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Hierarchical Layer-By-Layer Porous $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ Arrays for All-Solid-State Asymmetric Supercapacitors

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Engineering multicomponent active materials as electrodes with rational structured design is an effective strategy to meet the high-performance requirements of supercapacitors. In this report we describe the fabrication of a hierarchical layer-by-layer porous $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ three-dimensional (3D) network on nickel foam, which shows both an excellent specific capacitance of 2984 F g^{-1} at 5 mA cm^{-2} and cyclic stability over 5000 cycles. The outstanding performance is ascribed to the distinctive self-supported structure and the synergistic effect between FeCo_2S_4 and $\text{Ni}(\text{OH})_2$. Moreover, the all-solid-state $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ /reduced graphene oxide asymmetric supercapacitor exhibits a high energy density of 64 Wh kg^{-1} at a power density of 800 W kg^{-1} and excellent cyclic stability (92.9% of capacity retention after 10000 cycles), while the output voltage can reach 1.6 V. This rational design of the layer-by-layer structured electrode provides an innovative strategy for fabricating

electrodes for the future energy storage devices.

Introduction

Along with the depleting fossil fuel and the increasing ecological challenges, high-performance energy storage devices, such as Li-ion batteries (LIBs), and metal-air batteries (MABs), are widely researched.^{1,2} Recently, supercapacitors (SCs) have attracted intense attention because of their excellent cyclic stability, rapid recharging properties and high safety compared with the LIBs, MABs and other commercial batteries.³⁻⁵ Generally, there are two kinds of SCs based on different charge storage mechanisms, faradaic supercapacitors and electrical double layer capacitors (EDLCs).⁶⁻⁹ EDLCs mainly use carbonaceous materials (graphene,¹⁰ carbon nanotubes,¹¹ porous carbon,¹² etc.) as electrodes which exhibit good cycling stability, but are usually limited by low energy density. Compared with carbonaceous materials, metal oxide electrodes (Ni,¹³ Co,¹⁴ Mn,¹⁵ Zn,¹⁶ etc.) produce faradaic pseudo-capacitances and offer considerable potential due to their higher theoretical capacities based on the redox reactions.¹⁷⁻²¹ However, metal oxide electrodes pose other challenges due to their usually poor intrinsic conductivity and unstable electrochemical performance.²² Developing new materials for SCs with optimal architecture to meet high demands of energy storage devices is therefore extremely important.

Recently, transition metal sulfides have emerged as promising materials for SCs benefiting from their high intrinsic conductivity and electrochemical activity.²³⁻²⁵ Particularly, bimetallic sulfides such as MCo_2S_4 ($\text{M} = \text{Cu}^{26}$, Ni^{27} , Zn^{28} , etc.) exhibit

higher specific capacitances and higher electrochemical activity compared with monometallic sulfides. This is mostly attributed to the availability of several oxidation states leading to reinforced synergic effect.²⁹⁻³² One example of such sulfide material, FeCo_2S_4 ($M=\text{Fe}$) has been reported as the SC electrode material due to the multiple valences of Fe versus Ni in the electrochemical reactions.²⁹⁻³¹ However, further enhancing the cycling life of bimetallic sulfides without compromising the electrochemical activity is a pressing issue.

It seems that hybrid architectures that combine sulfides with metal hydroxides is a way to solve effectively this problem.³³ $\text{Ni}(\text{OH})_2$ which has a high specific capacitance can form multiple morphologies and easily be brought to wrap other materials, making it an excellent choice for SC electrode applications.³⁴ Porous structures of bimetallic sulfides combined with deformable $\text{Ni}(\text{OH})_2$ can therefore be designed to meet the high-performance indicators of SCs.^{34, 35} However, controlling the heterogeneous growth process of the hydroxides and bimetallic sulfides is a challenge because of the distinctly different structures.³³ To the best of our knowledge, there are only very few reports on controlled synthesis of rationally designed hybrid structures that combine FeCo_2S_4 and $\text{Ni}(\text{OH})_2$ with high electrochemical performance, although FeCo_2S_4 ,²⁹⁻³¹ $\text{Ni}(\text{OH})_2$,³⁶ and metal sulfides with nickel hydroxide³⁷ have been researched separately in this context in the past.

In light of these perspectives, we report here a comprehensive study of the chemical synthesis and the structural and electrochemical properties of a new hybrid $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ layered material. Hierarchical layer-by-layer porous

$\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ 3D nanoarrays were first synthesized using a simple method. This method which is quite general integrates naturally an intersecting FeCo_2S_4 nanosheet assembly and petal-like structured $\text{Ni}(\text{OH})_2$. The resulting hybrid electrode offers excellent electrochemical performance. The all-solid-state $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2/\text{rGO}$ asymmetric supercapacitors (ASC) also deliver a considerable energy density of 64 Wh kg^{-1} at 800 W kg^{-1} and outstanding cyclic stability (92.9% of capacity retention after 10000 cycles at 6 A g^{-1}). This strategy provides an effective general method for synthesizing hierarchical multicomponent electrode materials and the excellent electrochemical properties of which are rooted in their unique structures.

Experimental section

Synthesis of FeCo_2S_4 nanosheet arrays

0.5 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 1 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 25 mL of deionized (DI) water which contained 2.5 mmol urea and 1 mmol NH_4F , with magnetic stirring for 20 minutes. The prepared solution was then poured into a 50 mL Teflon-lined autoclave with a piece of cleaned nickel foam ($2\text{cm} \times 3\text{cm}$), followed by hydrothermal treatment at 120°C for 12 h. After hydrothermal treatment, the nickel foams obtained were naturally cooled, washed with DI water, and dried in vacuum at 50°C for 10 h. The nickel foam obtained was placed into a 50 mL autoclave with 30 mL 0.1 M Na_2S solution and maintained at 120°C for 8 h. The mass loading of FeCo_2S_4 materials was 2 mg cm^{-2} .

Synthesis of $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ 3D network

1 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1 mmol urea were dissolved in 30 mL DI water and stirred for 20 minutes to get a light-green clear solution. The solution was then poured into a 50 mL autoclave which contained a nickel foam grown with FeCo_2S_4 nanosheet arrays and kept at 120 °C for various times ($t=3, 6$, and 9 h). The mass loadings of $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ with $\text{Ni}(\text{OH})_2$ growth time of 3, 6, and 9 h were about 2.6, 3.1, and 3.4 mg cm^{-2} , respectively.

Synthesis of reduced graphene oxide (rGO) negative electrode

Graphene oxide (GO) solution was obtained as trial products from Institute of Coal Chemistry, Chinese Academy of Science. The GO solution was freeze-dried and heated in argon atmosphere at 350 °C for 2 h. A mixture of GO powder, acetylene black and polytetrafluoroethylene in a mass ratio of 8:1:1 was next prepared with ethanol as solvent. The Ni foam was coated with the slurry and dried in vacuum at 50 °C for 10 h.

Materials Characterization

The morphologies of the synthesized samples were characterized using scanning electron microscopy (SEM, HITACHI SU-70, FEI QUANTA FEG 250), and transmission electron microscopy (TEM, Tecnai G2 T20). The X-ray diffraction (XRD) patterns were determined using Miniflex 600. X-ray photoelectron spectroscopic (XPS) was carried out to analyze the elemental valence in a Thermo-Scientific system (Al- $K\alpha$ radiation). The N_2 sorption isotherms were tested using Micromeritics ASAP 2020 at 77 K and calculated based on the BET method.

Electrochemical Measurements

The electrochemical tests were carried out in 6M KOH aqueous solution using CHI 660E electrochemical workstation (Shanghai, China). In a typical three-electrode system, the $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ was the working electrode, a saturated calomel electrode worked as the reference electrode and a platinum plate was used as the counter electrode. Cyclic voltammetry (CV) tests were recorded from -0.2 to 0.8 V and galvanostatic charge/discharge (GCD) tests measured from 0 to 0.45 V. The values of the specific areal capacitances (C_a) and the specific gravimetric capacitances (C_g) were calculated as follows:

$$C_a = \frac{I\Delta t}{S\Delta V}$$
$$C_g = \frac{I\Delta t}{m\Delta V}$$

in which I represents the current, Δt is the discharge time, S is the electrode area, ΔV is the voltage change excluding the IR drop in the discharge curves, and m is the mass of the active material. Electric impedance spectroscopy (EIS) was tested from 100 kHz to 0.1 Hz with an AC amplitude of 5 mV. The cycling stability was measured on a LANHE Battery Test System (Wuhan LAND electronics, China).

Assembly of all-solid-state asymmetric supercapacitors (ASCs)

The ASC devices were fabricated using $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ or FeCo_2S_4 as positive electrodes and rGO as negative electrodes, respectively. Polyvinyl alcohol (PVA)/KOH gel was the solid electrolyte and laboratory filter paper was the separator. The solid electrolyte was prepared by heating 10 mL DI water containing 1 g PVA and 1 g KOH to 95 °C for 2 h under continuous stirring. The gel was coated onto the two electrodes and the separator and then assembled into one single ASC device with the

polyester tape (PET) as outer packing. Considering the different charge storage performance of the two electrodes in ASCs, the mass ratio was determined as:

$$\frac{m_+}{m_-} = \frac{C_{g-}\Delta V_-}{C_{g+}\Delta V_+}$$

in which m_+ and m_- are the mass of active materials of the positive and negative electrodes respectively, ΔV_+ and ΔV_- are the operating potential ranges of the positive and negative electrodes respectively. The energy density (E) and power density (P) were calculated as follows:

$$E = \frac{1}{2} C \Delta V^2$$

$$P = \frac{E}{\Delta t}$$

where C, ΔV , and Δt were all the corresponding parameters of ASC devices.

Results and Discussion

The fabrication of porous $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ self-supported electrode is briefly illustrated in Fig. 1. In the first step, the metal ions in the solution combine with the OH^- group to form Fe-Co precursor nanoparticles during the hydrothermal process. The nanoparticles can adhere to the surface of the nickel foam, and serve as crystal nuclei grown further into two-dimensional nanosheets.³⁸ Next, Fe-Co precursors are transformed to FeCo_2S_4 via the hydrothermal sulfurization.³⁹ Finally, the Ni^{2+} reacted with OH^- groups to form nuclei and grew into nanosheets on the FeCo_2S_4 layer on spontaneous oriented attachment.⁴⁰ In this way a distinctive layer-by-layer structure was synthesized successfully via a self-assembly process.

The surface morphologies of the as-synthesized materials were analyzed by SEM. The ultrasmall nanosheets of FeCo_2S_4 are seen to have grown uniformly on Ni foam (Fig. 2a). The average length of the nanosheets is about 200 nm (Fig. 2b). The densely interlaced FeCo_2S_4 nanosheets assemble into 3D regular arrays which maintain the structure of the Fe-Co precursors (Fig. S1, Supporting Information).

By varying the hydrothermal reaction time (i.e. 3, 6, and 9 hours), $\text{Ni}(\text{OH})_2$ was synthesized with morphologies shown in Fig. S2 (Supporting Information), followed by detailed analyses. $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ with growth time of 6 h shows more uniform structures than that of 3 h and 9 h. Moreover, the electrode with the growth time of 6 h exhibits better electrochemical performances as well. We will therefore discuss in detail the samples with growth time of 6 h.

Fig. 2c-2f illustrate the $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ sample morphologies from different perspectives. When $\text{Ni}(\text{OH})_2$ grew on FeCo_2S_4 nanosheets, it assembled into a layered structure located on the FeCo_2S_4 nanosheets. This morphology is different from pure $\text{Ni}(\text{OH})_2$ grown directly on Ni foam (Fig. S3, Supporting Information). Fig. 2c shows that the nickel foam was uniformly covered with $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ hybrid arrays. Fig. 2d shows that the average length of the upper petal-like $\text{Ni}(\text{OH})_2$ nanosheet in the hybrid is around 1500 nm, and that the average height of the $\text{Ni}(\text{OH})_2$ nanosheet is about 1700 nm, while the FeCo_2S_4 nanosheet is 1000 nm, which could also be observed in the cross-section SEM image (Fig. 2e). For comparison, the SEM image of the cross section for the FeCo_2S_4 layer alone is shown in Fig. S4 (Supporting Information). Tilted top view SEM image shows that the surface density of the upper

Ni(OH)₂ layer is smaller than that of the lower FeCo₂S₄ layer (Fig. 2f). These two different nanosheets combine naturally to form the highly organized 3D network with plentiful voids in between the interconnected nanosheets, offering open space to facilitate the transmission of the electrolyte.

Detailed morphologies of the as-synthesized FeCo₂S₄ and FeCo₂S₄@Ni(OH)₂ were further examined by TEM. Fig. 3a depicts the morphology of the FeCo₂S₄@Ni(OH)₂ hybrid structure, and the selected regions highlighted in yellow boxes are shown in Fig. 3b and 3d. Obviously, the nanosheet with well-distributed pores about several nanometers in diameter (black circles in Fig. 3b) corresponds well with the FeCo₂S₄ nanosheets shown in Fig. S5a (Supporting Information). This morphology is mainly attributed to the liberation of gases and water during the hydrothermal sulfurization, and the pores can effectively increase the specific surface area and transmission channels of ions which could lead to a superior capacitance.^{40, 41} The high resolution TEM (HRTEM) image (Fig. 3c) shows the interplanar spacing of FeCo₂S₄ in the hybrid, i.e., 0.287 nm, which agrees well with the XRD result and the interplanar spacing of the pure FeCo₂S₄ shown in Fig. S5b. The inset of Fig. 3c shows the corresponding selected area electron diffraction (SAED) pattern. The concentric circles represent the polycrystalline nature of the FeCo₂S₄ nanosheets. Fig. 3d shows the ultrathin and smooth Ni(OH)₂ nanosheets. The HRTEM in Fig. 3e shows clear lattice fringes with interplanar spacing of 0.219 nm and 0.254 nm, which correspond with (103) and (111) planes of Ni(OH)₂. The corresponding SAED pattern (Fig. 3f) shows a

series of bright diffraction rings representing planes of (111), (103), (300), (220), (410), and (316) for Ni(OH)_2 in the hybrid structure, pointing clearly to polycrystallinity.

STEM-EDS color mapping was conducted to investigate the elements distribution in the $\text{FeCo}_2\text{S}_4@\text{Ni(OH)}_2$ hybrid nanosheets, as shown in Fig. S6. The elemental mapping shows that Fe, Co, and S are mainly distributed in the regions encircled in red, especially Fe, suggesting that these parts are the FeCo_2S_4 nanosheets. The uniform distribution of Ni indicates that the Ni(OH)_2 nanosheets tightly adhere to the FeCo_2S_4 nanosheets which accords well with the SEM images, further verifying the layer-by-layer structure of the hybrid. The nanosheets in the STEM-EDS sample was fabricated by ultrasonic vibrations. Since the large size of the Ni(OH)_2 nanosheet upon the FeCo_2S_4 layer makes it more easier to flake off from the nickel foam, the content of Ni element may be higher than other elements.

XRD patterns of FeCo_2S_4 and $\text{FeCo}_2\text{S}_4@\text{Ni(OH)}_2$ are shown in Fig. 4a. These two patterns show diffraction peaks at 21.81° , 31.09° , 37.83° , 49.73° , and 55.21° , consistent with the patterns of FeCo_2S_4 in previous reports.^{29,31} Apart from these peaks, the $\text{FeCo}_2\text{S}_4@\text{Ni(OH)}_2$ hybrid (red curve) shows diffraction peaks at 11.63° , 23.77° , 33.67° , and 35.19° , which represent the (001), (002), (110), and (111) planes of a hexagonal Ni(OH)_2 phase (JCPDS card No. 22-0444). Other peaks at 44.51° , 51.85° , and 76.37° are the pristine Ni foam phase (JCPDS card No. 04-0850). This analysis suggests the existence of FeCo_2S_4 , Ni(OH)_2 and pure

nickel foam without other redundant peaks, indicating that the hybrid is composed of FeCo_2S_4 and $\text{Ni}(\text{OH})_2$. The XRD pattern agrees well with the TEM analyses and further verify that $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ has been fabricated successfully.

N_2 sorption isotherms were recorded to further study the structural nature of the materials. As shown in Fig. 4b, isotherms with hysteresis loops can be classified as type IV, suggesting the presence of abundant mesoporous areas in the samples. The $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ hybrid gives a Brunauer-Emmett-Teller (BET) surface area of $136.9 \text{ m}^2 \text{ g}^{-1}$. This result is much higher than that of the individual components, FeCo_2S_4 ($46.7 \text{ m}^2 \text{ g}^{-1}$) and $\text{Ni}(\text{OH})_2$ ($44.4 \text{ m}^2 \text{ g}^{-1}$) (Fig. S7a, Supporting Information). The pore structure was investigated by the Barrett-Joyner-Halenda (BJH) method, which demonstrates that superior mesoporous structure in the 2-5 nm range was formed, as depicted in Fig. S7b (Supporting Information). The unique layer-by-layer structure greatly improves the specific surface area which provides more active sites for the redox reactions.³⁸

The chemical valence states of each element in the mixed-valence $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ hybrid was analyzed by XPS using Gaussian fitting. The Fe 2p spectrum (Fig. 4c) was divided into two main peaks and two satellite peaks (identified as “Sat.”). The main peaks at 711.5 and 724.3 eV correspond to Fe $2p_{2/3}$ and Fe $2p_{1/2}$ for Fe^{2+} , respectively, while the two satellite peaks disclose the existence of Fe^{3+} .^{38, 42} Fig. 4d shows the Co 2p spectrum that was divided in a similar way. The deconvolution peaks at 779.6 and 794.5 eV agree with Co^{3+} , and the peaks at 782.5

and 798.3 eV are ascribed to Co^{2+} .³⁸ Generally, the energy difference between the satellite and main peaks is significant and confirms the oxidation state of Co.³¹ If the energy difference is ~ 6.0 eV, then the cation is likely to be Co^{2+} ; while the cation is likely to be Co^{3+} , if the difference is 9-10 eV.^{43, 44} Herein, the energy gap is about 9 eV, indicating that the main cation is Co^{3+} . The S 2p spectrum (Fig. 4e) was fitted with two peaks at 161.7 and 162.7 eV indexed to S 2p_{2/3} and S 2p_{1/2}, respectively, indicating the presence of S^{2-} species.²⁹ The 163.8 eV peak represents a bond between metal and sulfur (M-S) in ternary transition metal sulfides,^{29, 31, 45} while the peak at 168.9 eV is a satellite peak. The Ni 2p spectrum (Fig. 4f) shows peaks at 855.6 and 873.2 eV, which accord with Ni 2p_{2/3} and Ni 2p_{1/2} for Ni^{2+} , respectively, along with two satellite peaks.^{40, 46, 47} The XPS results correspond well with the XRD pattern of the as-prepared $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$.

The electrochemical performance of the synthesized electrodes was tested by a three-electrode system. The materials used in this work (except for the rGO material) were all grown on nickel foam that can be directly used as electrodes. The pure nickel foam gives very small currents compared with the prepared active materials (Fig. S8, Supporting Information), so the capacitance of the nickel foam is negligible.⁴⁸ CV and GCD curves of $\text{Ni}(\text{OH})_2$ samples with different growth time were also recorded to further study their effects on electrochemical performance, which are shown in Fig. S9 (Supporting Information). The electrodes made of samples with 6 h $\text{Ni}(\text{OH})_2$ growth time shows clearly superior electrochemical properties compared with that of 3h and 9 h $\text{Ni}(\text{OH})_2$ growth time, again confirming that 6 h is the optimum growth

time for growing Ni(OH)₂.

Fig. 5a displays the CV of FeCo₂S₄@Ni(OH)₂, FeCo₂S₄ and Ni(OH)₂ at 20 mV s⁻¹. The apparent redox peaks suggest pseudocapacitive behavior for all the three electrodes. Clearly, there are differences in redox potentials because of the different polarization performances of the three electrodes.⁴⁹ Notably, FeCo₂S₄@Ni(OH)₂ possesses a larger CV area and higher redox peaks than FeCo₂S₄ and Ni(OH)₂, implying the remarkable performance of the hybrid electrode. This is mainly due to the synergy between the FeCo₂S₄ and Ni(OH)₂ nanosheets. The CV measurements of FeCo₂S₄ and Ni(OH)₂ are depicted in Fig. S10 (Supporting Information) for comparison. The mechanisms of charge storage in alkaline electrolyte for FeCo₂S₄ and NiCo₂S₄ have much in common.³⁰ And the electrochemical mechanism of Ni(OH)₂ to store charges can be attributed to the generation of NiOOH.⁵⁰ The faradaic redox reactions of the hybrid electrode can be expressed as:^{30, 38, 50}

Fig. 5b displays CV curves of FeCo₂S₄@Ni(OH)₂ electrode at different scan rates in the potential window -0.2 ~ 0.8 V. Due to the overlap of the successive redox reactions of the three kinds of metal ions, there is just one obvious couple of redox peaks.^{51, 52} Notably, with the scan rate increasing, CV curves have drastically increased areas and still show one couple of integrated faradaic redox peaks at high scan rates. This indicates high rate capability and reversibility of the electrode.^{28, 51}

Moreover, when the scan rate increases, the oxidation and reduction peaks are shifted in the direction of higher and lower potentials respectively, which is related to the internal resistance.⁵³ The CV curves can be used to analyze the electrochemical reaction kinetics. According to previous reports,^{54, 55} the relationship between electrochemical response current (*i*) and sweep rates (*v*) can be described by the following formula:

$$i = av^b \quad (4)$$

in which *a* and *b* are adjustable variables. When the redox reaction in the electrochemical process is controlled by diffusion, *b* = 0.5; while *b* = 1 when the electrochemical process is surface-controlled redox reaction.⁵³ The value of *b* therefore dictates different reaction mechanisms in the electrochemical process. Obviously, there is a linear relationship between *i* and *v*^{1/2} (Fig. S11, Supporting Information), i.e., *b* = 0.5, indicating that diffusion-controlled intercalation or deintercalation is the primary storage mechanism of this hybrid electrode.⁵⁶

The GCD curves of FeCo₂S₄@Ni(OH)₂ at various current densities with the potential window 0 ~ 0.45 V are shown in Fig. 5c. The charge curves are symmetric to the relevant discharge curves, suggesting reversible electrochemical characteristics and excellent coulombic efficiency. The nonlinear curves indicate pseudocapacitive characteristic of FeCo₂S₄@Ni(OH)₂ which accords well with the CV tests. The values of *C_a* are 9.25, to 6.69 F cm⁻² at current densities of 5 to 50 mA cm⁻² with the corresponding *C_g* values of 2984 to 2158 F g⁻¹. It can thus be noted that FeCo₂S₄@Ni(OH)₂ can still deliver excellent capacitances even at high current

densities.

Fig. 5d shows the relationships between the specific gravimetric capacitance and the current density of the $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$, FeCo_2S_4 and $\text{Ni}(\text{OH})_2$. The C_g values of the $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ are approximately 2.5 times that of pure $\text{Ni}(\text{OH})_2$ and 1.5 times that of pure FeCo_2S_4 (the GCD curves of FeCo_2S_4 and $\text{Ni}(\text{OH})_2$ are given in Fig. S12, Supporting Information). Encouragingly, the capacity retention of the $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ is 72% with the current density increasing from 5 to 50 mA cm^{-2} , implying excellent rate capability of the hybrid electrode, which is enhanced compared with FeCo_2S_4 (68%) and $\text{Ni}(\text{OH})_2$ (64.5%).

Fig. 5e displays EIS and the corresponding Nyquist plots for $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$, FeCo_2S_4 and $\text{Ni}(\text{OH})_2$ electrodes, with the inset showing the equivalent electrical circuit. The diameter of the semicircle in the Nyquist plot represents the charge transfer resistance (R_{ct}) which mostly originates from the ionic transfer between electrode and electrolyte.³⁸ The R_{ct} values of $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$, FeCo_2S_4 and $\text{Ni}(\text{OH})_2$ are 0.27, 0.67, 2.11 Ω . The intersection with the abscissa axis represents the bulk resistance (R_s) which originates from the intrinsic resistance of electrode and electrolyte.⁵⁷ The R_s values of $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$, FeCo_2S_4 and $\text{Ni}(\text{OH})_2$ electrode are 1.43, 2.31, and 1.54 Ω , respectively. The slope at the low frequency shows the Warburg impedance (W) reflecting the electrolyte diffusion efficiency. Obviously, the slope of the oblique line for the $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ hybrid is larger than those of FeCo_2S_4 and $\text{Ni}(\text{OH})_2$. The organized hybrid nanoarrays with porous structure thus provide enough space for the transmission of electrolyte ions that can lead to the

lower resistance.

The cyclic stability is a significant indicator to evaluate SCs. $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ and FeCo_2S_4 electrodes were tested through continuous GCD cycling, Fig. 5f. These two electrodes show outstanding cyclic performances as the loss of capacity is less than 10% even after 5000 cycles. However, the retention rate of the $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ electrode is 95.7% which is higher than that of FeCo_2S_4 (90.2%), indicating improved cycling stability after the growth of $\text{Ni}(\text{OH})_2$. The capacitance of the $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ electrode increased approximately 6% during the initial 700 cycles mainly because the activation of the layer-by-layer distributed materials is slower and the electrolyte needs sufficient time to permeate the FeCo_2S_4 layer which is located below the $\text{Ni}(\text{OH})_2$ layer, as reported.^{33, 58} This phenomenon can also be observed for the pure FeCo_2S_4 electrode but only in the first few cycles because the FeCo_2S_4 nanosheets are activated in a shorter time and the electrolyte permeates faster. The electrochemical performance of the $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ electrode is overall much better compared with other reported bimetallic sulfides, iron-cobalt-based composites and nickel hydroxide hybrids (Table S1, Supporting Information).

Moreover, the porous structure of $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ hybrid shows no obvious change during cycling (Fig. S13a, Supporting Information). The morphology after 5000 GCD cycles is also not much affected and maintained well. The XRD pattern shows that the crystalline structure of $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ is still retained only with the reduced peak intensities because of the electrochemical oxidation in the cycling tests,⁵⁹ Fig. S13b (Supporting Information). The $\text{Ni}(\text{OH})_2$ layer plays a buffer role

during the charging and discharging process. As a result, the cycle stability of the hybrid electrode is improved. Fig. S13c (Supporting Information) shows that the resistance of the hybrid electrode is little affected after cycling, with $R_{ct} = 0.38 \Omega$ and $R_s = 1.59 \Omega$ as compared to $R_{ct} = 0.27 \Omega$ and $R_s = 1.43 \Omega$ before the tests.

The outstanding electrochemical properties are mainly due to the following reasons: (1) FeCo_2S_4 nanosheets make a great contribution to the high capacitance because the bimetallic sulfides possess higher capacitance compared with the monometallic sulfides, double hydroxides and the corresponding oxides.³¹ (2) The $\text{Ni}(\text{OH})_2$ layer offers an increased surface area which creates more active sites, and the robust $\text{Ni}(\text{OH})_2$ layers can protect the FeCo_2S_4 layer from corrosion of the electrolyte, thus increasing the stability of the hybrids. (3) The two layered nanoarrays are not disordered accumulation but highly organized, so that the porous structure can provide enough space for transmitting ions from the electrolyte which decreases the diffusion resistance and accommodates the volume change during long-term cycling. (4) The hybrids grown directly on Ni foams efficiently avoid the “dead surface” usually encountered in conventional slurry-coating. Meanwhile, the tight adhesion between the active materials and the Ni foam contributes to the improved cycling life.³⁵

To verify the practical applications of $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ electrode, the ASC device was assembled as shown in Fig. 6a. Fig. S14 (Supporting Information) gives detailed information of the electrochemical performance for rGO. The CV curves of rGO are nearly rectangular and the GCD curves linear, reflecting the electrical double

layer capacitive properties. Fig. 6b compares the CV tests of rGO (-1.0 ~ 0 V) and $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ (-0.2 ~ 0.8 V) at 20 mV s^{-1} , and suggests that the possible voltage window may be 1.8 V. CV curves of the prepared ASC device at various voltage windows at 20 mV s^{-1} were also recorded, Fig. 6c. The obvious polarization can be observed with the voltage increasing to 1.8 V. The maximum working potential is therefore determined to be 1.6 V. CV curves of the ASC device from 0 to 1.6 V at various scan rates are depicted in Fig. 6d. The shapes of these CV curves are similar while the areas are increased, substantiating the fast charging/discharging reactions. The CV redox peaks are not obvious and in accordance with the nonlinear GCD curves, Fig. 6e, suggesting that the electric double layer capacitance and the pseudocapacitance make joint contribution in the ASC device. The C_g values of the ASC are 181 F g^{-1} at the current density of 1 A g^{-1} , with 61% capacity retention when the current density reaches up to 10 A g^{-1} (Fig. 6f). The capacitance decreases because of the redox reactions are inadequate at high current densities.²⁸

Ragone plots (Fig. 6g) of asymmetric $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2/\text{rGO}$ and $\text{FeCo}_2\text{S}_4/\text{rGO}$ devices display the relation of power density and energy density which are both crucial factors to evaluate the properties of SCs. It is worth noting that the ASC shows a high energy density of 64 Wh kg^{-1} at a power density of 800 W kg^{-1} , even retained at about 40 Wh kg^{-1} at a high power density of 10.2 kW kg^{-1} . Notably, these two electrochemical properties of the ASC device in this work are superior compared with the similar reports, such as for $\text{MnCo-LDH}@\text{Ni}(\text{OH})_2//\text{AC}$ ASC (47.9 Wh kg^{-1} at 750.7 W kg^{-1}),⁴⁰ $\text{NiCo}_2\text{S}_4@\text{Ni}(\text{OH})_2//\text{AC}$ ASC (53.3 Wh kg^{-1} at 290 W kg^{-1}),⁵⁷

MnCo₂S₄//rGO ASC (31.3 Wh kg⁻¹ at 800 W kg⁻¹),⁶⁰ NiCo₂S₄//AC ASC (17.3 Wh kg⁻¹ at 180 W kg⁻¹),⁶¹ and other reports (Table S2, Supporting Information). The cycling stability of the ASC is also an important indicator to assess its practical application. Notably, the capacitance of FeCo₂S₄@Ni(OH)₂//rGO ASC maintains about 92.9% after 10000 continuous GCD tests at 6 A g⁻¹ (black curve in Fig. 6h), indicating excellent cycling performance and reversibility. The Coulombic efficiency, η can be determined as: $\eta = t_d/t_c \times 100\%$, in which t_d and t_c are the discharge and charge times.³⁰ The Coulombic efficiency is approximately 96.3% after 10000 cycles. The two assembled all-solid-state FeCo₂S₄@Ni(OH)₂//rGO ASC devices (working areas were 2 × 2 cm) which were connected in series and fixed on the watch band make the digital watch work properly, as shown in the inset (□) of Fig. 6h. The toy motor fan, the calculator and the LEDs arranged in the pattern of SDU can also be actuated by the devices successfully (the inset (□) to (□) of Fig. 6h).

Conclusions

In summary, a hierarchical porous FeCo₂S₄@Ni(OH)₂ 3D network as a self-supported electrode for SCs has been fabricated successfully using a simple method. The bimetallic sulfide (FeCo₂S₄) generated through the ion exchange in the sulfurized process maintains the lamellar morphology of the precursor. By controlling the hydrothermal reaction time, the organized Ni(OH)₂ arrays with an appropriate surface density are then brought to grow on the FeCo₂S₄ layer to form the hybrid material. The synthesized electrode shows a high specific capacitance of 2984 F g⁻¹ at

5 mA cm⁻² and excellent cycling stability of 95.7% after 5000 cycles. This notable electrochemical performance is mainly ascribed to the sophisticated layer-by-layer structure and the mixed-valence synergistic effect between FeCo₂S₄ and Ni(OH)₂. The FeCo₂S₄@Ni(OH)₂/rGO ASC device has also been fabricated which maximum working potential can reach up to 1.6 V. This ASC device delivers a maximum energy density of 64 Wh kg⁻¹ and a maximum power density of 10.2 kW kg⁻¹ with excellent cyclic performance of 92.9% after 10000 cycles, which is much higher compared with the reported related materials. This work therefore provides an innovative method to design novel structures excellently suited for hybrid electrodes to meet the high-performance requirements of energy storage devices in the future.

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Fig. 1 Schematic illustration of the synthesis of layer-by-layer and self-supported

$\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ 3D nanosheet arrays.

Fig. 2 a, b) SEM images of FeCo_2S_4 with the inset in b) showing magnified FeCo_2S_4 arrays. c,d) SEM images of $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ arrays with the inset in d) showing magnified hybrid arrays. e) SEM image of the cross section for $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ hybrid. f) Tilted top-view SEM image of the layer-by-layer $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ hybrid arrays.

Fig. 3 a) TEM image of the nanosheets for layer-by-layer $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ hybrid. b) Magnified TEM and c) HRTEM images with the corresponding SAED pattern (inset) of FeCo_2S_4 nanosheets in the hybrid structure. d) Magnified TEM image, e) HRTEM image and f) the corresponding SAED pattern of the $\text{Ni}(\text{OH})_2$ nanosheets in the hybrid structure.

Fig. 4 a) XRD patterns of FeCo₂S₄ and FeCo₂S₄@Ni(OH)₂. b) N₂ sorption isotherms of FeCo₂S₄ and FeCo₂S₄@Ni(OH)₂. XPS spectrum of c) Fe 2p, d) Co 2p, e) S 2p, and f) Ni 2p for FeCo₂S₄@Ni(OH)₂ hybrid.

Fig. 5 a) CV curves of FeCo₂S₄, Ni(OH)₂, and FeCo₂S₄@Ni(OH)₂ electrodes at 20 mV s⁻¹. b) CV curves of FeCo₂S₄@Ni(OH)₂ electrode at various scan rates. c) GCD curves of FeCo₂S₄@Ni(OH)₂ electrode at various current densities. d) Specific capacitance of FeCo₂S₄, Ni(OH)₂, and FeCo₂S₄@Ni(OH)₂ electrodes at various current densities. e) EIS curves of FeCo₂S₄, Ni(OH)₂, and FeCo₂S₄@Ni(OH)₂ electrodes. The inset shows the electrochemical equivalent circuit. f) Cyclic stability of FeCo₂S₄ and FeCo₂S₄@Ni(OH)₂ electrodes at 50 mA cm⁻² for 5000 cycles.

Fig. 6 a) Fabrication of the $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2/\text{rGO}$ ASC device. b) CV of $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2$ and rGO electrodes at different potential windows tested at a scan rate of 20 mV s^{-1} . c) CV of the $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2/\text{rGO}$ ASC tested at various voltage windows at 20 mV s^{-1} . d) CV curves of the $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2/\text{rGO}$ ASC tested at various scan rates from 0 to 1.6 V. e) GCD curves of the $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2/\text{rGO}$ ASC at different current densities. f) Specific capacitance of the $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2/\text{rGO}$ and $\text{FeCo}_2\text{S}_4/\text{rGO}$ ASCs at different current densities. g) Ragone plots of two ASCs with comparison to similar ASCs reported previously. h) Coulombic efficiency and cyclic stability of the $\text{FeCo}_2\text{S}_4@\text{Ni}(\text{OH})_2/\text{rGO}$ ASC device at 6 A g^{-1} for 10000 cycles (the insets show the practical applications of the two ASCs connected in series on operating (□) a digital watch, (□) a toy motor fan, (□) a calculator and (□) 27 red LEDs arranged in the pattern of SDU.).

A comprehensive study of the chemical synthesis and electrochemical properties of a new FeCo₂S₄@Ni(OH)₂ layer-by-layer material for high-performance all-solid-state supercapacitor.