



Article

Synthesis of Hierarchical Porous Ni_{1.5}Co_{1.5}S₄/g-C₃N₄ Composite for Supercapacitor with Excellent Cycle Stability

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Abstract: In this work, the hierarchical porous Ni_{1.5}Co_{1.5}S₄/g-C₃N₄ composite was prepared by growing Ni_{1.5}Co_{1.5}S₄ nanoparticles on graphitic carbon nitride (g-C₃N₄) nanosheets via a hydrothermal route. Due to the self-assembly of larger size g-C₃N₄ nanosheets as a skeleton, the prepared nanocomposite possesses a unique hierarchical porous structure that can provide short ions diffusion and fast electron transport. As a result, the Ni_{1.5}Co_{1.5}S₄/g-C₃N₄ composite exhibits a high specific capacitance of 1827 F g⁻¹ at a current density of 1 A g⁻¹, which is 1.53 times that of pure Ni_{1.5}Co_{1.5}S₄ (1191 F g⁻¹). In particular, the Ni_{1.5}Co_{1.5}S₄/g-C₃N₄/activated carbon (AC) asymmetric supercapacitor delivers a high energy density of 49.0 Wh kg⁻¹ at a power density of 799.0 W kg⁻¹. Moreover, the assembled device shows outstanding cycle stability with 95.5% capacitance retention after 8000 cycles at a high current density of 10 A g⁻¹. The attractive performance indicates that the easily synthesized and low-cost Ni_{1.5}Co_{1.5}S₄/g-C₃N₄ composite would be a promising electrode material for supercapacitor application.

Keywords: g-C₃N₄; metal sulfide; supercapacitor; cycle stability

1. Introduction

Supercapacitor has attracted great attention in recent years, due to its high-power density, excellent cycling stability, fast charge-discharge and environmental friendliness [1]. The electrode materials for supercapacitor application mainly include carbon materials [2], metal oxides [3], conductive polymers [4], transition metal sulfides [5,6], and their composites [7]. Among various electrode materials, transition metal sulfides have a broad application prospect because of its inherent characteristics and excellent electrochemical performance [8]. Compared with oxide counterparts, the transition metal sulfides possessed better electrical conductivity, richer electrochemical activity and higher theoretical capacitance. Furthermore, ternary Ni-Co-S sulfides such as NiCo₂S₄ and Ni₂CoS₄ have been demonstrated to be more attractive than corresponding binary Ni or Co sulfides (e.g., NiS, CoS, Ni₃S₄, ect.) [9–13], thanks to their rich redox reaction sites and the advantage in terms of electronic conductivity [14]. Recently, several groups have reported that the atomic ratio of nickel and cobalt plays an important role in optimizing the electrochemical performance of electrodes [15–17]. The nonstoichiometric Ni_{1.5}Co_{1.5}S₄ showed a higher specific capacitance, attributing to the synergistic effects of nickel species and cobalt species.

Graphitic carbon nitride (g-C₃N₄) is a two-dimensional graphite structure composed of sp²-hybridized carbon and nitrogen atoms [18,19]. The presence of high content nitrogen in g-C₃N₄

can enhance the electron-donor property of the carbon matrix, resulting in an improvement the electron transport between the active materials [20,21]. Therefore, g-C₃N₄ is considered a promising candidate material for electrochemical applications because of its rapid charge separation and relatively slow charge recombination property in the electron transfer process [22]. Some recent research has revealed that the combination of pseudocapacitive materials and g-C₃N₄ can effectively enhance the electrochemical performance of electrode materials for supercapacitor applications. For example, Shi et al. synthesized flower-like Ni(OH)₂/g-C₃N₄ via a facile hydrothermal route. This hybrid structure exhibited a specific capacitance of 505.6 F g⁻¹ at a current density of 0.5 A g⁻¹ [23]. Dong et al. reported g-C₃N₄@Ni(OH)₂ with interconnect honeycomb nanostructure, which exhibited a high specific capacitance of 1768.7 F g⁻¹ as well as a better cycling performance with 84% retentions after 4000 cycles [24]. Guan et al. found that the electrochemical performances of NiCo₂O₄/g-C₃N₄ were extremely dependent on their morphology. The nanoneedle-assembled NiCo₂O₄/g-C₃N₄ possessed higher specific capacitance, while nanosheets-assembled NiCo₂O₄/g-C₃N₄ exhibited a better cycling durability [25]. The hybrid structures of metal sulfides and carbon nanomaterials (such as CNTs and graphene) have attracted much attention for high performance supercapacitor [26]. However, to the best of our knowledge, the combination of nonstoichiometric Ni_{1.5}Co_{1.5}S₄ and g-C₃N₄ has been rarely reported.

Herein, we report the hierarchical porous Ni_{1.5}Co_{1.5}S₄/g-C₃N₄ composite by a simple solvothermal method. The prepared composite shows a high specific capacitance of 1827 F g⁻¹ owing to interconnecting porous structure assembled by Ni_{1.5}Co_{1.5}S₄ nanoparticles and 2D g-C₃N₄ nanosheets. More impressively, an asymmetric supercapacitor (denoted as Ni_{1.5}Co_{1.5}S₄/g-C₃N₄//AC) assembled using the optimized Ni_{1.5}Co_{1.5}S₄/g-C₃N₄ and activated carbon exhibits great practical application value in energy conversion and storage due to its high energy density and power density, and excellent cycling stability.

2. Experimental Section

2.1. Preparation of Samples

The g-C₃N₄ nanosheets were prepared through a simple improved calcination method as reported in the literature [27]. In brief, 1 g of melamine and 3 g of ammonium chloride were mixed and ground thoroughly in an agate mortar. Then the mixtures were put into a quartz boat and heated at 550 °C with a heat rate of 10 °C min⁻¹ for 4 h in a tube furnace. After cooling to room temperature, the yellow g-C₃N₄ was obtained. Finally, the g-C₃N₄ were washed with deionized water and absolute ethanol several times, and ground into powders for further use.

The Ni_{1.5}Co_{1.5}S₄/g-C₃N₄ composites were prepared through a modified one-step hydrothermal method as described in our previous paper [28]. Typically, 3 mmol of NiCl₂6H₂O, 3 mmol of CoCl₂6H₂O and 20 mmol of CS(NH₂)₂ were dispersed in a mixture solution of 30 mL water and 50 mL ethylene glycol. Then, 60 mg of g-C₃N₄ nanosheets was added to the above solution and stirred magnetically for 30 min. The pH value of the mixed solution was adjusted to 11 using NaOH. Afterwards, the mixed solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave (Xi'an Changyi Instrument Equipment Co., Ltd, Xian, China) and reacted at 200 °C for 24 h. After cooling to ambient temperature, the black precipitates were collected, washed with deionized water and ethanol several times, and dried at 60 °C for 12 h. The preparation process is shown in Figure 1.



Figure 1. Schematic illustration of the synthesis of $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$.

2.2. Characterizations of Samples

The X-ray diffraction (XRD) patterns of the samples obtained on an X-ray diffractometer (Bruker D8 ADVANCE, Bruker Daltonics Inc., Bruker, Germany) instrument. The X-ray photoelectron spectra (XPS) were collected using a spectrometer (Escalab 250XI, Thermo Fisher Scientific Inc., Walsham, MA, USA) with monochromatic aluminum target. The morphologies of the samples were observed using a field-emission scanning electron microscope (FESEM, JSM-6701F, JEOL Ltd., Tokyo, Japan) at an accelerating voltage of 5 kV, and a transmission electron microscope (TEM, JEM2010, JEOL Ltd., Tokyo, Japan), respectively. The Brunauer-Emmett-Teller (BET) surface area and Barret-Joyner-Halenda (BJH) pore size distribution of the samples were measured by nitrogen adsorption-desorption isotherms at 77 K using a gas sorption analyzer (Micromeritics ASAP 2020, Micromeritics Instrument Inc., Atlanta, GA, USA).

2.3. Electrochemical Measurement

A three-electrode system and two-electrode system were used to test the electrochemical performance of the samples on a CS350H electrochemical workstation with 2 M KOH aqueous as electrolyte. The working electrode was prepared via mixing the active material (2.0 mg, 80 wt.%), Super P conductive carbon black (10 wt.%) and polyvinylidene fluoride binder (10 wt.%). Then, the slurry was coated on a piece of nickel foam current collector (1 cm × 1 cm), and dried at 60 °C for 12 h under vacuum. Finally, the working electrode was fabricated by pressing nickel foam loaded with active material at a pressure of 10 MPa. Platinum plate and saturated Ag/AgCl were used as counter electrode and reference electrode, respectively. An asymmetric supercapacitor (ASC) cell was assembled by using $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ as the positive electrode and commercial AC as the negative electrode. The electrochemical performance of the electrodes was characterized by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) methods. The specific capacitances (C) of the electrodes are calculated based on the GCD curves according to the following Equation [29].

$$C = (I \times \Delta t) / (m \times \Delta V) \quad (1)$$

where I is the constant discharging current (mA), Δt is the discharge time (s), the potential window (ΔV), and m is the mass of active materials in the electrode (mg). For two-electrode testing, the mass of active materials includes the electroactive materials of both the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ and AC.

3. Result and Discussion

The phase purity and crystal structure of the samples were analyzed using XRD patterns, and the results are shown in Figure 2. Six diffraction peaks can be perfectly indexed to the (111), (220), (311), (400), (511) and (440) of spinel structured NiCo_2S_4 (JCPDS# 20-0782) or Ni_2CoS_4 (JCPDS# 24-0334), respectively. In addition, no other metal sulfides such as NiS and Ni_3S_2 were observed in the pattern, which indicates the pure spinel structure. Figure S1 shows the XRD pattern of the prepared $\text{g-C}_3\text{N}_4$. Two diffraction peaks at around 13.1° and 27.3° in $\text{g-C}_3\text{N}_4$ correspond to the in-plane structure packing of aromatic systems of (100) plane and the interlayer stacking of conjugated aromatic systems of (002)

plane, respectively [30,31], which reveals that the prepared g-C₃N₄ nanosheets is the typical graphitic structure. No diffraction peaks of g-C₃N₄ were found in the XRD pattern of the Ni_{1.5}Co_{1.5}S₄/g-C₃N₄, which is probably due to weak scattering intensity and relatively low content of g-C₃N₄.

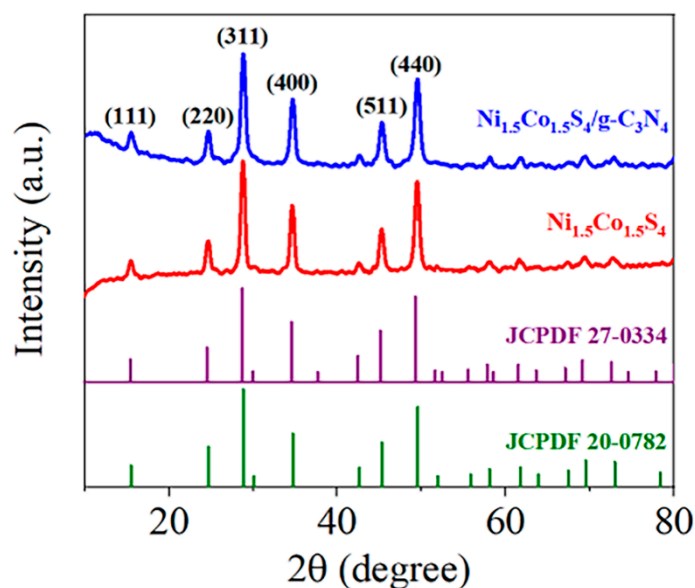


Figure 2. XRD patterns of the Ni_{1.5}Co_{1.5}S₄ and Ni_{1.5}Co_{1.5}S₄/g-C₃N₄.

In order to determine the chemical bonds of the corresponding elements in the Ni_{1.5}Co_{1.5}S₄/g-C₃N₄ composite, the XPS spectra of the sample are shown in Figure 3. The XPS survey spectrum (Figure 3a) shows the presence of Ni, Co, S, C, N, and O elements in the sample. The O 1s peak is mainly attributed to contamination when the sample is exposed to ambient air. The high-resolution XPS spectra of Ni 2p, Co 2p, S 2p, C 1s, N 1s are fitted with Gaussian functions to acquire detail information of chemical bonding. For Ni 2p spectrum, the fitting peaks at 853.3 and 856.2 eV are assigned to Ni²⁺ and Ni³⁺, respectively. For Co 2p spectrum, the fitting peaks at 778.7 and 780.9 eV are assigned to Co³⁺ and Co²⁺, respectively. Moreover, two satellite peaks can be observed in each high-resolution Ni 2p and Co 2p spectra. Obviously, the low-valent and high-valent metal ions coexist in the Ni_{1.5}Co_{1.5}S₄/g-C₃N₄ composite, which is similar to previous reports [28]. Chen et al. believed that the easily valence-changed nickel can contribute the most faradaic capacity of the active materials, while the low-valent cobalt can offer the high electronic conductivity and assist the charge-transfer process in the binary metal sulfides based active materials [17]. Two peaks S 2p (Figure 3d) located at binding energy of 161.4 and 162.5 eV are typical of metal-sulfur bonds [32,33]. The C 1s spectrum (Figure 3e) is fitted into three peaks which could be attributed to sp² C-C (284.8 eV), C-O (286.5 eV) and N-C=N or C-(N)₃ (288.5 eV) bonds, respectively [22]. Figure 3f shows the three different kinds of chemical states of nitrogen species in the g-C₃N₄. According to the literature [34–36], the peaks at binding energy of 398.4, 399.8 and 401.3 eV are assigned to sp² nitrogen in carbon containing triazine rings (C=N-C), bridged graphitic tertiary nitrogen bonded with carbon atom (N-(C)₃), and amino functional groups (C-N-H), respectively. These peaks are agreement with the characteristics of nitrogen species in g-C₃N₄.

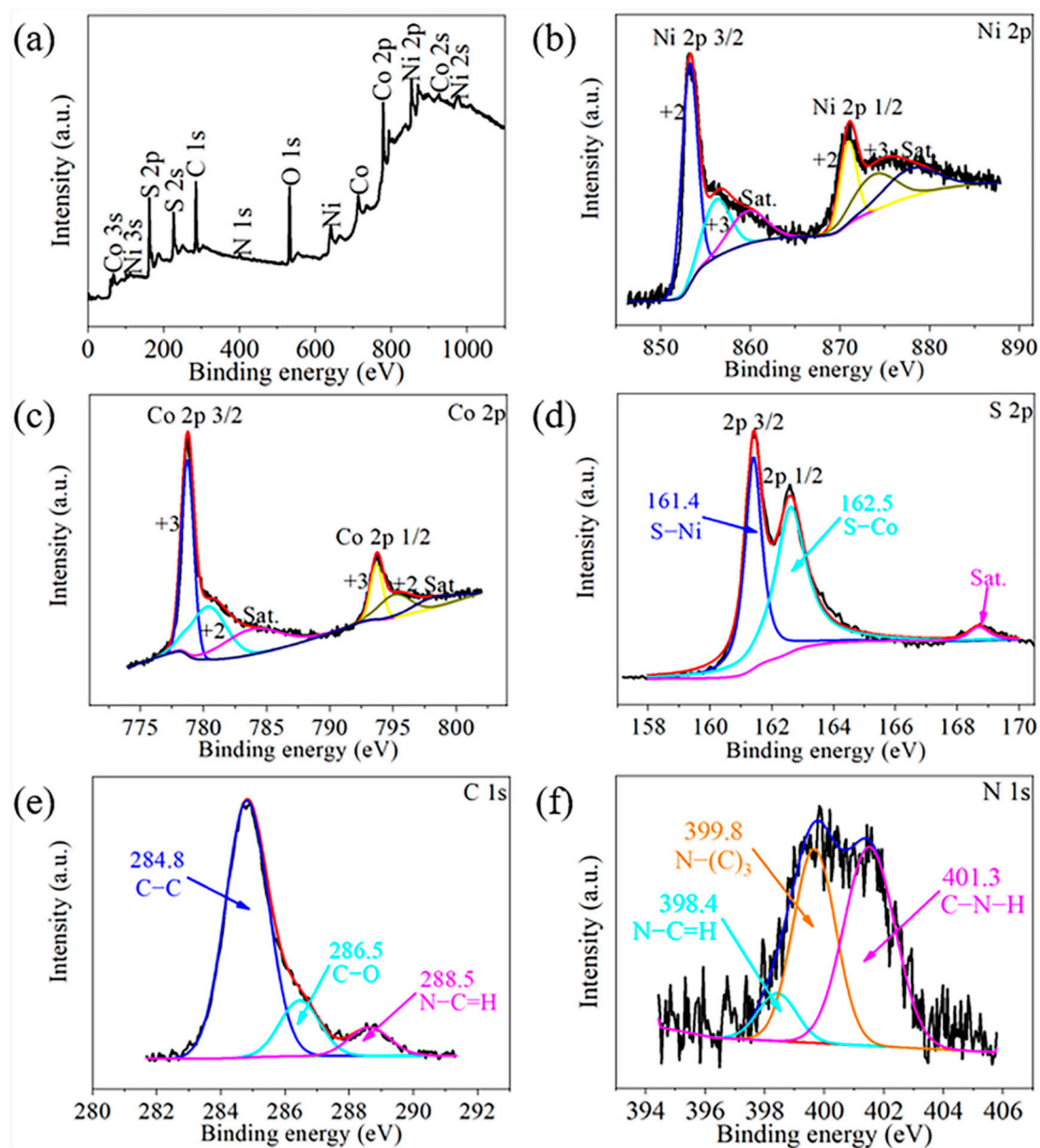


Figure 3. X-ray photoelectron spectra (XPS) of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$: (a) survey spectrum; (b) Ni 2p; (c) Co 2p; (d) S 2p; (e) C 1s and (f) N 1s.

Figure 4a,b shows the morphology of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$. The as-prepared composite is composed of $\text{g-C}_3\text{N}_4$ nanosheets and $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ nanoparticles. Compared with the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ (Figure S2), some macroporous structure is clearly observed in the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ due to self-assemble of larger size $\text{g-C}_3\text{N}_4$ nanosheets as skeleton. The $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ has higher porosity which is also confirmed by the gas sorption experiments in Figure 5. It is seen from TEM images (Figure 4c,d) that a large number of $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ nanoparticles (30–60 nm) were anchored on the surface of $\text{g-C}_3\text{N}_4$ nanosheets (0.8–2.0 μm). The selected area electron diffraction (SAED) pattern displays two sets of diffraction rings that can be indexed to the graphic structure $\text{g-C}_3\text{N}_4$ (yellow rings) and the spinel structure $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ (blue rings), respectively. The high-resolution transmission electron microscope (HRTEM) image shows the formation of the distinct nanoparticle-on-nanosheet heterostructure.

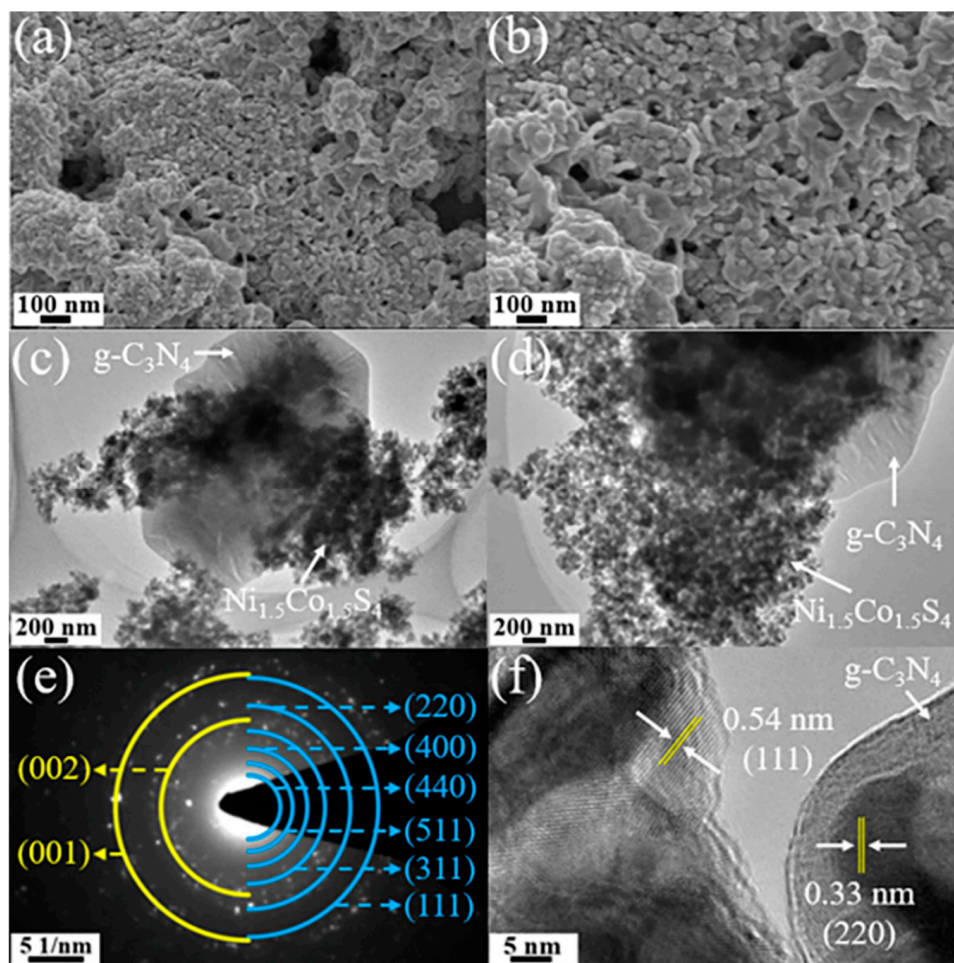


Figure 4. (a,b) SEM images; (c,d) TEM images; (e) SAED (selected area electron diffraction) pattern and (f) TEM image of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$.

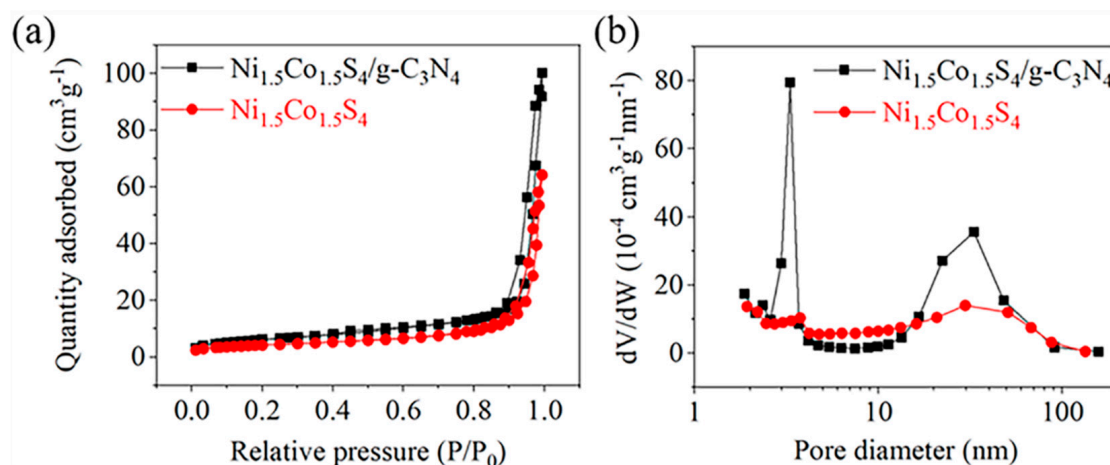


Figure 5. (a) Nitrogen adsorption-desorption isotherm and (b) Pore-size distribution curves of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ and the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$.

The pore structures of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ and the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ were tested by nitrogen adsorption-desorption at 77 K. As shown in Figure 5a, the samples display type IV isotherm with typical H1 hysteresis loop at a relative pressure of 0.8–1.0, which is characteristic for mesoporous materials [37]. The BET specific surface area of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ is $22.5 \text{ m}^2 \text{ g}^{-1}$, which is much higher than that of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ ($15.2 \text{ m}^2 \text{ g}^{-1}$). It is seen from Figure 5b that two samples are mainly composed of mesoporous and macropores, suggesting a hierarchical porous structure (Table S1). The BJH desorption cumulative volume of pores between 1.7 nm and 300.0 nm notably increases from $0.100 \text{ cm}^3 \text{ g}^{-1}$ for $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ to $0.124 \text{ cm}^3 \text{ g}^{-1}$ for the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$, while the average pore diameter slightly decreases from 25.5 nm to 24.9 nm. These results indicate that the addition of $\text{g-C}_3\text{N}_4$ can not only increase the specific surface area, but also optimize the structure of pores. Consequently, an increase of the mesoporous channels in the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ is more beneficial for the fast ion transportation to improve the electrochemical activity of the electrodes.

Figure 6 shows electrochemical properties of the samples tested through the three-electrode system. The CV curves was performed at a scan rate of 50 mV s^{-1} within potential window of -0.4 – 0.6 V . As shown in Figure 6a, the redox peaks of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ is similar to those of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$, which can be attributed to the reversible process of $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$ associated with the insertion and extraction of OH^- anions to and from the electrode materials [38]. The integral area of the CV loop of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ is larger than that of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$, indicating superior electrochemical performance. This result can be further confirmed by GCD tests in Figure 6b. Figure 6c,d show the CV and GCD curves of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ at different scan rates and current densities. They almost maintain the symmetric shape without visible distort, suggesting that the electrode has excellent pseudocapacitive behavior and high coulombic efficiency. The anodic peak current shows a linear relationship with the square root of scan rate (Figure 6e), which indicates that the electrochemical kinetics is a diffusion-controlled process. The specific capacitances of the samples were calculated at the current densities ranging from 1 A g^{-1} to 20 A g^{-1} according to the GCD curves. The $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ composite exhibits a high specific capacitance of 1827 F g^{-1} at a current density of 1 A g^{-1} (Figure 6f), which is 1.53 times that of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ (1191 F g^{-1}). Even if the current density increases 20 times, the specific capacitance still reaches to 1348 F g^{-1} , demonstrating a good rate performance. This result is superior to those of the most recently reported composites such as Ni-Co-S/graphene and $\text{NiCo}_2\text{S}_4/\text{g-C}_3\text{N}_4$ composites [36,39]. Moreover, the CV and GCD curves of pure $\text{g-C}_3\text{N}_4$ nanosheets is shown Figure S3 for a comparison. The specific capacitance of $\text{g-C}_3\text{N}_4$ nanosheets is only 11 F g^{-1} at a current density of 1 A g^{-1} , which is far lower than that of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ composite. In order to further explore the effect of $\text{g-C}_3\text{N}_4$ content on the electrochemical properties, the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ composites with different $\text{g-C}_3\text{N}_4$ content were also prepared and evaluated, shown in Figure S4. When the amount of $\text{g-C}_3\text{N}_4$ is 60 mg, the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ composite shows the highest specific capacitance, owing to maximizing synergetic effects of $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ nanoparticles and $\text{g-C}_3\text{N}_4$ nanosheets. However, the specific capacitance decreases when 90 mg of $\text{g-C}_3\text{N}_4$ is introduced. This superior supercapacitive performance of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ can be mainly ascribed to two reasons. On the one hand, $\text{g-C}_3\text{N}_4$ nanosheets can increase the specific surface area and mesoporous number, which provides more active sites for interface reaction and shortens the pathway of the electrolyte ion diffusion. On the other hand, $\text{g-C}_3\text{N}_4$ nanosheets can improve electrical conductivity of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$, which facilitates for electron transport. As shown in Figure S5, the impedance plots imply that the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ composite possesses smaller internal resistance, faster ion diffusion process and lower charge transfer resistance during the faradic reaction.

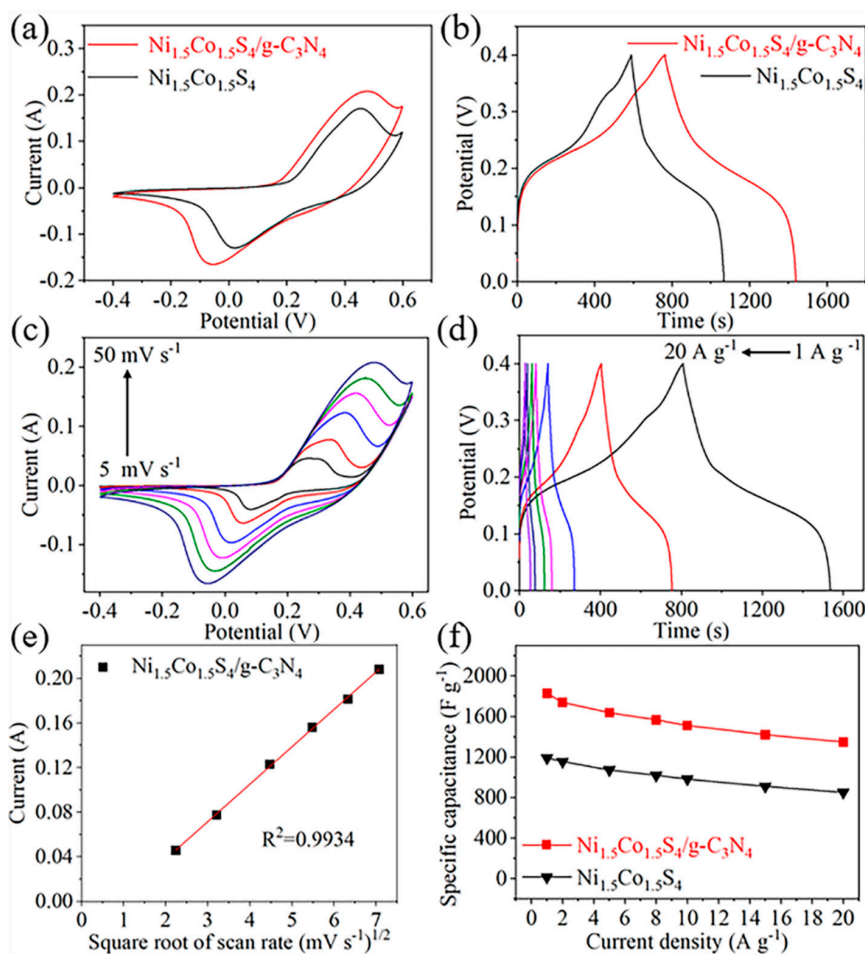


Figure 6. Electrochemical properties of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ and the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$: (a,c) cyclic voltammetry (CV) curves; (b,d) galvanostatic charge-discharge (GCD) curves; (e) the linear relation between the anodic peak current and square root of scan rate; (f) the specific capacitance at different current densities.

Figure 7 shows the performance of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4//\text{AC}$ supercapacitor. The working voltage window of the device was extended to 1.6 V (Figure 7a), because the potential window of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4$ and AC is in the range of -0.4 to 0.6 V and -1 to 0 V, respectively. Apparently, the capacitance of the device comes from the combined contribution of pseudocapacitive and electrical double behaviors. Furthermore, the charge-discharge curves are good symmetric with a coulombic efficiency of over 98.0% at different scan rate, demonstrating its high electrochemical reversibility (Figure 7b). The specific capacitance of the device is calculated to be 138 F g^{-1} at 1 A g^{-1} , and it still retains 76 F g^{-1} even at a high current density of at 20 A g^{-1} (Figure 7c). Figure 7d shows the Nyquist plot of device in the frequency range of 10^{-2} to 10^5 Hz. The equivalent series resistance (R_s) and the charge transfer resistance (R_{ct}) are as low as 0.73 and 1.55Ω , respectively, which are considered to be good for improved charge-discharge rate and power density of the device. The impedance phase angle of the device is approximately -52.16° at a frequency of 0.01 Hz, and reaches -45° at a frequency of 0.04 Hz (Figure 7e). The resistance and reactance of the capacitor have equal magnitudes at the phase angle of -45° , so the frequency at this point is convenient for comparison [40]. This frequency of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4//\text{AC}$ device is comparable to that of an activated carbon-based electric double-layer capacitor (0.05 Hz) [41]. Figure 7f shows the cycling stability of the device at a current density of 10 A g^{-1} . After 8000 cycles, the capacitance retention and the coulombic efficiency still kept about 95.5% and 98.4%, respectively, indicating outstanding long-term stability. Energy density (E) and power density (P) are used as two major parameters to evaluate the performance of supercapacitor

in practical applications [31]. Figure 8 shows a Ragone plot of energy density and power density. The $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4//\text{AC}$ supercapacitor delivers high energy density of 49.0 Wh kg^{-1} at a power density of 799.0 W kg^{-1} . These values surpass those of previously reported symmetric and asymmetric supercapacitors based on $\text{g-C}_3\text{N}_4$ composites, such as $\text{g-C}_3\text{N}_4@\text{Ni}(\text{OH})_2$ [24], $\text{ZnS}/\text{g-C}_3\text{N}_4$ [42] and porous $\text{g-C}_3\text{N}_4$ [43–45].

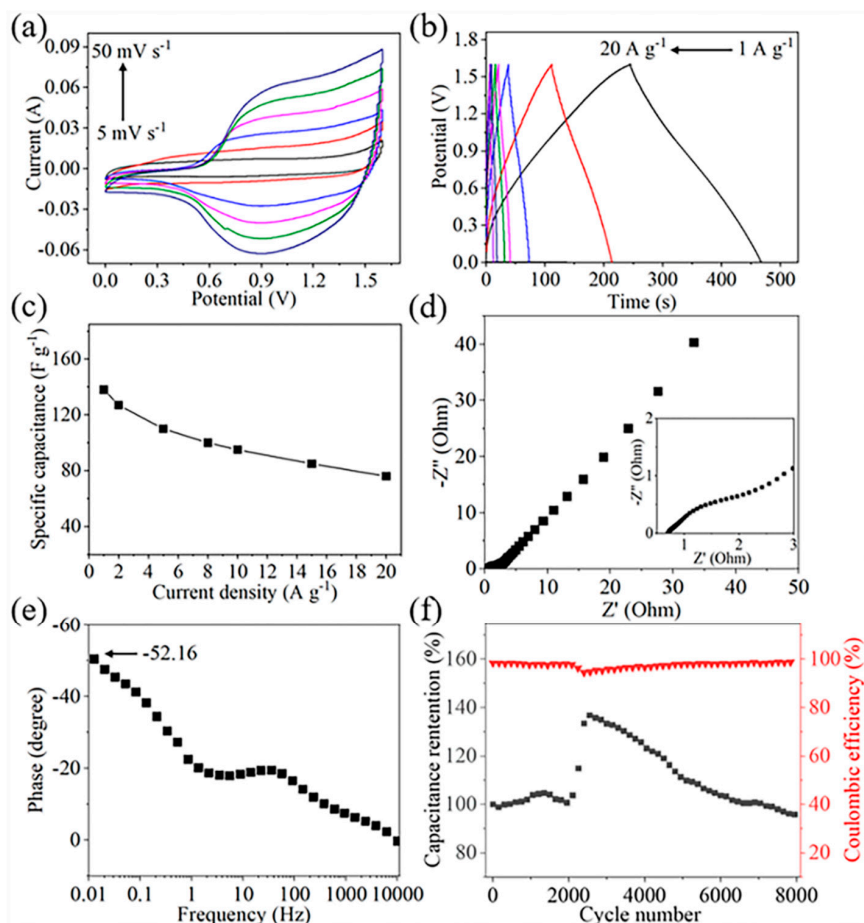


Figure 7. Electrochemical characterizations of the $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4/\text{g-C}_3\text{N}_4//\text{AC}$ supercapacitor (a) CV curves; (b) GCD curves; (c) specific capacitance at different current densities; (d) Nyquist plot; (e) plot of phase angle versus frequency; (f) cycling stability at a current density of 10 A g^{-1} .

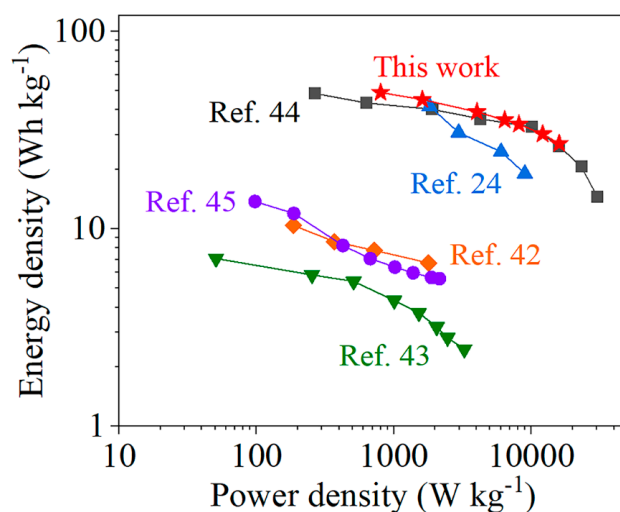


Figure 8. Ragone plot of energy density and power density.

4. Conclusions

In summary, we have prepared the hierarchical porous Ni_{1.5}Co_{1.5}S₄/g-C₃N₄ composite by growing Ni_{1.5}Co_{1.5}S₄ nanoparticles on g-C₃N₄ nanosheets using a hydrothermal method. Compared with pure Ni_{1.5}Co_{1.5}S₄, the Ni_{1.5}Co_{1.5}S₄/g-C₃N₄ composite possesses larger surface area and optimized porous structures. The specific capacitance of the composites is strongly depended on the content of g-C₃N₄ nanosheets. When the adding amount of g-C₃N₄ is 60 mg, the Ni_{1.5}Co_{1.5}S₄/g-C₃N₄ composite exhibits the highest specific capacitance of 1827 F g⁻¹ at a current density of 1 A g⁻¹, which is 1.53 times that of pure Ni_{1.5}Co_{1.5}S₄. The enhancement in specific capacitance could be attributed to maximizing synergetic effects of Ni_{1.5}Co_{1.5}S₄ nanoparticles and g-C₃N₄ nanosheets. A Ni_{1.5}Co_{1.5}S₄/g-C₃N₄//AC asymmetric supercapacitor exhibits a high energy density of 49.0 Wh kg⁻¹ at a power density of 799.0 W kg⁻¹, and outstanding cycle stability with 95.5% capacitance retention after 8000 cycles at a current density of 10 A g⁻¹.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2079-4991/10/9/1631/s1>, Figure S1: XRD pattern of g-C₃N₄, Figure S2: SEM images of pure Ni_{1.5}Co_{1.5}S₄, Figure S3: Electrochemical properties of the Ni_{1.5}Co_{1.5}S₄@g-C₃N₄ with different content of g-C₃N₄: (a) CV curves, (b) GCD curves, Figure S4: Electrochemical properties of the Ni_{1.5}Co_{1.5}S₄/g-C₃N₄ with different content of g-C₃N₄: (a) CV curves, (b) GCD curves, (c) the specific capacitance at different current densities, and (d) the dependence of specific capacitance on g-C₃N₄ content, Figure S5: Nyquist plot of pure Ni_{1.5}Co_{1.5}S₄ and Ni_{1.5}Co_{1.5}S₄@g-C₃N₄, Table S1: The cumulative pore volume of Ni_{1.5}Co_{1.5}S₄ and Ni_{1.5}Co_{1.5}S₄@g-C₃N₄.

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