One-step electrodeposition fabrication of Ni_3S_2 nanosheet arrays on Ni foam as an advanced electrode for asymmetric supercapacitors

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ABSTRACT Ni_3S_2 nanosheet (NS) arrays on Ni foam were fabricated by a simple one-step electrodeposition strategy, and used as a kind of electrode material for asymmetric supercapacitors. The Ni_3S_2 NS arrays are interconnected, which can be regarded as bridges between these individual nanoparticle units. The electrochemical performances were evaluated by cyclic voltammetry and chronopotentiometry techniques in a three-electrode system. The Ni_3S_2 NS arrays display a specific capacitance of 773.6 F g^{-1} at 1 A g^{-1} , and excellent rate property of 84.3% at 10 A g^{-1} . The performance of the Ni_3S_2 NS arrays was further investigated in an asymmetric supercapacitor for potential practical application. The asymmetric supercapacitor using the Ni_3S_2 electrode and reduced graphene oxide electrode as positive and negative electrodes, respectively, exhibits an energy density of 41.2 W h kg^{-1} at 1.6 kW kg^{-1} . When up to 16 kW kg^{-1} , it holds 25.3 W h kg^{-1} . These excellent electrochemical performances are attributed to the improved electronic conductivity and rich redox reaction sites from Ni_3S_2 NS arrays. Our results indicate that the Ni_3S_2 NS arrays have great potential for supercapacitors.

Keywords: nickel subsulfide, electrodeposition, nanosheet arrays, asymmetric supercapacitors

INTRODUCTION

The consumption of petroleum and natgas fuels and emission of harmful soot gas lead to the urgent need for research and development of alternative and green energy conversion and storage devices [1–10]. Supercapacitors, an alternative efficient and emerging energy storage system, have drawn intensive attention, owing to their safe operation mode, long cycle life and fast charge rate/high power density [11–16]. Supercapacitors are generally di-

vided into two types—the pseudocapacitance and double electric layered capacitance [17–22]. Pseudocapacitance type electrode delivers a larger specific capacitance and higher energy density from the rich Faradic redox reactions of metal oxides [23–27]. To date, various transition metal materials have been extensively explored and demonstrated to be promising electrode materials for advanced supercapacitors applications [28–33]. However, the relatively poor electrochemical capacity or low conductivity of electrode materials still limits their large-scale practical applications for energy storage devices [34–36]. Thus, development of high-performance electrode materials, such as large capacitance, high electrical conductivity and good electrochemical stability, is highly demanded.

In recent years, transition metal sulfides have been widely explored and researched as the candidate of electrode materials [37–43]. Transition metal sulfides exhibit much smaller band gap compared with transition metal oxides, resulting in higher conductivity [44,45]. The substitution of sulfur, possessing the lower electronegativity, leads to a flexible phase structure, which can prevent the structure destruction and facilitate a pathway for the transport of electrons [46]. These excellent properties endow them with better and high electrical conductivity and electrochemical performance, providing the potential as electrode materials. Ni_3S_2 (nickel subsulfide) is regarded as an advanced energy storage material of supercapacitors because it possesses excellent theoretical capacity, higher electrical conductivity and abundant reserves in nature [47,48]. The micro/nanostructured Ni_3S_2 electrodes with different morphologies have been designed and fabricated through various ap-

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proaches. For example, Chen *et al.* [49] prepared self-supported Ni_3S_2 nanosheets (NSs) on Ni foam electrode through the wet-chemical method following a hydrothermal process. Yang *et al.* [50] reported the mushroom-like $\text{Ni}_3\text{S}_2/\text{Ni}$ foam through a solvothermal method. Huo *et al.* [51] prepared the NS $\text{Ni}_3\text{S}_2/\text{Ni}$ foam electrode through a high-temperature hydrothermal method.

However, the above-mentioned fabricated processes require tedious chemical treatments, complex multi-step and complicated procedures which are time-consuming and give rise to a lot of energy consumption and high fabrication cost. Furthermore, these processes are not suitable for large-scale production, limiting the industrial development of Ni_3S_2 electrode for supercapacitors. Therefore, developing a low consumption, cost-effective and easy-control route to fabricate Ni_3S_2 electrode materials and systematically studying their electrochemical capacitance is still a challenge for supercapacitors.

The electrodeposition method is widely used for the fabrication of nanomaterials, which can easily control the nanocrystal growth and their morphologies compared with chemical hydrothermal or solvothermal routes. In this work, we fabricated the interconnected Ni_3S_2 NS arrays on Ni foam through a simple one-step electrodeposition strategy. This process only includes an electrodeposition step for the electrolyte with the presence of nickel chloride hexahydrate and thiourea. The relationship between microstructures and electrodeposition cycles was investigated. The effect of different morphologies on the electrochemical performances was also discussed. The Ni_3S_2 electrode displays a specific capacitance of 773.6 F g^{-1} at 1 A g^{-1} and excellent rate performance of 84.3% at 10 A g^{-1} . The assembled NS@NF-20//rGO reveals a power density of 41.2 W h kg^{-1} at 1.6 kW kg^{-1} (25.3 W h kg^{-1} at 16 kW kg^{-1}). These results indicate that the Ni_3S_2 NS arrays will be a promising electrode material for energy conversion and storage devices.

EXPERIMENTAL SECTION

Reagents

The chemicals were used without further purification unless otherwise described. Nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), potassium hydroxide (KOH) and thiourea ($\text{CH}_4\text{N}_2\text{S}$, TU) were purchased from Tianjin Guangfu Technology Development Co. Ltd., Tianjin, China. *N*-methyl pyrrolidone (NMP) was purchased from Aladdin Biochemical Technology Co. Ltd., Shanghai, China. Poly(vinylidene fluoride) (PVDF), Ni foam, poly(vinyl alcohol) (PVA), acetylene black (AB) and the cel-

lulose separator were bought from Taiyuan Liyuan Lithium Technology Co., Ltd., Taiyuan, China. Reduced graphene oxide (rGO) was purchased from The Sixth Element Materials Technology Co. Ltd., Changzhou, China. De-ionized water ($18.3 \text{ M}\Omega \text{ cm}$) was obtained by Milli-Q water purification system.

Fabrication of Ni_3S_2 electrodes

One-step electrodeposition of the Ni_3S_2 electrodes was carried out on a CHI660D electrochemical instrument (CH Instruments, Shanghai, China). The procedure was controlled through a CH Instruments Model software within the three-electrode cell system at 15°C . The silver/silver(I) chloride (Ag/AgCl) with saturated KCl solution, platinum plate ($20 \text{ mm} \times 20 \text{ mm} \times 0.2 \text{ mm}$) and 100 mL of de-ionized water containing 2 mmol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 150 mmol $\text{CH}_4\text{N}_2\text{S}$ were used as the reference electrode, counter electrode and electrolyte, respectively. A Ni foam ($10 \text{ mm} \times 20 \text{ mm} \times 1 \text{ mm}$, more details are shown in Table S1 and Fig. S1, Supplementary information) was cleaned by sonication in 3 mol L^{-1} HCl, and then washed in ethanol and de-ionized water. The cleaned Ni foam was adopted as the work electrode. Cyclic voltammetry (CV) technique was carried out to fabricate Ni_3S_2 electrode at a 10 mV s^{-1} sweep rate for 10, 20 and 40 sweep cycles within a potential window of -1.2 to 0.2 V in the deposition bath. These obtained Ni_3S_2 electrodes were washed several times with de-ionized water, and then dried at 40°C in vacuum for 2 h. These Ni_3S_2 samples obtained by the 10, 20 and 40 cycles were named as NS@NF-10, NS@NF-20 and NS@NF-40, respectively. The mass loadings of the NS@NF-10, NS@NF-20 and NS@NF-40 electrode were ca. 0.6, 1.2 and 3.5 mg cm^{-2} , respectively.

Materials characterization

X-ray diffraction (XRD) patterns of Ni_3S_2 NS arrays on Ni foam were measured using a diffractometer equipped with Rigaku RAD-3C (Cu $\text{K}\alpha$, $\lambda = 1.5405 \text{ \AA}$, 35 kV, 20 mA, 2-Theta angles: 10° – 70°). The morphologies and structures were examined using a JEOL S-4800 field-emission scanning electron microscope (FE-SEM) under the operating voltage of 3.0 kV, and a JEOL JEM-2100F transmission electron microscope (TEM) under the accelerating voltage of 200 kV. Energy dispersive spectrometer (EDS) was also carried out using the JEOL S-4800 equipment with an EDS detector (Oxford). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALB-MKII250 photoelectron spectrometer by a monochromatic radiation with Al $\text{K}\alpha$ source at 150 W.

Electrochemical measurements

Electrochemical measurements were performed on a CHI660D instrument at 15°C. These Ni₃S₂ NS arrays on Ni foam electrodes (NS@NF-10, NS@NF-20 and NS@NF-40) were directly used as the working electrodes. Platinum plate (20 mm×20 mm×0.2 mm) was the counter electrode. Hg/HgO (1 mol L⁻¹ KOH) was the reference electrode. The 2 mol L⁻¹ KOH was used as the electrolyte for this three-electrode cell. CV, chronopotentiometry (CP), cycling galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) were executed to evaluate their electrochemical performances.

The specific capacitances of these electrodes and NS@NF-20//rGO asymmetric supercapacitor were calculated based on the GCD curves at various current densities using the following Equation (1) [52]:

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

where C is the specific electrochemical capacitance (F g⁻¹); I is the electric current (A) for the charge/discharge measurement; Δt is the time (s) during discharge measurements; m is the mass (g) of active material; ΔV is the window voltage (V) in the CP measurement.

The NS@NF-20//rGO asymmetric supercapacitor was assembled using NS@NF-20 as positive electrode, rGO as negative electrode and PVA/KOH gel as electrolyte on a CHI660D workstation system. The fabrication details of the rGO electrode were given in the Supplementary information (Page S3). 4.0 g of PVA powder was dissolved into 40 mL de-ionized water under vigorous magnetic stirring at 90°C. After 1 h, 4.5 g KOH powder was added into the as-dissolved PVA solution until the mixture turned into the PVA/KOH gel. The NS@NF-20 electrode, the rGO electrode and the cellulose separator (more details are shown in Table S2) were immersed into the as-prepared PVA/KOH gel for 10 min. Then, they were taken out from the PVA/KOH gel and assembled to the NS@NF-20//rGO asymmetric supercapacitor. It was tested on a CHI660D workstation.

The energy densities and power densities of the NS@NF-20//rGO asymmetric supercapacitor were calculated based on the following Equations (2) and (3):

$$E = \frac{1}{7.2} C \Delta V^2, \quad (2)$$

$$P = \frac{3600E}{t}, \quad (3)$$

Where E is the energy density (W h kg⁻¹); P is the power density (W kg⁻¹); C is the specific capacitance (F g⁻¹) of the Ni₃S₂@Ni₃S₂//rGO asymmetric supercapacitor; ΔV is

the window voltage (V); t is the discharging time (s) during charge/discharge measurements.

RESULTS AND DISCUSSION

One-step electrodeposition strategy for the fabrication of Ni₃S₂ electrodes is illustrated in Fig. 1. This electrodeposition strategy was executed in the three-electrode cell system as described in EXPERIMENTAL SECTION. CV was performed to deposit the Ni₃S₂ NS arrays on the surface of Ni foam substrate within -1.2 to 0.2 V at 10 mV s⁻¹ for 10, 20 and 40 sweep cycles in the deposition bath. The relevant chemical reactions involved in the electrodeposition process can be expressed as following Equation (4) [53,54]:

The CV curves of these samples in the electrodeposition process are shown in Fig. S2. The Ni foam substrates are uniformly covered with the Ni₃S₂ NS arrays. The different microstructures and morphologies of electrodes can be achieved at different sweep cycles (10, 20, 40 cycles).

The crystal phase and composition of Ni₃S₂ electrode were characterized through XRD measurements and the XRD patterns are shown in Fig. 2. Two diffraction peaks located at 45.1° and 52.5° are the characteristic peaks of Ni foam (marked by rectangular frames). Another eight diffraction peaks located at 21.8°, 31.2°, 37.7°, 38.2°, 44.4°, 49.7°, 50.1°, 55.2° and 55.4° are the characteristic peaks of the Ni₃S₂ NS arrays (marked by asterisks), which match well with the standard Ni₃S₂ phase (JCPDS card No. 44-1418). These diffraction peaks correspond to the reflections of (101), (110), (003), (002), (113), (211) (122) and (300) planes of the Ni₃S₂ NS arrays, respectively. Notably, these diffraction peaks of the Ni₃S₂ NS arrays are weak, indicating the low crystallinity of the Ni₃S₂ NS arrays [55].

SEM images of these different morphological Ni₃S₂ electrodes (NS@NF-10, NS@NF-20 and NS@NF-40) are shown in Fig. 3. Fig. 3a–d show the SEM images of the NS@NF-10 electrode. The panorama image of NS@NF-10 (Fig. 3a) shows almost the same surface morphology as pure Ni foam (Fig. S1), and irregular Ni₃S₂ nanoparticles are grown on the surface of Ni substrate (nucleation, Fig. 3b and c). From the high magnification SEM image (Fig. 3d), it is observed that some cross-linked and smaller NSs are formed and grown on the Ni foam substrate. These sparse Ni₃S₂ nuclei on the surface of current collector substrate display an embryonic form for the honeycomb-like Ni₃S₂ NSs.

The SEM images of NS@NF-20 are shown in Fig. 3e–h. The surface of Ni foam is different from that of NS@NF-

Figure 1 Schematic illustrations of the electrodeposition process for the Ni_3S_2 NS arrays on Ni foam substrate.

Figure 2 XRD patterns of the Ni_3S_2 NS arrays on Ni foam. The diffraction peaks of Ni_3S_2 are marked by asterisks and those of Ni foam are marked by rectangular frame. Several vertical lines at the bottom are the standard diffraction peaks of Ni_3S_2 from JCPDS card No. 44-1418.

10. The enlarged SEM image in Fig. 3g clearly shows that the Ni_3S_2 NSs become much denser and larger to form the honeycomb-like Ni_3S_2 NS arrays structure, which indicates the growth of Ni_3S_2 from nanoparticles to NSs on Ni foam. Fig. 3h shows high-magnification SEM image of NS@NF-20. The honeycomb-like Ni_3S_2 nanostructure is composed of interconnected Ni_3S_2 NSs, which can be regarded as the bridges between the individual nanoparticle units, beneficial for improving structural stability of the NS arrays and enhancing the electrochemical performances. These Ni_3S_2 NSs possess a relatively uni-

form thickness of ~ 50 nm. The high magnification SEM image shows that the rough surface of Ni_3S_2 NSs is covered with smaller Ni_3S_2 NSs. The sufficient open space between Ni_3S_2 NSs is also regarded as the electrolyte ion reservoir, which will be of benefit to the fast diffusion and transfer of ions and electrons.

With the prolongation of the CV sweep cycles to 40, the surface of Ni foam with Ni_3S_2 coating (Fig. 3j) is getting rougher than those with less cycling time for electrodeposition (10 and 20 cycles). The transformation (from NS to microsphere) of the surface morphology in the NS@NF-40 electrode is observed in Fig. 3k. To gain more detail about the microsphere, Fig. 3l displays a high-resolution SEM image which presents the presence of Ni_3S_2 NSs on the surface of these microspheres. It is further observed that the Ni_3S_2 microspheres consist of aggregates of many Ni_3S_2 NSs because the Ni_3S_2 NSs become a larger and denser structure on surface of Ni foam substrate with the increase of CV sweep cycles. The Ni_3S_2 microsphere growth possibly originates from the nuclei on surface of Ni_3S_2 NSs. These microspheres result in decreased the space between interconnected Ni_3S_2 NSs.

The structure and morphology of Ni_3S_2 NSs are also characterized by TEM. Fig. 4 shows the typical TEM images of Ni_3S_2 NSs scratched from the NS@NF-20 electrode. Fig. 4a displays the overall contour of Ni_3S_2 NSs with bending and wrinkles. The enlarged TEM images in Fig. 4b and c reveal that the thickness of Ni_3S_2 NSs is ca. 30 nm. It appears that Ni_3S_2 NSs are also wrapped with tiny NSs (the regions marked by red rectangles and red

Figure 3 SEM images of Ni_3S_2 NS arrays on Ni foam with different morphologies by altering the sweep cycles in the electrodeposition process. (a–d) Low- and high-magnification SEM images of Ni_3S_2 NS arrays after 10 cycles (NS@NF-10), scale bars = 20 μm , 10 μm , 1 μm and 200 nm, respectively. (e–h) Low- and high-magnification SEM images of Ni_3S_2 NS arrays after 20 cycles (NS@NF-20), scale bars = 30 μm , 10 μm , 1 μm and 100 nm, respectively. (i–l) Low- and high-magnification SEM images of Ni_3S_2 sample after 40 cycles (NS@NF-40), scale bars = 20 μm , 10 μm , 1 μm and 200 nm, respectively.

dashed lines show the core-shell structure). The tiny Ni_3S_2 NSs are homogeneously distributed on the surface of large-sized Ni_3S_2 NSs to form $\text{Ni}_3\text{S}_2@\text{Ni}_3\text{S}_2$ core-shell structure, which is consistent with the corresponding SEM images. This $\text{Ni}_3\text{S}_2@\text{Ni}_3\text{S}_2$ core-shell structure can increase the surface area more than single Ni_3S_2 NSs, which shortens the distance of ion/electron transportation and enhance the electrochemical performance. As can be observed in the high magnification TEM image of Ni_3S_2 NSs (Fig. 4d), the tiny Ni_3S_2 nuclei are formed and anchored over the surface of Ni_3S_2 NSs (the regions marked by blue circles). These nuclei play a vital role in the growing process for Ni_3S_2 NS arrays and the $\text{Ni}_3\text{S}_2@\text{Ni}_3\text{S}_2$ core-shell structure. The tiny Ni_3S_2 nuclei have a narrow distribution in size of ca. 2 nm to 5 nm. Fig. 4e and f display the high-resolution TEM (HRTEM) images of Ni_3S_2 NSs. The characteristic lattice spacing of Ni_3S_2 NSs are measured to be 2.87, 4.06 and 2.38 Å, which well match with the spacing of the (110), (101) and (003) planes of Ni_3S_2 NSs, respectively. Inset in Fig. 4f shows

corresponding selected area electron diffraction (SAED) patterns of Ni_3S_2 NSs, revealing that the diffraction rings are well indexed as those of the (110), (202) and (211) planes of the Ni_3S_2 NSs, respectively. These characterizations are well consistent with XRD patterns.

The electrodeposition growth of Ni_3S_2 can be divided into two steps: the initial Ni_3S_2 nucleation and the subsequent growth of the individual Ni_3S_2 nucleus. At first, the formation of tiny Ni_3S_2 nuclei, also called as seed crystals, occurs on surface of Ni foam substrate with high density, which play a vital role in growth of Ni_3S_2 NS arrays. Subsequently, as the CV sweep cycle increases, the Ni_3S_2 nuclei grow to Ni_3S_2 NS arrays. When increasing the CV sweep cycles to 40, the Ni_3S_2 microspheres are assembled from the dense Ni_3S_2 NSs, and Ni foam is almost fully coated and clad by denser Ni_3S_2 NSs.

EDS mappings of the Ni_3S_2 sample are shown in Fig. 5 and the corresponding mappings of Ni and S clearly indicate the homogeneous distribution of Ni and S elements. To further analyze their elemental compositions

Figure 4 (a–d) The typical TEM images with different resolution of the Ni_3S_2 NSs, scale bars = 100, 50, 50 and 20 nm, respectively. (e, f) High-resolution TEM images of the Ni_3S_2 NSs, scale bar = 5 nm. The inset shows the corresponding selected area electron diffraction (SAED) pattern of the Ni_3S_2 NSs. (The regions marked by red rectangles and red dashed lines show the core-shell structure; the regions marked by blue circles show some nuclei on the surface of NS).

and valence states, NS@NF-20 electrode was characterized by XPS. Fig. 6a displays the full survey XPS spectrum of the NS@NF-20 electrode, which shows the elements of S and Ni. Other peaks of the C, N and O elements are most likely from the air [56,57]. Fig. 6b shows the Ni spectrum of NS@NF-20 electrode, which consists of two peaks at 856.3 and 874.0 eV with a spin orbit energy separation of 17.7 eV, corresponding to Ni $2p_{3/2}$ and Ni $2p_{1/2}$ components of the Ni^{2+} in Ni_3S_2 , respectively [58].

Figure 6 (a) XPS full spectra of Ni_3S_2 NS arrays. (b) Ni 2p spectrum. (c) S 2p spectrum.

Figure 5 (a) SEM image of the Ni_3S_2 NS arrays. (b) Overlapped EDS mapping of the Ni_3S_2 sample taken from the rectangular frame in (a). (c) S mapping. (d) Ni mapping.

Two peaks located at 861.9 and 880.2 eV are the satellite (Sat.) peaks of the Ni $2p_{3/2}$ and Ni $2p_{1/2}$, respectively [59]. Fig. 6c displays S spectrum of NS@NF-20 electrode. The S peaks observed at 162.7 and 164.0 eV correspond to S $2p_{1/2}$ and S $2p_{3/2}$, respectively, consistent with the nickel subsulfide in the previous reports [58–60]. The S peak at 168.7 eV is attributed to the presence of sulfate radical ion, indicating that partial S^{2-} are likely oxidized to sulfate in air [38,60].

Typical CV curves of the NS@NF-20 electrode within -0.2 to 0.9 V at various sweep rates in the range of 5 – 100 mV s^{-1} are shown in Fig. 7a. CV curves of this NS@NF-20 electrode with a couple of redox peaks are attributed to reversible Faradic behavior of electrode in alkaline electrolyte as expressed in Equation (5) [61]:

The shape of CV curves of NS@NF-20 electrode almost does not change when the sweep rate increases, indicating

Figure 7 (a) CV curves of NS@NF-20 electrode at various sweep rates. (b) GCD curves of NS@NF-20 at various current densities. (c) Comparative CV curves of NS@NF-10, NS@NF-20 and NS@NF-40 electrodes at a sweep rate of 5 mV s^{-1} . (d) GCD curves of the three electrodes at a current density of 1 A g^{-1} . (e) The specific capacitances of the three electrodes as a function of the current density. (f) Nyquist plots of the three electrodes. The inset shows the enlarged plots in the high frequency part.

that the NS@NF-20 electrode possesses low resistance between electrode and electrolyte, fast Faradic reactions as well as good rate capability [62]. The anodic peaks of CV curves shift to negative potential and the cathodic peaks shift to positive potential. The absolute values of the response currents of the anodic and cathodic peaks correspondingly increase with the increase of sweep rate. These results may be owing to the polarization effect.

Fig. 7b displays the GCD curves of NS@NF-20 electrode at $1\text{--}10 \text{ A g}^{-1}$. According to the Equation (1), the specific capacitances of NS@NF-20 are calculated to be 773.6, 755.2, 734.4, 676.8, 662.4 and 652.5 F g^{-1} at 1, 2, 4, 6, 8 and 10 A g^{-1} , respectively. Above calculated specific capacitances of NS@NF-20 electrode are shown in Fig. 7e. The NS@NF-20 electrode possesses a larger specific capacitance compared with the NS@NF-10 and NS@NF-40 electrodes. The pure Ni foam as working electrode is also tested at the same condition, indicating a negligible capacitance of Ni foam (Fig. S3).

To understand the effect of electrodeposition sweep cycles on the electrochemical performances, the NS@NF-10 and NS@NF-40 electrodes were also investigated by CV and CP tests, and compared with the NS@NF-10 electrode. Fig. 7c shows the CV curves of the three electrodes at 5 mV s^{-1} . We can observe that all the CV curves

have redox peaks, but the response currents of redox peaks and the enclosed areas of CV curves are different with increase of electrodeposition cycles. The NS@NF-20 electrode has the highest response current and the largest CV enclosed area, indicating a higher specific capacitance of NS@NF-20 electrode than that of the NS@NF-10 and NS@NF-40 electrodes. Figs S4 and S5 show the integrated CV curves of NS@NF-10 and NS@NF-40 electrodes at various current densities.

Fig. 7d displays the discharging curves of the NS@NF-10, NS@NF-20 and NS@NF-40 electrodes at 1 A g^{-1} . These discharging curves display two distinct voltage plateaus, which are attributed to the pseudocapacitive behavior arising from reversible Faradic redox. The discharge curves do not form a straight line, owing to their charge and discharge plateaus. The integrated GCD curves of NS@NF-10 and NS@NF-40 electrodes at various sweep rates are shown in Figs S6 and S7. From the GCD curves, the discharge time of NS@NF-20 electrode is 386.8 s, which is larger than those of NS@NF-10 (204.7 s) and NS@NF-40 electrodes (144.4 s), indicating that the specific capacitance of NS@NF-20 electrode (773.6 F g^{-1}) is larger than those of NS@NF-10 (409.4 F g^{-1}) and NS@NF-40 (323.2 F g^{-1}) electrodes at 1 A g^{-1} . For comparison, the specific capacitances of the

three electrodes at 1, 2, 4, 6, 8 and 10 A g⁻¹ are shown in Fig. 7e, which indicates that the specific capacitances of NS@NF-20 electrode are larger than those of NS@NF-10 and NS@NF-40 electrodes at 1, 2, 4, 6, 8 and 10 A g⁻¹. The specific capacitance of NS@NF-20 electrode is superior to those of the nickel sulfide based materials in previously reported literatures (Table S3).

Fig. 7e also displays the excellent rate capability of NS@NF-10, NS@NF-20 and NS@NF-40 electrodes. It is observed that with increasing from 1 to 10 A g⁻¹, the specific capacitance decreases from 406.3 to 250 F g⁻¹ for NS@NF-10 electrode, from 773.6 to 652.5 F g⁻¹ for NS@NF-20, from 323.2 to 170.0 F g⁻¹ for NS@NF-40. When up to 10 A g⁻¹ from 1 A g⁻¹, the specific capacitance of NS@NF-20 electrode still retains 773.6 F g⁻¹ with the good rate capacity of 84.3%. Rate capacities of the NS@NF-10 and NS@NF-40 electrodes are 61.5% and 52.6%, respectively, indicating the Ni₃S₂ electrode possesses high reversibility of the redox charge storage reactions. Furthermore, the volumetric capacitances of the NS@NF-20 electrode were also calculated (Fig. S8). The cycling stability is also an important parameter for supercapacitors. Fig. S9 shows the cycling GCD measurement of NS@NF-20 electrode, which retains 81.7% of initial capacitance after 5,000 cycles at 5 A g⁻¹, indicating a fine long-term stability of NS@NF-20 electrode.

Fig. 7f displays the Nyquist plots of NS@NF-10, NS@NF-20 and NS@NF-40 electrodes in 0.01 Hz to 100 kHz. EIS spectra are approximately divided into two regions: the semicircles in the high-frequency range and the straight lines in the low-frequency range. In the high-frequency part, the intercept at the real axis (Z') represents the intrinsic resistance of electrodes (R_s). R_s consists of intrinsic resistance of active material, ionic resistance of electrolyte as well as contact resistance between active material and Ni foam substrate [63]. The inset in Fig. 7f shows that the values of R_s of NS@NF-10, NS@NF-20 and NS@NF-40 electrodes are 0.86, 0.89, and 0.93 Ω , respectively. These Ni₃S₂ electrodes exhibit low intrinsic resistance, indicating the good conductivity of the Ni₃S₂ NS arrays with excellent pathways for electron transport. In the high-frequency range, a semicircle is observed and its diameter represents charge-transfer resistance (R_{ct}) between electrode and electrolyte associated with reversible Faradaic reactions [53]. The diameter of Nyquist plot of NS@NF-20 electrode is smaller than that of NS@NF-10 and NS@NF-40 electrodes, indicating the fast charge-transfer kinetics of NS@NF-20 electrode. In the low-frequency range, the slope indicates the diffusion behavior of electrode materials. The bigger the linear

slope, the faster it is for the diffusion of ion/electron. These large-slope lines reveal that the Ni₃S₂ electrodes have fast electron transport performances due to their high conductivity. The results based on EIS analysis show that the Ni₃S₂ NS arrays possess high ionic and electronic conductivities, which can effectively reduce resistances and provide a highway for ion and electron transfer in reversible Faradaic reactions.

To further evaluate the practical application performances of Ni₃S₂ NS arrays, the NS@NF-20//rGO asymmetric supercapacitor is assembled, and a diagram of its structure is shown in Fig. 8a. Fig. 8b shows a series of CV curves of NS@NF-20//rGO asymmetric supercapacitor under various voltage windows from 0–1.0 V to 0–1.8 V at 5 mV s⁻¹. The stable window voltage can reach 1.6 V for the NS@NF-20//rGO asymmetric supercapacitor. When window voltage increases to 1.8 V, the polarization of NS@NF-20 electrode leads to the instability for the device [45]. Therefore, a potential of 0–1.6 V is selected as the window voltage to investigate further electrochemical performances of the NS@NF-20//rGO device. Fig. 8c displays the CV curves of NS@NF-20//rGO asymmetric supercapacitor at sweep rates from 10 to 100 mV s⁻¹ within 0–1.6 V. The NS@NF-20//rGO asymmetric supercapacitor exhibits a pair of non-rectangular peaks in CV curves, which indicates a characteristic of pseudocapacitance originating from the reversible Faradic reactions. Up to 100 mV s⁻¹, CV curves of the NS@NF-20//rGO asymmetric supercapacitor still retain markedly redox Faradic reaction peak because the large surface area of the electrode provides the pathway for ion and electron transport.

Fig. 8d displays the GCD curves of the NS@NF-20//rGO asymmetric supercapacitor at 2, 4, 8, 12 and 20 A g⁻¹. From these GCD curves, high coulombic efficiency of NS@NF-20//rGO asymmetric supercapacitor is observed, which indicates the good electrochemical performance. Fig. 8e displays the specific capacitances of NS@NF-20//rGO as a function of the current densities. The specific capacitance of NS@NF-20//rGO asymmetric supercapacitor reaches 115.6 F g⁻¹ at 2 A g⁻¹. With up to 20 A g⁻¹, it still retains 71.2 F g⁻¹, suggesting the good rate capability for NS@NF-20//rGO asymmetric supercapacitor. The inset in Fig. 8e shows that two devices in series light up the red light-emitting diode (LED) for five minutes, suggesting the potential application of this NS@NF-20//rGO device.

The energy and power densities are closely related to the practical application for energy conversion and storage devices. The energy and power densities of NS@NF-

Figure 8 Electrochemical test of the NS@NF-20//rGO asymmetric supercapacitor. (a) Schematic illustration of the assembled NS@NF-20//rGO asymmetric supercapacitor. (b) CV curves at different voltages windows. (c) CV curves at various sweep rates. (d) GCD curves at different current densities of 2–20 A g^{-1} . (e) The specific capacitances at different current densities of 2–20 A g^{-1} . The inset shows a digital photograph of two NS@NF-20//rGO asymmetric supercapacitors in series lighting up a red light-emitting diode (LED). (f) Ragone plots of the NS@NF-20//rGO asymmetric supercapacitor.

20//rGO asymmetric supercapacitor are evaluated based on the GCD data using the Equations (2) and (3). Fig. 8f shows Ragone plot of NS@NF-20//rGO asymmetric supercapacitor, which exhibits its calculated energy and power densities based on GCD data. The NS@NF-20//rGO asymmetric supercapacitor shows the excellent energy density (41.2 W h kg^{-1} at 1.6 kW kg^{-1}). When its power density is up to 16 kW kg^{-1} , it still maintains 25.3 W h kg^{-1} . The high energy and power densities are attributed to the good rate properties of NS@NF-20 and

rGO electrode materials. This NS@NF-20//rGO asymmetric supercapacitor delivers superior energy density compared with the transition metal sulfide electrode materials in the previous reports, such as the nano-triangular $\text{Ni}_3\text{S}_2\text{@CoS//AC}$ (28.4 W h kg^{-1} at 0.134 kW kg^{-1}) [61], CoNi_2S_4 NSs//AC (33.9 W h kg^{-1} at 0.409 kW kg^{-1}) [62], the clustered network-like $\text{Ni}_3\text{S}_2\text{-Co}_9\text{S}_8\text{//AC}$ (17 W h kg^{-1} at 1.400 kW kg^{-1}) [64], the cliff-like $\text{NiO/Ni}_3\text{S}_2\text{//AC}$ ($43.99 \text{ W h kg}^{-1}$ at 0.230 kW kg^{-1}) [65], the porous $\text{Ni}_3\text{S}_2\text{//AC}$ (41.8 W h kg^{-1} at 0.155 kW kg^{-1}) [66],

Ni₃S₂/MWCNT-NC//AC (19.8 W h kg⁻¹ at 0.798 kW kg⁻¹) [67] and Ni₃S₂/CNFs//CNFs (25.8 W h kg⁻¹ at 0.425 kW kg⁻¹) [68] (the details are shown in Table S4). This NS@NF-20 with outstanding electrical properties will be a good potential material for the asymmetry supercapacitors.

CONCLUSIONS

Ni₃S₂ NS arrays on Ni foam have been devised and fabricated using one-step electrodeposition strategy. These Ni₃S₂ NS arrays are interconnected and deposited on the current collector of Ni foam. This cross-linked NS array structure is highly beneficial to the transport of ions and electrons between electrode and electrolyte during the charge/discharge process. These Ni₃S₂ NS arrays as a novel electrode material possess excellent electrochemical performances for supercapacitors. The Ni₃S₂ NS arrays electrode (NS@NF-20) shows 773.6 F g⁻¹ at 1 A g⁻¹ and an 84.3% rate capability from 1 to 10 A g⁻¹, and achieves a cycling retention of 81.7% over 5,000 cycles. The assembled NS@NF-20//rGO asymmetric supercapacitor device can reach a 0–1.6 V stable voltage window. This NS@NF-20//rGO device also exhibits a maximum energy density of 41.2 W h kg⁻¹ as well as a maximum power density of 16 kW kg⁻¹. These good performances endow the Ni₃S₂ NS arrays electrode material with a more practical and potential prospects for the asymmetric supercapacitors. It is suggested that the Ni₃S₂ NS arrays electrode material is a new candidate for the commercial application of supercapacitors.

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Author contributions Xu J conceived the idea of this study and revised the paper. Sun Y performed the synthesis of the electrode and prepared the manuscript. Liu X revised the paper and coordinated this work. The paper was discussed through contributions of all authors. All authors have given approval to the final version of the paper.

Conflict of interest The authors declare no conflict of interest.

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

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一步电沉积法制备 Ni_3S_2 纳米片阵列作为高性能非对称超级电容器的研究

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摘要 本文采用一步电沉积法制备了 Ni_3S_2 纳米片阵列超级电容器电极。 Ni_3S_2 纳米片彼此互连能够为电子传导提供快速通道, 有利于电子与离子传输, 提供了丰富的赝电容反应位点。采用不同电沉积次数探究了不同负载量的 Ni_3S_2 对其电化学性能的影响。性能最好的 Ni_3S_2 电极在 1 A g^{-1} 下展示出 773.6 F g^{-1} 的单位比电容, 在 10 A g^{-1} 时具有84.3%的优异倍率性能。组装的非对称超级电容器($\text{Ni}_3\text{S}_2/\text{rGO}$)表现出优良的使用性能。这些结果表明了所制备的 Ni_3S_2 超级电容器电极材料具有广阔的应用前景。电沉积法控制 Ni_3S_2 负载量的策略能够为电极材料制备提供一种新思路。