated in Fig. S3. The CCO@ZIF-T intermediates obtained from reaction for 3 and 6 h are

both converted to hybrid structures composed of nano-flowers and nanowires, while a unique honeycomb-like network structure can be observed after sulfurizing the intermediates for 10 and 15 h, indicating that more polyhedra help form a network structure after sulfidation treatment. When the CCO NWAs are used as the raw materials for sulfidation, the Co_xS_y NWAs maintain the nanowire structure of CCO NWAs with a rough surface (Fig. S4).

The microstructures of Co_xS_y -T NSs were further characterized by the TEM technique. As shown in Fig. 3a, b, the interlaced nanosheet structure of the as-prepared product was further revealed. The lattice fringe spacings of 0.285 and 0.181 nm in the HRTEM image are consistent well with distances of the (311) and (511) planes of Co_3S_4 , respectively (Fig. 3c). Moreover, the dim fringe spacings in the selected area electron diffraction (SAED) pattern confirm the successful transformation of Co_3S_4 (Fig. 3d). Fig. 3e–g show the elemental mapping images of Co_xS_y -T NSs, indicating that Co and S elements are uniformly distributed throughout the whole nanosheets. These results further evidence the formation of

Co_xS_y nanosheets.

XRD and Raman characterizations were further carried out to investigate the phases and compositions of the as-prepared samples. The XRD pattern of CCO NWAs shown in Fig. S5 is consistent with the standard card of $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})$ (JCPDS No. 48-0083). Following the conversion of CCO NWAs into CCO@ZIF and CCO@ZIF-T, the samples exhibit several new peaks corresponding to ZIF-67. After the sulfidation process, the CCO@ZIF-T are entirely transformed into Co_3S_4 (JCPDS 42-1448), while the CCO NWAs and CCO@ZIF are converted into Co_9S_8 (JCPDS 02-1459) (Fig. 4a). The Raman spectra of Co_xS_y -T NSs and Co_xS_y NSs are displayed in Fig. 4b. In the Raman spectrum of Co_xS_y -T NSs, the peaks centered at 462, 510, 604 and 664 cm^{-1} are assigned to the E_g , F_{2g} , F_{2g} and A_{1g} modes of Co_3S_4 , respectively, while the Co_xS_y NSs show the characteristic peaks of Co_9S_8 phase at 242, 303, 360, 474, 517 and 679 cm^{-1} [27–30]. Furthermore, XPS analysis was performed to measure the chemical states of the Co and S atoms in Co_xS_y -T NSs and Co_xS_y NSs. The Co 2p XPS spectra can be deconvoluted into two main peaks of

Figure 3 (a, b) TEM images, (c) HRTEM image, (d) the corresponding SAED pattern, and (e) scanning TEM (STEM) image of the Co_xS_y -T NSs. Elemental mapping images of (f) Co and (g) S elements.

Figure 4 (a) XRD patterns of the as-prepared Co_xS_y-T NSs, Co_xS_y NSs and Co_xS_y NWAs. (b) Raman spectroscopy of the Co_xS_y NSs and Co_xS_y-T NSs. High-resolution (c) Co 2p and (d) S 2p XPS spectra of the Co_xS_y-T NSs and Co_xS_y NSs.

Co 2p_{1/2} and Co 2p_{3/2} and the characteristic peaks of Co–S band (794.1/778.4 eV), with the satellite peaks at 803 and 786.2 eV (Fig. 4c) [31]. The high-resolution Co 2p_{1/2} and Co 2p_{3/2} spectra are further deconvoluted into two doublets at 780.5/796.1 eV and 782.3/797.5 eV, which are assigned to Co³⁺ and Co²⁺, respectively [15]. It can be found that the Co 2p_{1/2} and Co 2p_{3/2} peaks of Co_xS_y-T NSs both positively shift 0.4 eV to higher energy compared with those of Co_xS_y NSs, indicating the transfer of more electrons from Co to S atoms. Besides, the ratio of Co³⁺ to Co²⁺ in Co_xS_y-T NSs is 1.2, which is higher than 0.6 in Co_xS_y NSs. Fig. 4d illustrates the high-resolution XPS spectrum of S 2p, in which the deconvoluted peak at 168.9 eV is ascribed to the binding energy of the S–O bond, the peak at 163.6 eV to S₂²⁻, and the peaks at 161.7 and 162.9 eV to S²⁻ [32–34]. These results all demonstrate the successful transformation of CCO@ZIF-T to Co_xS_y-T NSs with high Co³⁺ ratio.

The electrochemical performances of Co_xS_y-T NSs, Co_xS_y NSs and Co_xS_y NWAs were then investigated and compared in a three-electrode system with 6 mol L⁻¹ KOH as the electrolyte. The comparative cyclic voltam-

metry (CV) plots of the three samples at 10 mV s⁻¹ in the potential range of 0–0.6 V are shown in Fig. 5a. The CV curves all exhibit a pair of redox peaks, demonstrating the reversible Faradaic behavior of Co_xS_y in alkaline electrolyte. The charge storage mechanisms can be explained by the following reactions [13]:

The typical Faradic pseudocapacitive behaviors are well retained at high scan rates, as demonstrated by the pair of redox peaks (Fig. S6). The redox peaks shift towards higher and lower potentials, respectively, with the increased scan rate, which is due to a diffusion-controlled electrochemical process. The larger CV-integrated area of Co_xS_y-T NSs compared with that of Co_xS_y NSs and Co_xS_y NWAs indicates an enhanced electrochemical capacity, which can be attributed to the higher ratio of Co³⁺ and the 3D network structure. Fig. 5b displays the galvanostatic charge/discharge (GCD) curves of Co_xS_y-T NSs, Co_xS_y NSs and Co_xS_y NWAs at 10 A g⁻¹. The GCD curves with clear battery-type nature of potential plateau regions

Figure 5 Electrochemical performance of the Co_xS_y-T NSs, Co_xS_y NSs and Co_xS_y NWAs electrodes. (a) CV curves at 10 mV s⁻¹. (b) GCD curves at 10 A g⁻¹. (c) Specific capacities at different current densities. (d) Nyquist plots. (e) Cycling performance at 10 A g⁻¹.

suggest an excellent reversibility of redox reaction. Also, the longer discharging time of Co_xS_y-T NSs than Co_xS_y NSs and Co_xS_y NWAs implies a superior energy storage property, which is consistent well with the CV results. A highest specific capacity of 351 mA h g⁻¹ at 5 A g⁻¹ is achieved for Co_xS_y-T NSs, which is 1.7 and 2.4 times that of Co_xS_y NSs (211 mA h g⁻¹ at 5 A g⁻¹) and Co_xS_y NWAs (149 mA h g⁻¹ at 5 A g⁻¹), respectively (Fig. 5c and Fig. S7). The value is also superior to those recently reported results for cobalt-based sulfide electrodes shown in Table S1. According to the GCD curves, the specific capacities for the Co_xS_y-T NSs electrode are calculated to be 351 (2635 F g⁻¹), 331 (2483 F g⁻¹), 303 (2275 F g⁻¹), 279 (2096 F g⁻¹), 240 (1800 F g⁻¹) and 182 mA h g⁻¹ (1365 F g⁻¹), corresponding to 0.66, 0.62, 0.57, 0.52, 0.45,

and 0.34 mA h cm⁻² at the current density of 5, 10, 15, 20, 30 and 50 A g⁻¹, respectively. The reduced specific capacity at larger current density is related to the shortened time for ion diffusion from the electrolyte solutions to the electrode materials. Remarkably, 51.8% of the capacity maintains at 50 A g⁻¹ for the Co_xS_y-T NSs electrode, which is higher than 13.8% for the Co_xS_y NSs and 18.6% for the Co_xS_y NWAs, indicating an excellent rate capability. The inherent electrochemical behaviors of Co_xS_y-T NSs, Co_xS_y NSs and Co_xS_y NWAs were further evaluated with EIS measurements. Fig. 5d shows their corresponding Nyquist plots, where the first intersection of the X axis (Z') in the high frequency region represents the internal resistance (R_s) of the electrode, the diameter of the semicircle refers to the charge transfer resistance (R_{ct})

of the device, and the straight line in the low frequency region indicates the diffusion resistance (R_w) [35,36]. A smaller R_s (0.44 Ω) and a lower R_{ct} (0.04 Ω) compared with those of Co_xS_y NSs ($R_s=0.51$ Ω and $R_{ct}=0.47$ Ω) and Co_xS_y NWAs electrode ($R_s=0.44$ Ω and $R_{ct}=0.06$ Ω) are observed for Co_xS_y -T NSs, indicating a more efficient reaction kinetics. Besides, the Co_xS_y -T NSs electrode shows a more vertical line in the low frequency region of Nyquist plot compared with Co_xS_y NSs and Co_xS_y NWAs, suggesting a faster ion diffusion into the electrode. Besides specific capacity and rate capability, electrochemical stability is a critical factor for evaluating the performance of the electrode materials. As depicted in Fig. 5e, the capacity of Co_xS_y -T NSs increases steadily at the initial 1000 cycles, which is attributed to the penetration of electrolyte ions into the pores to achieve a stable state. In addition, the Co_xS_y -T NSs show excellent cycling stability with 97.6% capacity retention after 7000 GCD cycles, which is better than those for Co_xS_y NSs (74.9%) and Co_xS_y NWAs (38.1%). All these results demonstrate that Co_xS_y -T NSs have prominent electrochemical performance including high capacity, good rate capability and excellent cycling stability, which can be attributed to the higher content of high-valence Co^{3+} and the 3D network structure. The higher content of Co^{3+} is beneficial for the Faradaic redox reactions, and the 3D network structure with cross-linked nanosheets can shorten the ion diffusion paths, provide abundant active sites, reduce the charge-transfer resistance, and accommodate the volume expansion. The compositional and structural advantages thus together accelerate the Faradaic reaction kinetics and improve the energy storage performance of the electrode materials.

The superior performance of Co_xS_y -T NSs was further investigated by CV measurements to understand the en-

ergy storage kinetics and mechanism. Generally, the current (i) obeys the power-law relationship with the sweep rate (v) [37,38]:

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

where a and b are adjustable values. The b values of 1 and 0.5 are indications of a capacitive nature and a semi-infinite linear diffusion, respectively. For Co_xS_y -T NSs, the b values for the cathodic and anodic peaks are 0.63 and 0.59, respectively, suggesting that a diffusion-controlled battery-type behavior dominates the energy storage process (Fig. S8). Since the charge storage of electrode materials usually consists of two components including a capacitive contribution and a diffusion-controlled effect, a more detailed kinetic analysis has been performed to understand the energy storage mechanism based on the relation [37]:

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

where $i(V)$ is the current at a constant potential V , v is the scan rate, and k_1 and k_2 are the surface capacitive and diffusion-controlled coefficients, respectively. The typical CV curve of Co_xS_y -T NSs at 5 mV s^{-1} reveals that the diffusion-controlled process contributes to 76% of the total capacity (Fig. 6a). The contributions of the two processes at higher scan rates are displayed in Fig. 6b. The results show that the diffusion-controlled contribution decreases with the increase of scan rate as a result of the shortened time for electrolyte ion diffusion. Based on the above results, the excellent electrochemical property of Co_xS_y -T NSs electrode can be attributed to the following factors. Firstly, the Co_xS_y -T NSs containing a larger ratio of high-valence Co^{3+} facilitate the Faradaic redox reactions. Secondly, the cross-linked nanosheet arrays *in-situ* grown on the highly conductive NF avoid the use of polymer binders, which enables the rapid electron

Figure 6 (a) Separation of the capacitive and diffusion-controlled currents for the Co_xS_y -T NSs at 5 mV s^{-1} . (b) The capacitive and diffusion-controlled contributions at different scan rates.

transfer and exposure of more active sites to the electrolyte. Thirdly, 3D honeycomb-like structure with large holes can provide more active sites, shorten the ion diffusion paths, and accommodate the volume expansion during the cycling, which lead to a high capacity and an outstanding cycling stability.

In order to evaluate the practical energy storage performance of the Co_xS_y -T NSs, a solid-state ASC was assembled by using the Co_xS_y -T NSs as the positive electrode, AC as the negative electrode and PVA-KOH

gel as the solid-electrolyte. The electrochemical performance of AC is shown in Fig. S9. The specific capacitance of AC is calculated to be 241 F g^{-1} at 2 A g^{-1} . According to the charge balance principle, the mass ratio of the Co_xS_y -T NSs and AC was optimized at 1:5. Fig. 7a shows the CV curves of Co_xS_y -T NSs and AC obtained at 20 mV s^{-1} with the potential window of 0–0.6 V and –1.0–0 V, respectively, illustrating a large voltage window of 1.6 V for the ASC. The CV curves of the solid-state Co_xS_y -T//AC ASC device exhibit a quasi-rectangle shape

Figure 7 Electrochemical performance of the as-assembled solid-state Co_xS_y -T NSs//AC ASC. (a) CV curves of AC and Co_xS_y -T NSs. (b) CV curves of the ASC at various scan rates. (c) GCD curves of the ASC at different current densities. (d) Specific capacitances and coulombic efficiencies at different current densities. (e) Cycling performance of the ASC at 5 A g^{-1} with an inset of the LED lights powered by two ASCs connected in series. (f) The Ragone plot of the ASC compared with the recently reported ASCs.

at various scan rates ranging from 5 to 100 mV s⁻¹, indicating a good charge balance between the positive and the negative electrodes (Fig. 7b). Also, the GCD curves exhibit a nearly symmetric behavior even at a high current density of 30 A g⁻¹, implying a prominent electrochemical reversibility of the ASC (Fig. 7c). The specific capacitance reaches 229.6 F g⁻¹ at 1 A g⁻¹ and maintains 115.1 F g⁻¹ at 20 A g⁻¹, demonstrating an excellent rate performance (Fig. 7d). Meanwhile, the coulombic efficiencies of the Co_xS_y-T NSs//AC ASC remain above 95%, which are consistent with the CV and GCD results. Furthermore, the ASC was stable after 7000 GCD cycles with 96.2% capacitance retention (Fig. 7e), demonstrating a robust durability. The Nyquist plot of the solid-state Co_xS_y-T NSs//AC ASC with a small R_s value of 0.97 Ω indicates a low R_s of the device (Fig. S10). In addition, as a demonstration of the potential for practical application, two solid-state Co_xS_y-T NSs//AC ASCs were assembled in series to power twenty-five green light emitting diodes (LEDs). As the significant parameters for evaluating the electrochemical properties of the ASCs, the energy density and power density of the device are calculated based on the GCD curves (Fig. 7f). Remarkably, the highest energy density of the ASC device reaches 81.62 W h kg⁻¹ at the power density of 0.81 kW kg⁻¹ and even maintains 41.28 W h kg⁻¹ at the power density of 23.97 kW kg⁻¹, which is superior or comparable to most of the recently reported cobalt-based ASCs, such as Co₉S₈@C//APDC HSC (58.00 W h kg⁻¹ at 1.00 kW kg⁻¹) [39], core-shell Co₃S₄//AC (54.78 W h kg⁻¹ at 0.40 kW kg⁻¹) [40], Co₃S₄/CoMo₂S₄//AC (33.10 W h kg⁻¹ at 0.85 kW kg⁻¹) [41], Ni₃S₂/CoNi₂S₄//AC (50.70 W h kg⁻¹ at 1.59 kW kg⁻¹) [42], NiCoP/carbon nanofibers (CNF)//NiCoP/CNF (36.00 W h kg⁻¹ at 1.20 kW kg⁻¹) [43], NiCo₂S₄//AC (44.80 W h kg⁻¹ at 0.79 kW kg⁻¹) [44], Co₉S₈/NiCo₂S₄//AC (56.44 W h kg⁻¹ at 0.80 kW kg⁻¹) [45], Zn-Co-S/Ni(OH)₂//Zn-Co-S/Ni(OH)₂ (74.93 W h kg⁻¹ at 0.65 kW kg⁻¹) [46], F-CoMn₂O_{4-x}//Fe₂O₃ (64.40 W h kg⁻¹ at 0.80 kW kg⁻¹) [47], NiCo₂S₄@graphene//porous carbon (PC) (43.40 W h kg⁻¹ at 0.25 kW kg⁻¹) [48], Ni-Co-S//graphene (60.00 W h kg⁻¹ at 1.80 kW kg⁻¹) [49], NiCo₂S₄/nitrogen-doped carbon foam (NCF)//ordered mesoporous (OMC)/NCF (45.50 W h kg⁻¹ at 0.51 kW kg⁻¹) [50], Cu-Co₉S₈ NTAs//AC (71.93 W h kg⁻¹ at 0.75 kW kg⁻¹) [15], CoO/Co-Cu-S//AC (90.70 W h kg⁻¹ at 0.80 kW kg⁻¹) [9], CF@NiCoZn-layered double hydroxides (LDH)/Co₉S₈-quantum dots (QD)//C (56.40 W h kg⁻¹ at 0.88 kW kg⁻¹) [51], Co₉S₈@NiCo₂O₄//AC (86.00 W h kg⁻¹ at 0.79 kW kg⁻¹) [13] and Ni-Co-S-W//AC (55.10 W h kg⁻¹ at 0.80 kW kg⁻¹) [52] (Table S2).

CONCLUSIONS

In summary, we have developed a simple TEOA-assisted MOF self-templating strategy to fabricate a unique 3D honeycomb-like network constructed with cross-linked Co_xS_y nanosheets. The introduction of TEOA in the reactions increases the content of high-valence Co³⁺ in the Co_xS_y-T NS product. Benefiting from the compositional and structural merits, the Faradaic reaction kinetics and the energy storage performance of Co_xS_y-T NSs are greatly enhanced. A high specific capacity of 351 mA h g⁻¹ at 5 A g⁻¹ and a long cyclic life with 97.6% capacity retention over 7000 cycles are achieved. Moreover, the solid-state ASC device assembled with Co₃S₄-10 NSs and AC exhibits a high energy density of 81.62 W h kg⁻¹ at the power density of 0.81 kW kg⁻¹, which is superior or comparable to most of the state-of-the-art ASCs. Also, the long-term stability with 96.2% capacitance retention is acquired after 7000 cycles. This work demonstrates a facile method to enhance the electrochemical performance of electrode materials by simultaneously modulating the oxidation state of transition metal species and constructing the 3D network structure, which is expected to shed light on the development of high-performance materials for future energy storage devices.

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

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

Haiyan Wang received her PhD degree in 2018 from Zhejiang University. From 2018 to 2019, she was a postdoctoral fellow at Zhejiang University and then she joined Zhejiang Normal University as a lecturer in 2019. Her interests mainly focus on electrode materials for energy storage and conversion devices, including supercapacitors, Zn-air batteries and water splitting.

Ying Yang is currently a graduate student under the guidance of Professor Yong Hu from the Department of Chemistry, Zhejiang Normal University. Her research interests focus on the design and manufacture of inorganic nanomaterials for supercapacitors and ionic hybrid supercapacitors.

Qinghao Li received his B. Eng degree in chemical engineering from Jiangxi University of Science and Technology and his MSc degree in chemistry from Zhejiang Normal University. His research interests include supercapacitors and electrochemical water splitting.

Yong Hu obtained his PhD degree in 2006 in inorganic chemistry from the University of Science and Technology of China. He then worked as a research fellow at Nanyang Technological University. Since 2008, he has been a full professor at the College of Chemistry and Life Science, Zhejiang Normal University, China. His current research interests are focused on the design and syntheses of nanomaterials for energy and environmental applications.

分子辅助制备富含高价态Co³⁺的三维蜂窝状钴硫化物网络结构用于高性能固态不对称超级电容器

王海燕^{1†}, 杨瑛^{1†}, 李擎昊^{1†}, 陆雯¹, 宁吉强², 钟依均¹, 张子旸², 胡勇^{1*}

摘要 过渡金属氧化态调控工程是一种很有前景的改善电极材料的氧化还原活性、增加活性位点的策略。本文提出了一种简单的三乙醇胺辅助自模板法, 制备了一种由交错钴硫化物纳米片(Co_xS_y-T NSs)组装而成的独特的三维蜂窝状网络结构。有趣的是, 我们首次发现在该体系中, 三乙醇胺可以有效地增加目标产物中的高价态Co³⁺的比例。Co_xS_y-T NSs电极具有高含量的Co³⁺和三维网络结构, 使得其在5 A g⁻¹的电流密度下表现出351 mA h g⁻¹(2635 F g⁻¹)的最大比容量和优异的循环稳定性。此外, 由Co_xS_y-T NSs和活性炭(AC)电极组装的固态不对称超级电容器在0.81 kW kg⁻¹功率密度下展现出81.62 W h kg⁻¹的高能量密度和卓越的长周期循环稳定性, 7000次循环后仍有96.2%的容量保持率。该结果证明同时调控高价态的金属物种并构筑三维网络结构是一种简单而有效的制备用于能源存储与转换的高活性电极材料的策略。