SPECIAL TOPIC: Graphene Oxides towards Practical Applications

A generalized one-step *in situ* formation of metal sulfide/reduced graphene oxide nanosheets toward high-performance supercapacitors

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ABSTRACT Metal sulfides are promising candidates for supercapacitors, but their slow reaction kinetics hinders their electrochemical performance. Large electrochemical surface area and combination with conductive carbon are potential methods to improve their capacitive performance. However, seeking for a generalized and simple approach to prepare two-dimensional composites of metal sulfide and conductive carbon for supercapacitors is challengeable. Herein, a generalized and facile one-step pyrolysis method was designed for *in situ* growth of cobalt nickel sulfides (CoNi₂S₄) on reduced graphene oxide (rGO) nanosheets (CoNi₂S₄/rGO) under mild conditions. The as-prepared CoNi₂S₄/rGO materials possess the nanoparticles-on-nanosheets structure, which is effective to provide a myriad of active sites and optimized electron/ion diffusion pathway. Benefiting from those advantages, the resultant CoNi₂S₄/rGO electrodes exhibit impressed specific capacitances of 1526 and 988 F g⁻¹ at 2 and 20 A g⁻¹, respectively. The supercapacitors based on CoNi₂S₄/rGO showcase an operation potential window of 1.6 V, and energy density of 54.8 W h kg⁻¹ at the power density of 798 W kg⁻¹. The capacitance retention of the supercapacitor is about 93.7% after 8000 cycles at 3 A g⁻¹. Moreover, a series of metal sulfide/rGO hybrids are obtained by this generalized strategy, which could be extended to construct electrode materials for various energy devices.

Keywords: metal sulfide, reduced graphene oxide, *in situ* growth, two-dimensional, supercapacitors

INTRODUCTION

Developing sustainable energy resources is one of the

significant channels to meet the challenge of fossil fuel overconsumption [1–4]. Supercapacitors (SCs) have attracted extensive attentions due to their special advantages including high security, low cost, high power density and long discharging/charging cycles [5–8]. However, the feature of low energy density restricts further development of SCs [9–11]. Adopting high capacitance materials is an effective way to expanding energy density of SCs according to the equation $E=0.5CV^2$, where C and V are the specific capacitance and voltage window of the devices, respectively [12–14]. Transitional metal sulfides possess higher capacitance than their oxide counterparts because of the lower electronegativity of sulfur, rendering them promising candidates for SCs [15–17]. Especially, mixed metal sulfides such as NiCo₂S₄ [18–20], MnCo₂S₄ [21], CuCo₂S₄ [22] possess much more significant electrochemical activity and specific capacitance in contrast to single-metallic sulfides because of the synergistic effect among different components [23,24].

Ternary nickel cobalt sulfides (NCSs), a typical class of electrode materials, have been extensively investigated in the field of SCs [25]. Although NCS is a kind of promising material for SCs, it suffers low electronic conductivity and unstable volume expansion. As a result, the diffusion of electron/ion through the materials will be retarded and the energy density will be further reduced [26]. One way to boost the electron/ion diffusion is adopting rational nanostructural design for advanced NCS electrodes, which can enhance the electrical con-

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ductivity and shorten the electron/ion diffusion path [27]. As a consequence, NCSs with various nanostructures like nanosheets [28], nanotubes [29], nanoparticles [30], have been frequently applied as positive electrode materials in the field of SCs. In particular, NCS nanoparticles have attracted much attention because the nanoparticle structure owns larger electrochemical surface area [31]. However, the applications of NCS nanoparticles were restricted due to the serious aggregation during the preparation and practical application processes. Therefore, the electrochemical performance significantly shrank, as well as showed poor cyclic stability and inferior rate performance attributed to the sluggish electron/ion transfer kinetics [32]. To address this obstacle, an effective approach is introducing carbon substrate to simultaneously enhance the conductivity and well distribute the NCS nanoparticles [33].

Two-dimensional (2D) graphene oxide (GO) is commonly employed as a template for planar growth of metal sulfides [34,35]. The metal sulfide precursors could gather on the surface of GO *via* strong interactions between the precursors and the abundant oxygenated functional groups on the surface of GO [36,37]. After heating treatment, the conductivity of GO will be enhanced because the oxygenated functional groups are partially reduced to form thermal reduced GO (rGO). Therefore, GO as an eminent support for transition metal sulfide nanoparticles is extensively applied to SCs. Most recently, many studies have been devoted to the preparation of metal sulfide/rGO composites [38–43]. Nevertheless, most of approaches are restricted by the following intrinsic limitations: i) as the precursors do not contain sulfur element, the introduction of other sulfur sources like thioacetamide (TAA) or Na_2S is indispensable. ii) The reactions need to be carried out under harsh conditions, such as electrodeposition, and hydrothermal condition. iii) The synthetic procedure is usually complex. It is still a challenge to prepare 2D composite materials based on metal sulfide/rGO by the one-step method under mild conditions.

Herein, we present a facile one-step pyrolysis method for the preparation of $\text{CoNi}_2\text{S}_4/\text{rGO}$ hybrids by *in situ* growth of homogeneously dispersed CoNi_2S_4 nanoparticles on rGO nanosheets under mild conditions. The metal ethylxanthate deposited on GO nanosheets was used as the precursor for the formation of metal sulfide/rGO hybrids. The distribution of the CoNi_2S_4 nanoparticles can be regulated by adjusting the contents of GO. As a universal method, various metal sulfide/rGO hybrids with different morphologies can be prepared

successfully. Reviewed in a three-electrode configuration, the as-prepared $\text{CoNi}_2\text{S}_4/\text{rGO}$ hybrids show high specific capacitance of 1526 F g^{-1} at 2 A g^{-1} . More prominently, an asymmetric supercapacitor (ASC) was fabricated with $\text{CoNi}_2\text{S}_4/\text{rGO}$ as the positive electrode and active carbon (AC) as the negative electrode, achieving a high energy density of 54.8 W h kg^{-1} at a power density of 798 W kg^{-1} with outstanding electrochemical stability. Meanwhile, quasi-solid-state devices were prepared to demonstrate their practical application in flexible devices.

EXPERIMENTAL SECTION

Synthesis of $\text{CoNi}_2\text{S}_4/\text{rGO}$

In a typical synthesis for $\text{CoNi}_2\text{S}_4/\text{rGO}$, GO was dispersed in deionized water with the assistance of sonication for 30 min to form GO suspension (1 mg mL^{-1}). Then, 0.33 mmol of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.66 mmol of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were added to the GO suspension and stirred for 10 min. Then, 32 mL of potassium ethylxanthate solution (0.1 g mL^{-1}) was added into the above solution dropwise with vigorously stirring for 8 h to form CoNi_2S_4 -Precursor/GO. After drying, the sample was annealed in a furnace with a ramping rate of 2°C min^{-1} to 500°C and kept for 2 h under N_2 atmosphere. The final products were washed with deionized water and ethanol for six times. A series of the $\text{CoNi}_2\text{S}_4/\text{rGO}$ hybrids were fabricated based on the same procedure with different amounts of GO (8, 16, 24 mg), yielding samples labeled as $\text{CoNi}_2\text{S}_4/\text{rGO}$ -1, $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2, and $\text{CoNi}_2\text{S}_4/\text{rGO}$ -3, respectively.

Syntheses of CoS , $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$, and NiS at different temperatures

Typically, 1 mmol of metal salt was prepared with different feed ratios of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ from 1:0, 2:1, 1:1, 1:2, and 0:1 under stirring for 30 min. Then, 32 mL of potassium ethylxanthate solution (0.1 g mL^{-1}) was dropwise added into the above solution. The products were filtrated and washed several times with deionized water and dried under vacuum for 6 h. The dried sample was annealed in a furnace with a ramping rate of 2°C min^{-1} to $400/500/600^\circ\text{C}$ and kept for 2 h under N_2 atmosphere. The final products were washed with deionized water and ethanol for six times, and the corresponding samples were named as CoS -400, NiCo_2S_4 -400, $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ -400, CoNi_2S_4 -400, NiS -400, CoS -500, NiCo_2S_4 -500, $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ -500, CoNi_2S_4 -500, NiS -500, CoS -600, NiCo_2S_4 -600, $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ -600, CoNi_2S_4 -600, and NiS -600.

Synthesis of other metal sulfide/rGO

Typically, 1 mmol of metal salt was added into 15 mL of GO suspension (1 mg mL^{-1}) and stirred for 10 min, and then 32 mL of potassium ethylxanthate solution (0.1 g mL^{-1}) was dropwise added into the above solution. The dried sample was annealed in a furnace with a ramping rate of 2°C min^{-1} to 300°C and kept for 2 h under N_2 atmosphere. The final products are named as CdS/rGO, $\text{Cu}_{1.8}\text{S/rGO}$, $\text{In}_2\text{S}_3/\text{rGO}$, FeS/rGO, MnS/rGO, and ZnS/rGO, which were prepared by using the corresponding metal salts $\text{CdCl}_2 \cdot 1/2\text{H}_2\text{O}$, $(\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O})$, $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, MnCl_2 , and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, respectively.

Characterizations

The phase and structure were examined by X-ray powder diffraction (XRD, PERSEE, XD-3 with Cu K α radiation). Raman spectra were conducted on a Horiba Micro Raman HR Evolution System with an excitation wavelength of 514.5 nm. X-ray photoelectron spectroscopy (XPS, Thermo-VG; ESCALAB250Xi with Al K α radiation) was used to investigate the elemental species and their chemical states. The morphologies of samples were investigated by field-emission scanning electron microscopy (FESEM, FEI, QuanTA-200F) and transmission electron microscopy (TEM, JEOL, JEM-2100F). The crystal structure information on nanoscale was examined by a high resolution TEM (HRTEM, JEOL, JEM-2100F). The porosity measurements and Brunauer-Emmett-Teller (BET) surface area of the as-synthesized electrode materials were examined by N_2 sorption isotherms (Quantachrome, Autosorb-iQ at the testing temperature of 77 K).

Electrochemical measurements

The electrochemical performances were evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements using a CHI660D electrochemical workstation (Chenhua, Shanghai) in a three-electrode system, and a two-electrode system for ASC devices. For preparing the working electrodes, the electroactive materials, acetylene black conductor and poly(vinylidene fluoride) (PVDF) were mixed in *N*-methyl pyrrolidone (NMP) with a weight ratio of 80:10:10. The mixture was first coated onto the Ni foam surface ($1 \times 1 \text{ cm}^2$), and the working electrode was obtained by drying at 60°C for 12 h. The mass loading of the active material was $\sim 2 \text{ mg cm}^{-2}$. A platinum plate, an Ag/AgCl electrode, and 6 mol L^{-1} KOH solution were used as the counter electrode, reference electrode and electrolyte, respectively, in

a three-electrode system. The ASC devices were fabricated with $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2 hybrids ($\sim 0.6 \text{ mg cm}^{-2}$) as the cathode and AC ($\sim 2.3 \text{ mg cm}^{-2}$) as the anode, and 6 mol L^{-1} KOH solution was used as the electrolyte. Sodium carboxymethyl cellulose (CMC)-KOH gel was used as electrolyte for quasi-solid-state devices. The CMC-KOH gel electrolyte was prepared by adding 6 g of CMC and 10 g of KOH into 100 mL of deionized water under stirring at 90°C for 3 h until the gel became transparent.

Calculations

The specific capacitance of the single electrode (C_s) was examined by the GCD curves according to Equation (1):

$$C_s = \frac{1}{m \Delta V / \text{d}t}, \quad (1)$$

where I , m , and $\text{d}V/\text{d}t$ are the current during the discharge process, the mass of the active electrodes, and the slope of the discharge curve, respectively.

The mass loading of the positive electrode to the negative electrode follows the following Equation (2):

$$\frac{m_+}{m_-} = \frac{C_s \Delta V_-}{C_{s+} \Delta V_+}. \quad (2)$$

Specific capacitance (C), energy density (E), and power density (P) of the ASC devices follow Equations (3–5), respectively:

$$C = \frac{1}{m \Delta V / \text{d}t}, \quad (3)$$

$$E = \frac{C(\Delta V)^2}{2 \times 3.6}, \quad (4)$$

$$P = \frac{E \times 3600}{\Delta t}, \quad (5)$$

where m , ΔV , and Δt are the total mass of the active materials (g), the potential voltage (V), and the discharge time (s), respectively. The mass of the active materials was calculated by subtracting the mass of the substrate from the coated substrate. The units of specific capacitance, energy density and power density are F g^{-1} , Wh kg^{-1} and W kg^{-1} , respectively.

RESULTS AND DISCUSSION

The preparation of $\text{CoNi}_2\text{S}_4/\text{rGO}$ hybrids is illustrated in Fig. 1. At first, Co^{2+} and Ni^{2+} were anchored on GO by intensively interaction with the oxygen-containing functional groups of $-\text{OH}$ and $-\text{COOH}$. Then, potassium ethylxanthate reacted with metal ions to form chelates on the surface of GO to form CoNi_2S_4 -Precursor/GO. After annealing, the CoNi_2S_4 -Precursor/GO was transformed into $\text{CoNi}_2\text{S}_4/\text{rGO}$. The growth of the CoNi_2S_4 nanoparticles could be regulated by changing the concentra-

Figure 1 Schematic representation of the preparation of CoNi₂S₄/rGO.

tion of the GO suspension. Three different CoNi₂S₄/rGO hybrids referred to CoNi₂S₄/rGO-1, CoNi₂S₄/rGO-2, and CoNi₂S₄/rGO-3 have been investigated corresponding to the different quantities of GO. For comparison, the pristine CoS, NiCo₂S₄, Ni_{1.5}Co_{1.5}S₄, CoNi₂S₄, NiS were synthesized by the same method but without the addition of GO at different temperatures. At the same time, this generalized method can be used to synthesize other metal sulfides, including CdS, Cu_{1.8}S, In₂S₃, FeS, MnS, and ZnS, which can be compounded with rGO to form composite materials with different morphologies.

The crystal structures of CoNi₂S₄ and CoNi₂S₄/rGO

were investigated by XRD in Fig. 2a. The diffraction peaks located at 26.7°, 31.5°, 38.2°, 50.3°, and 55.0° are assigned to the (220), (311), (400), (511), and (440) planes of the cubic CoNi₂S₄ (JCPDF No. 24-0334) [31]. The diffraction peaks for rGO in the CoNi₂S₄/rGO were covered by the stronger diffraction peaks of CoNi₂S₄. Furthermore, there are no other peaks attributed to impurities, confirming the high purity. Crystalline structures of the pristine CoS, Ni_xCo_{3-x}S₄, and NiS formed at different temperatures (400/500/600°C) are detailed in Fig. S1. Obviously, the crystal phase and crystallinity are affected by the annealing temperature and the ratio of Ni

Figure 2 (a) XRD patterns of the CoNi₂S₄-500 and CoNi₂S₄/rGO hybrids. (b) Raman spectra of GO and CoNi₂S₄/rGO hybrids. (c) XPS survey scan spectrum of CoNi₂S₄/rGO-2. (d-g) High resolution XPS spectra of Ni 2p, Co 2p, S 2p, and C 1s. (h) N₂ adsorption/desorption isotherms and (i) the corresponding pore size distribution profiles of CoNi₂S₄-500 and CoNi₂S₄/rGO-2.

to Co. Hence, the reaction process principally requires optimal Ni to Co ratio and annealing temperature. Besides, the XRD patterns of other metal sulfide/rGO obtained by this generalized method are detailed in Fig. S2. These results prove that this generalized method has been successfully used to prepare a variety of metal sulfide/rGO hybrids, including CdS/rGO, $\text{Cu}_{1.8}\text{S}$ /rGO, In_2S_3 /rGO, FeS/rGO, MnS/rGO, and ZnS/rGO. The local structures of GO and CoNi_2S_4 /rGO were further investigated by Raman spectrum (Fig. 2b). Two characteristic peaks of the D and G bands of the CoNi_2S_4 /rGO-2 hybrids are centered at about 1350 and 1585 cm^{-1} , respectively. The two peaks at 240 and 375 cm^{-1} in the Raman spectrum are assigned to the E_g and A_{1g} modes of CoNi_2S_4 nanoparticles, respectively. In contrast to the GO, the I_D/I_G ratios of the CoNi_2S_4 /rGO hybrids increase slightly from 1.03 to 1.31, 1.25 and 1.19, respectively, proving that more structural defects exist in CoNi_2S_4 /rGO hybrids than pure GO. The increase of I_D/I_G ratio is obviously associated with the compact anchoring of CoNi_2S_4 nanoparticles on the rGO surface [38].

The surface information of the CoNi_2S_4 /rGO-2 hybrids was investigated by XPS. The presence of Ni, Co, S, and C in CoNi_2S_4 /rGO-2 hybrids is supported by the XPS survey spectrum, as shown in Fig. 2c. The Ni, Co, S, and C contents are estimated to be 4.00, 2.77, 28.26, and 64.96 at%, respectively. The Ni 2p spectrum could be deconvoluted into two shakeup satellites and two spin-orbit doublets (Fig. 2d). The binding energies at 853.3 and 870.7 eV are ascribed to Ni^{2+} , and the peaks located at 856.4 and 875.7 eV are ascribed to Ni^{3+} . The peaks at 882.9 and 863.5 eV are assigned to the satellite peaks [44]. For the Co 2p spectrum (Fig. 2e), the binding energy located at 783.9 and 798.2 eV are attributed to Co^{2+} ions, and the peaks at 778.8 and 793.9 eV belong to Co^{3+} . Besides, two peaks at 787.7 and 803.6 eV corresponding to satellite peaks are observed [45]. The S 2p spectrum exhibits two main binding energies located at 161.7 and 162.8 eV (Fig. 2f) ascribed to the S 2p_{3/2} and S 2p_{1/2}, respectively [34]. The deconvoluted C 1s spectrum (Fig. 2g) include four peaks, corresponding to C=C (284.5 eV), C-C (285.1 eV), C-O (286.0 eV), and C=O (288.5 eV), respectively [46]. The relatively high intense and narrow peak of C=C bond demonstrates that most of the carbons in rGO have been restored to sp² hybridized carbons [47]. The XPS spectra of the CoS, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$, and NiS are detailed in Figs S3–S7, which can demonstrate elemental components and chemical states of the corresponding compounds.

Note that enlarging the surface area of active materials

with porous structure can provide a myriad of active sites and superior electrochemical performance [48]. Fig. 2h displays the N₂ adsorption and desorption isotherms of CoNi_2S_4 and CoNi_2S_4 /rGO-2 hybrids. The CoNi_2S_4 /rGO-2 hybrids show the type IV isotherm. The existence of a large number of mesopores is proved by high uptakes of N₂ at $P/P_0 \sim 1$ [49]. The pore-size distribution curves based on Barrett-Joyner-Halenda (BJH) method in Fig. 2i present narrow pore-size distribution concentrated at 2.8 nm, indicating that there is large amount of mesopores within this range. Moreover, compared with the pristine CoNi_2S_4 sample with a surface area of 36.8 $\text{m}^2 \text{g}^{-1}$, the composite CoNi_2S_4 /rGO-2 shows a higher specific surface area of 121.9 $\text{m}^2 \text{g}^{-1}$. The porous structure of CoNi_2S_4 /rGO-2 with larger specific surface area has promotive effect on the rapid diffusion of electron/ions [50].

The morphologies of the obtained samples were examined by FESEM. The FESEM images of pure GO and the CoNi_2S_4 -Precursor/GO are displayed in Fig. S8. Obviously, the CoNi_2S_4 -Precursor/GO has a rougher surface than GO, indicating that the precursor was successfully loaded onto the GO surface. As shown in Fig. 3a, b, the FESEM images show that the pristine CoNi_2S_4 tends to form bulky aggregations without rGO. These aggregated CoNi_2S_4 will trigger reduced contact area with the electrolyte to retard the redox reaction kinetics of the electroactive materials. The FESEM images of CoNi_2S_4 /rGO-1 (Fig. 3c, d) composite with the least rGO content show that spherical structure was fixed on the surface of rGO, and vigorous agglomeration occurs due to the insufficient rGO. Fig. 3e, f displays the FESEM images of the CoNi_2S_4 /rGO-2. Evidently, the CoNi_2S_4 nanoparticles are ultra-dispersed on rGO owing to the content of rGO reaching the appropriate level. Moreover, the FESEM images of the CoNi_2S_4 /rGO-3 (Fig. 3g, h) with excessive rGO show that small amount of CoNi_2S_4 particles are distributed unevenly on the surface of rGO. Besides, more exquisite differences of CoNi_2S_4 nanoparticles dispersion are shown by the model structure of pristine CoNi_2S_4 , CoNi_2S_4 /rGO-1, CoNi_2S_4 /rGO-2, and CoNi_2S_4 /rGO-3 in Fig. 3b-1, d-1, f-1 and h-1, respectively.

The morphologies and structures of CoNi_2S_4 /rGO were further examined by TEM and HRTEM. The TEM image of CoNi_2S_4 /rGO-1 depicted in Fig. 4a reveals that the CoNi_2S_4 nanoparticles are aggregated on the rGO nanosheets. In sharp contrast, the TEM image of CoNi_2S_4 /rGO-2 (Fig. 4b) shows that small-sized CoNi_2S_4 nanoparticles are uniformly distributed on the rGO nanosheets. The TEM image of CoNi_2S_4 /rGO-3 (Fig. 4c)

Figure 3 (a, b) FESEM images and (b-1) model structure of CoNi_2S_4 -500. (c, d) FESEM images and (d-1) model structure of $\text{CoNi}_2\text{S}_4/\text{rGO}$ -1. (e, f) FESEM images and (f-1) model structure of $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2. (g, h) FESEM images and (h-1) model structure of $\text{CoNi}_2\text{S}_4/\text{rGO}$ -3.

shows that slight and uneven CoNi_2S_4 nanoparticles are fixed on the rGO nanosheets. The TEM images in Fig. 4-c are in agreement with the corresponding FESEM results. Besides, the structure of the nanoparticles-on-nanosheets can be favorably maintained in a large scale (Fig. S9). As a result, the FESEM and TEM images show that the optimal product possesses ultradispersed CoNi_2S_4 nanoparticles on rGO with appropriate amount of GO. At the same time, these images reveal that the $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2 feature the rich active sites, which is propitious to improve the specific capacitance. As depicted in Fig. 4d, the statistical size distribution of $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2 displays the mean size of CoNi_2S_4 nanoparticles is 16.7 nm. The HRTEM image of $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2 (Fig. 4e) confirms the rGO nanosheets flawlessly encapsulate the CoNi_2S_4 nanoparticles, implying the strong association of CoNi_2S_4 and rGO. The interplanar spacings of about 0.184 and 0.166 nm correspond to (511) and (440) planes of

CoNi_2S_4 , respectively. At the same time, the corresponding selected area electron diffraction (SAED) image depicted in Fig. 4f reveals the polycrystalline nature of $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2. The diffraction rings can be well indexed to (111), (220), (311), (400), (551), and (440) crystal planes of CoNi_2S_4 . Besides, the obvious hexagonal ring can be assigned to the structure of rGO. The $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2 was further analyzed by high-angle annular dark-field scanning TEM (HAADF-STEM) with energy dispersive spectrometer (EDS) analysis (Fig. 4g). The EDS mapping shows the coexistence of C, Co, Ni, and S elements which are homogeneously distributed throughout the $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2 nanosheets, further confirming the uniformly dispersion of CoNi_2S_4 nanoparticles on rGO nanosheets. The EDS line scanning (Fig. S10) was further used to reveal the element distribution, which also demonstrated the well-proportioned dispersion of C, Co, Ni, and S.

Figure 4 TEM images of (a) CoNi₂S₄/rGO-1, (b) CoNi₂S₄/rGO-2, and (c) CoNi₂S₄/rGO-3. (d) The statistical size distribution of CoNi₂S₄/rGO-2 obtained from TEM photographs. (e) HRTEM image of CoNi₂S₄/rGO-2 hybrids. (f) SAED pattern for CoNi₂S₄/rGO-2. (g) HAADF-STEM image and the corresponding elemental mapping images of CoNi₂S₄/rGO-2.

The morphological characteristics of other metal sulfide/rGO hybrids prepared by this method are detailed in Figs S11–S16. Apparently, the CdS/rGO, Cu_{1.8}S/rGO, MnS/rGO, and ZnS/rGO also show the morphology of nanoparticles anchored on the surface of rGO. In addition, the morphological images of In₂S₃/rGO and FeS/rGO show unique nanoflower and nanocluster structures, respectively. The corresponding SAED images reveal the crystalline natures of the metal sulfides. It shows that complex morphologies can also be prepared by this simple method under mild conditions.

The electrochemical performances of CoS, Ni_xCo_{3-x}S₄, and NiS were firstly analyzed in a standard three electrode systems by CV, GCD and EIS, as shown in Figs S17–S21. These results clearly demonstrate that both temperature and ratio of nickel to cobalt play very important function on specific capacitance and electron/ion diffusion. The specific capacitance data under different conditions are summarized in Fig. 5a. Obviously, the optimal products are obtained at the annealing temperature of 500°C and the ratio of nickel to cobalt of 2:1, which delivers the highest capacitance of 1304 F g⁻¹ at

2 A g⁻¹.

The electrochemical performances of CoNi₂S₄/rGO were further systematically investigated. The integrated CV area of CoNi₂S₄/rGO-2 is obviously larger than CoNi₂S₄/rGO-1, CoNi₂S₄/rGO-3, and CoNi₂S₄-500, which proves that CoNi₂S₄/rGO-2 shows a larger specific capacitance (Fig. 5b). As displayed in Fig. 5c, the representative CV curves of CoNi₂S₄/rGO-2 at scan rates ranging from 5 to 100 mV s⁻¹ in -0.1–0.5 V show obvious redox peaks, resulting from the Faradaic reactions of Ni²⁺/Ni³⁺ and Co²⁺/Co³⁺ transitions associated with OH⁻ during the electrochemical process. The similar CV curve shapes were observed even at high scan rate, indicating that CoNi₂S₄/rGO-2 hybrids delivered excellent pseudocapacitance behavior and rate capability. The Faradaic redox processes follow the reaction below [24]:

The GCD measurements of CoNi₂S₄/rGO-2 were implemented in -0.1–0.4 V at different current densities (Fig. 5d). Based on the GCD profiles, the specific capacitances of CoNi₂S₄/rGO-2 are 1526, 1430, 1382, 1208,

Figure 5 (a) Specific capacitances of CoS, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$, and NiS prepared at different temperatures. (b) CV curves of CoNi_2S_4 -500, and $\text{CoNi}_2\text{S}_4/\text{rGO}$ hybrids. (c) CV curves of $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2 electrode at various scan rates. (d) GCD curves of $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2 at various current densities. (e) Specific capacitances of CoNi_2S_4 -500 and $\text{CoNi}_2\text{S}_4/\text{rGO}$ hybrids at different current densities. (f) EIS curves of CoNi_2S_4 -500 and $\text{CoNi}_2\text{S}_4/\text{rGO}$ hybrids.

1103, and 988 F g^{-1} at 2, 3, 5, 10, 15, and 20 A g^{-1} , respectively. This suggests that small CoNi_2S_4 nanoparticles homogeneously dispersed on rGO provide more active sites which play a decisive role in enhancing the specific capacitance. Integrating the GCD curves, the corresponding specific capacitances of CoNi_2S_4 -500 and $\text{CoNi}_2\text{S}_4/\text{rGO}$ electrodes are displayed in Fig. 5e. Apparently, when the current density rises from 2 to 20 A g^{-1} , the specific capacitance of the $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2 electrode drops by 35%, indicating good rate capability. Moreover, the $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2 electrode delivers high capacitance retention and coulombic efficiency, which can be attributed to the highly reversible Faradaic reaction (Fig. S22).

The superior electrochemical performance of $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2 hybrids could be attributed to the following factors: i) rGO could provide a myriad of nucleation sites for CoNi_2S_4 , greatly inhibiting the aggregation of CoNi_2S_4 and forming small-sized CoNi_2S_4 nanoparticles. Numerous small CoNi_2S_4 nanoparticles on rGO nanosheets could vitally shorten the diffusion distance of active electron/ion. ii) The rGO nanosheets could effectively withstand the serious volume expansion of CoNi_2S_4 nanoparticles during rapid charge/discharge process. Hence, the rate capability of $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2 can be obviously improved. iii) CoNi_2S_4 nanoparticles deposited on the rGO nanosheets greatly inhibited the accumulation of rGO nanosheets, resulting in high double-layer capacitance.

To better understand the influence of rGO, the electrochemical impedances of CoNi_2S_4 and $\text{CoNi}_2\text{S}_4/\text{rGO}$ hybrids were tested by using EIS. As shown in Fig. 5f, the impedance spectra show a semicircle in the high frequencies and a sloped straight line in the low frequencies [51]. In the high frequency region, the $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2 electrode delivers the equivalent series resistance of 1.6Ω , which is lower than 1.8Ω of $\text{CoNi}_2\text{S}_4/\text{rGO}$ -1 and 2.3Ω of CoNi_2S_4 -500, and higher than 1.2Ω of $\text{CoNi}_2\text{S}_4/\text{rGO}$ -3. In the low frequency region, the slope of $\text{CoNi}_2\text{S}_4/\text{rGO}$ -3 shows the lowest diffusion resistance. In addition, the equivalent circuit diagram is shown in Fig. S23. The equivalent series resistances of CoNi_2S_4 , $\text{CoNi}_2\text{S}_4/\text{rGO}$ -1, $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2, and $\text{CoNi}_2\text{S}_4/\text{rGO}$ -3 are 0.69, 0.68, 0.71, and 0.74Ω , respectively, and the charge transfer resistances are 3.14, 2.57, 1.82, and 1.16Ω , respectively (Table S1). These phenomena are because the composites with more rGO have better conductivity. Moreover, the electrochemical properties of other metal sulfide/rGO hybrids are detailed in Figs S24–28, which prove that these metal sulfide/rGO hybrids are valuable in the field of SCs.

To further evaluate $\text{CoNi}_2\text{S}_4/\text{rGO}$ for practical application, ASCs were assembled with the $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2 hybrids and AC as the cathode and anode, respectively. The CV curves of the AC and $\text{CoNi}_2\text{S}_4/\text{rGO}$ -2 electrodes with different mass loadings are displayed in Fig. 6a. The specific capacitance and potential window of AC are

Figure 6 (a) CV curves of AC and CoNi₂S₄/rGO-2 at scan rate of 20 mV s⁻¹. (b) CV curves of the ASC under various potential windows. (c) CV curves of the ASC at different scan rates. (d) GCD curves of the ASC at different current densities. (e) Specific capacitances of the ASC calculated from GCD curves. (f) EIS curves of the ASC. (g) Ragone plot of energy and power densities of the ASC compared with literature results. (h) Cycling performance at a constant current density of 3 A g⁻¹. (i) Photographic image of a red LED operated by two ASC devices in series.

185 F g⁻¹ and 1 V, respectively. To obtain an excellent performance of ASCs, the optimal mass ratio of the positive to negative electrodes (m⁺/m⁻) was adjusted to around 1:4. To evaluate the maximum potential window of the ASCs, CV curves under various potential windows at 50 mV s⁻¹ were recorded (Fig. 6b). The CV curves demonstrate the ASCs show an outstanding capacitive behavior during 10–50 mV s⁻¹ in the working voltage windows of 0–1.6 V (Fig. 6c). The shape of CV curves changes slightly with the enhancement of current density, proving a superior rate capability of the ASCs. The GCD curves of the device at different current densities are shown in Fig. 6d. The device exhibits relatively low internal resistance drop, benefiting from the reduced electron/ion diffusion pathway. The specific capacitances of the supercapacitor device were calculated by the discharge curves. In Fig. 6e, the ASC device possesses specific capacitances of 154, 140, 133, 120, 100, 86, and

79 F g⁻¹ at 1, 2, 3, 5, 10, 15, and 20 A g⁻¹, respectively. The capacitance retention and coulombic efficiency of the ASC at different current densities are shown in Fig. S29. The coulombic efficiency at a current density of 1 A g⁻¹ is only 82%, which can be attributed to the incomplete discharge caused by some side reactions in the electrochemical redox reaction at low current density. The Nyquist plot (Fig. 6f) shows the charge-transfer resistance value is 7.9 Ω for the ASC devices. Fig. 6g shows the Ragone plots of the energy and power density of the ASC device. The asymmetric supercapacitor delivers a high energy density of 54.8 W h kg⁻¹ at a power density of 798 W kg⁻¹. Notably, the energy density of ASC devices is more preferable than that of nickel/cobalt composites-based devices, such as NiCo₂S₄/PRGO//AC (27.5 W h kg⁻¹ at 446.5 W kg⁻¹) [39], Co₃O₄/Graphene//Co₃O₄/Graphene (43.1 W h kg⁻¹ at 4000 W kg⁻¹) [52], NiCo₂O₄@CNT/CNT//treated carbon cloth (27.6 W h kg⁻¹ at 550 W kg⁻¹)

[53], Co-Mn-DHS//CMK-3 (33.8 W h kg^{-1} at 1602 W kg^{-1}) [54], and $\text{CoNi}_2\text{S}_4/\text{BC} // \text{BC}$ (38.9 W h kg^{-1} at 850 W kg^{-1}) [55]. The cycling stability of the ASC was further investigated by the capacitance retention at current density of 3 A g^{-1} (Fig. 6h). Remarkably, the ASC maintains 93.7% of its original capacitance after 8000 cycles, demonstrating the outstanding long-term stability. To further prove the practical use of the $\text{CoNi}_2\text{S}_4/\text{rGO}-2 // \text{AC}$ ASC device, a red light emitting diode (LED) can be lightened up by double ASC devices (Fig. 6i).

In view of developing flexible quasi-solid-state supercapacitors, we have fabricated supercapacitor devices using sodium carboxymethyl cellulose/KOH (CMC/KOH) electrolyte separating $\text{CoNi}_2\text{S}_4/\text{rGO}-2$ electrode from AC coated on carbon cloth. The electrochemical performance of the device is detailed in Fig. S30. The specific capacitances of the $\text{CoNi}_2\text{S}_4/\text{rGO}-2 // \text{AC}$ flexible ASC device are as high as 46.3, 43.6, 37.2, and 30.5 F g^{-1} at the current densities of 2, 3, 5, and 10 A g^{-1} , respectively. The flexible ASC device delivers a maximum energy density of 16.4 W h kg^{-1} at a power density of 1599 W kg^{-1} . Thus, this method is feasible in the preparation of flexible and wearable supercapacitors, which brings great potential for wearable electronic technologies. The electrochemical performance of quasi-solid-state supercapacitor is inferior to that of liquid supercapacitor, which can be attributed to the relatively poor ionic conductivity of gel electrolyte compared with that of aqueous electrolyte. Moreover, gel electrolyte may have worse Ohmic contact with the electrode materials and current collectors than aqueous electrolyte, resulting in decreased diffusion rate of ions and enhanced charge-transfer resistance, and thus poor rate capability.

CONCLUSIONS

In this work, 2D $\text{CoNi}_2\text{S}_4/\text{rGO}$ has been successfully constructed by a one-step pyrolysis approach. The as-prepared $\text{CoNi}_2\text{S}_4/\text{rGO}$ hybrids with nanoparticles-on-nanosheets structure, which is effective to provide a large number of active sites and shorten the electron/ion diffusion distance. Thus, the $\text{CoNi}_2\text{S}_4/\text{rGO}$ exhibits impressed specific capacitance of 1526 at 2 A g^{-1} as well as excellent rate performance. The fabricated ASC devices with $\text{CoNi}_2\text{S}_4/\text{rGO}$ as the positive electrode and AC as the negative electrode exhibits an energy density of 54.8 W h kg^{-1} at a power density of 798 W kg^{-1} . Moreover, the $\text{CoNi}_2\text{S}_4/\text{rGO}$ electrode can also be used to fabricate flexible supercapacitors with remarkable performance. In addition, this simple one-step pyrolysis method was extended to fabricate various metal sulfide/

rGO hybrids. Therefore, this study provides a universal strategy to fabricate metal sulfide-based composites for energy conversion/storage.

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Author contributions Chen Y and Yuan K conceived and designed the experiments. Zhang K, Wei Y, Huang J, Xiao Y, Yang W and Hu T conducted the experiments, analyzed the data and wrote the manuscript. Chen Y and Yuan K supervised the project. All the authors participated in the discussions of the research.

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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一种通用的一步原位合成策略制备金属硫化物/还原氧化石墨烯纳米片用于高性能超级电容器

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摘要 金属硫化物在超级电容器领域具有良好的应用前景, 但缓慢的反应动力学抑制了其电化学性能。增加电化学表面积并与碳材料结合可以改善其电化学性能。然而, 寻求一种简单通用的方法制备金属硫化物和导电碳的复合材料仍具有挑战性。本文设计了一种简单的一步热解法, 在温和的条件下将硫化钴镍(CoNi_2S_4)原位生长在还原氧化石墨烯(rGO)纳米片上。制备的硫化镍钴/还原氧化石墨烯($\text{CoNi}_2\text{S}_4/\text{rGO}$)材料具备纳米片结构, 可以提供大量的活性位点, 有效地缩短电子/离子的扩散路径。得益于这些优点, 所制备的 $\text{CoNi}_2\text{S}_4/\text{rGO}$ 电极材料在电流密度分别为2和20 A g^{-1} 时具有1526和988 F g^{-1} 的高比电容。基于 $\text{CoNi}_2\text{S}_4/\text{rGO}$ 的非对称超级电容器工作电压窗口为1.6 V, 在功率密度为798 W kg^{-1} 时能量密度高达54.8 Wh kg^{-1} 。在3 A g^{-1} 下循环8000次后, 其容量保持率为93.7%。利用该方法可获得一系列金属硫化物/rGO复合材料, 此通用策略可推广应用于各种能源器件电极材料的制备。