

Article

Facile Route to Achieve Self-Supported Cu(OH)₂/Ni₃S₂ Composite Electrode on Copper Foam for Enhanced Capacitive Energy Storage Performance

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Abstract: Herein, a Cu(OH)₂/Ni₃S₂ composite was successfully prepared through facile two-step electrodeposition. As the electrode substrate and the only copper source, the copper foam underwent surface oxidation by galvanostatic deposition technology to form Cu(OH)₂, and the subsequent coverage of Ni₃S₂ was achieved by potentiostatic deposition. The Cu(OH)₂ acts as a skeleton, providing support for Ni₃S₂ growth, thus providing more abundant electrochemical active sites. By virtue of the in situ growth strategy and the synergy of different components, the optimized Cu(OH)₂/Ni₃S₂ electrode illustrates significantly enhanced pseudocapacitance performance, with an areal specific capacitance of 11.43 F cm⁻² at 2 mA cm⁻², good coulombic efficiency of 94.55%, and remarkable cyclic stability (83.33% capacitance retention after 5000 cycles).

Keywords: electrode material; copper foam; galvanostatic deposition; potentiostatic deposition



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1. Introduction

Ni-based transition metal sulfides, including NiS, Ni₃S₂, and NiS₂ are now widely used as active electrode materials owing to their rapid faradaic redox reactions, high electrochemical activities, and abundant resources [1–3]. Researchers have explored various ways to prepare nickel sulfides with various morphologies, including the hydrothermal method, electrodeposition technology, and microwave-assisted solvothermal [4–6]. However, the single nickel sulfide component as an electrode material still has the problems of low conductivity and insufficient electrochemical active sites, which could usually be solved from two aspects: one is to adjust the composition of electrode materials, and the other is to improve the preparation strategy [7–9]. The former aims to promote electrochemical performance by doping or compounding. For instance, Sun et al. fabricated a ZnO@Ni₃S₂ array on nickel foam [10]. Although the capacitance characteristics of ZnO are relatively weak, the ZnO array provides skeleton support for the subsequent growth of Ni₃S₂ and facilitates the electrons transport during the process of electrochemical reaction owing to its good conductivity. The electrode exhibited the specific capacitance of 1529 F g⁻¹ at 2 A g⁻¹. As another example, Yang et al. designed core-shell Ni₃S₂@NiCo₂O₄ nanoflakes on nickel foam with 13.4 F cm⁻² at 1 mA cm⁻² [11]. The enhanced energy storage characteristic is ascribed to the synergetic effect of individual constituents. In addition, the specific core-shell structure creates abundant electrochemical active sites for charge storage. The above examples have realized the direct formation of binder-free electrodes for electrochemical characterizations. Furthermore, the researchers realized that the growth of Ni₃S₂

on nickel substrate does not require the additional introduction of a nickel source, that is, the nickel foam as the sole source of Ni in Ni_3S_2 , which has the advantage of reducing the contact resistance, avoids introducing impurities, and provides an unimpeded path for the electronic transmission and thus exhibits enhanced electrochemical characteristics [12,13].

Apart from nickel foam, the traditional electrode substrate includes copper foam, carbon cloth, stainless steel mesh, and so on [14–16]. Among them, the copper foam has similar advantages to nickel foam. In particular, copper foam is easily oxidized to form $\text{Cu}(\text{OH})_2$ (calcined to CuO) at room temperature owing to the active nature of metal copper, and the products have a uniform morphology with high yield [17]. Meanwhile, the copper foam is the reactant and the only copper source that participates in the electrodeposition reaction, which is bound to further reduce the contact resistance and increase the stability of the product. Furthermore, $\text{Cu}(\text{OH})_2$ can be used as a skeleton support for further deposition of other components to obtain composite electrode materials. Therefore, considering the two aspects of the composition and the preparation strategy of the composite materials, the $\text{Cu}(\text{OH})_2$ -based electrode materials derived from copper foam have typical advantages. In general, the process of constructing $\text{Cu}(\text{OH})_2$ from copper foam as the spontaneous source is achieved by surface oxidation in an alkaline solution [14,18]. One way is to add oxidants directly, such as $(\text{NH}_4)_2\text{S}_2\text{O}_8$, and the other is to use electrodeposition. The advantages of the latter are simple operation, high efficiency, and good repeatability [19].

Inspired by the above analysis, herein, $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ composite was designed to grow on copper foam substrate by electrodeposition technique. In detail, galvanostatic deposition was performed to realize the direct formation of $\text{Cu}(\text{OH})_2$ nanostructures on copper substrate, and then the further coating of Ni_3S_2 was completed by potentiostatic deposition. Copper foam functions as a substrate and the only copper source. The $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ electrode illustrates that the enhanced pseudocapacitance performance is owing to the in situ growth technique and composite structure, which reduces the contact resistance and provides more active sites for electrochemical reaction.

2. Materials and Methods

2.1. Materials

After cutting the copper foam (130 PPI, 1.5 mm thick) into $1\text{ cm} \times 1.5\text{ cm}$ pieces, they were washed with dilute hydrochloric acid, acetone, ethanol, and deionized water to remove surface impurities, and they were finally vacuum dried. The chemical reagents included NaOH, nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), and thiourea ($\text{CH}_4\text{N}_2\text{S}$).

2.2. Synthesis of $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ Composite Electrode

The direct growth of $\text{Cu}(\text{OH})_2$ nanostructure on copper substrate was realized by using an in situ electrodeposition technology according to previous reports, with some modifications [20,21]. Briefly, a three-electrode setup was exploited to perform galvanostatic deposition for 300 s at a current density of 0.05 A in 2 M NaOH electrolyte. The three-electrode system was composed of copper foam, saturated calomel electrode (SCE) 0.2415 V vs. reversible hydrogen electrode (RHE), and a Pt plate. They served as working electrode, reference electrode, and counter electrode, respectively.

According to previous reports with some modifications [22,23], the second step for Ni_3S_2 potentiostatic deposition was carried out for 1200 s at -1.1 V versus SCE by the same system as above, except the $\text{Cu}(\text{OH})_2$ deposited on copper substrate obtained previously was used as the working electrode. The electrolyte contains 0.05 M NiCl_2 and 0.5 M $\text{CH}_4\text{N}_2\text{S}$. In addition, for comparison, the controlled samples were obtained from different potentiostatic deposition times. The samples obtained from 60, 600, 1200, and 2400 s are abbreviated as S-1, S-10, S-20 and S-40, respectively.

2.3. Characterization

The products were characterized by X-ray diffraction (Cu $\text{K}\alpha$ radiation with $\lambda = 1.5406\text{ \AA}$, Shimadzu Co., Ltd, Kyoto, Japan), field-emission scanning electron microscopy (FE-SEM

JSM-7610F, Tokyo, Japan), and X-ray photoelectron spectroscopy (ESCALAB 250Xi, ThermoFisher Scientific Co., Ltd, Waltham, MA, USA). The electrochemical characterizations, including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and cycling performance, were conducted on a CHI 760E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd, Shanghai, China). The test system was composed of $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ supported by copper foam, Ag/AgCl (saturated KCl solution, 0.197 V vs. RHE), and a Pt plate. They served as working, reference, and counter electrode in 2 M NaOH solution.

3. Results

Figure 1 illustrates the stepwise preparation process for the $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ electrode. Firstly, galvanostatic deposition was applied to deposit $\text{Cu}(\text{OH})_2$ nanorods on copper substrate. The copper foam functioned as electrode substrate and copper source. Potentiostatic deposition was then adopted through a similar three-electrode system, which realized the deposition of the Ni_3S_2 layer on the $\text{Cu}(\text{OH})_2$ surface, and the amount of Ni_3S_2 increased gradually with the increase of the deposition time.

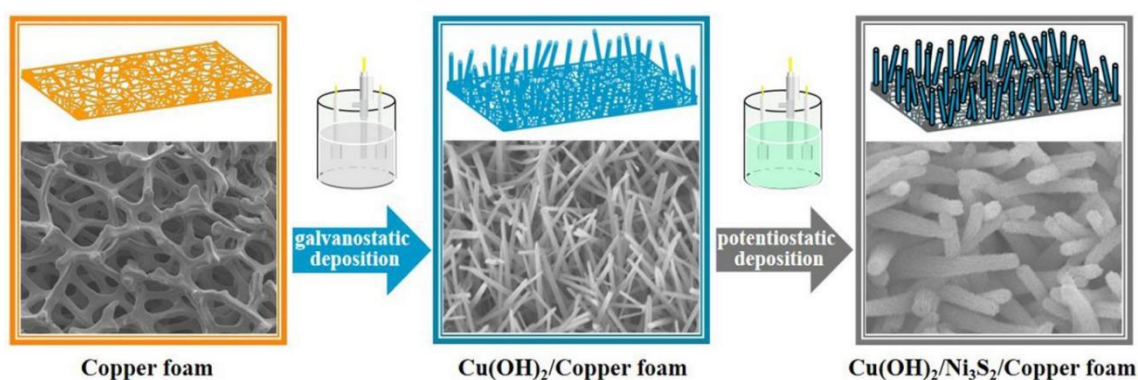


Figure 1. Schematic preparation of $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ electrode.

The FE-SEM images of $\text{Cu}(\text{OH})_2$ are revealed in Figure 2. As seen in Figure 2a, the copper foam maintains a 3D structure as the working electrode, and the surface becomes rough due to the galvanostatic deposition of $\text{Cu}(\text{OH})_2$. The high magnification image in Figure 2b exhibits highly ordered densely $\text{Cu}(\text{OH})_2$ nanorod arrays, growing outward from the surface of the copper substrate. The nanorods have a smooth surface with a diameter of ca. 130 nm accompanied by regular prismatic protrusions (Figure 2c,d).

Ni_3S_2 was further grown on the surface of $\text{Cu}(\text{OH})_2$ nanorods by subsequent potentiostatic deposition that lasted for 20 min. Figure 3 reveals the typical FE-SEM images of the $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ composite. As can be seen in Figure 3a, dense Ni_3S_2 uniformly and completely coats the surface of the $\text{Cu}(\text{OH})_2$ nanorods (Figure 3b). The high magnification image in Figure 3c demonstrates that $\text{Cu}(\text{OH})_2$ nanorods turn thicker because they are wrapped of a layer of Ni_3S_2 nanoflakes, and they are up to approximately 250 nm in diameter. Furthermore, these bent Ni_3S_2 nanoflakes with a thickness of ca. 6 nm are connected to form an irregular network structure (Figure 3d).

The X-ray diffraction (XRD) patterns of $\text{Cu}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ composite on copper foam are shown in Figure 4a, in which the two strongest diffraction peaks marked with squares can be indexed to the (111) and (200) planes of cubic Cu metal (JCPDS No. 01-1241), originating from the copper substrate. In addition, the black line illustrates seven diffraction peaks, marked with asterisks, which are in good agreement with (020), (021), (002), (111), (041), (130), and (150) planes of orthorhombic $\text{Cu}(\text{OH})_2$ (JCPDS No. 13-0420) [14,18]. This proves that galvanostatic deposition realizes the formation of a relatively high purity of the $\text{Cu}(\text{OH})_2$ phase on the surface of copper substrate. After potentiostatic deposition, besides the above two categories, the additional diffraction peaks marked with triangles on the red line match the (101), (110), (003), (202), (211), and (122)

crystalline planes of Ni_3S_2 (JCPDS card No. 44-1418) [4,24] further confirms the formation of $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ composite.

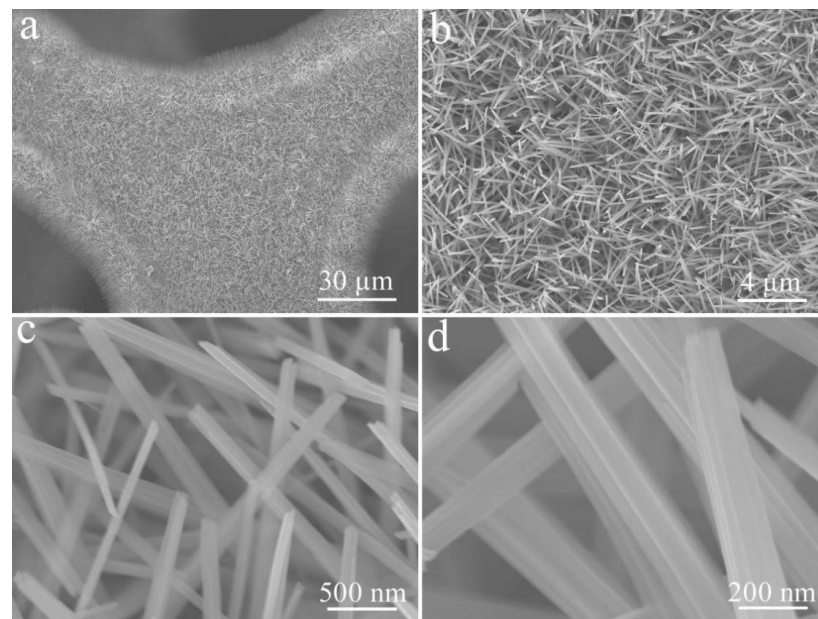


Figure 2. (a,b) Low-magnification and (c,d) high-magnification FE-SEM images of $\text{Cu}(\text{OH})_2$ nanorods grown on copper foam.

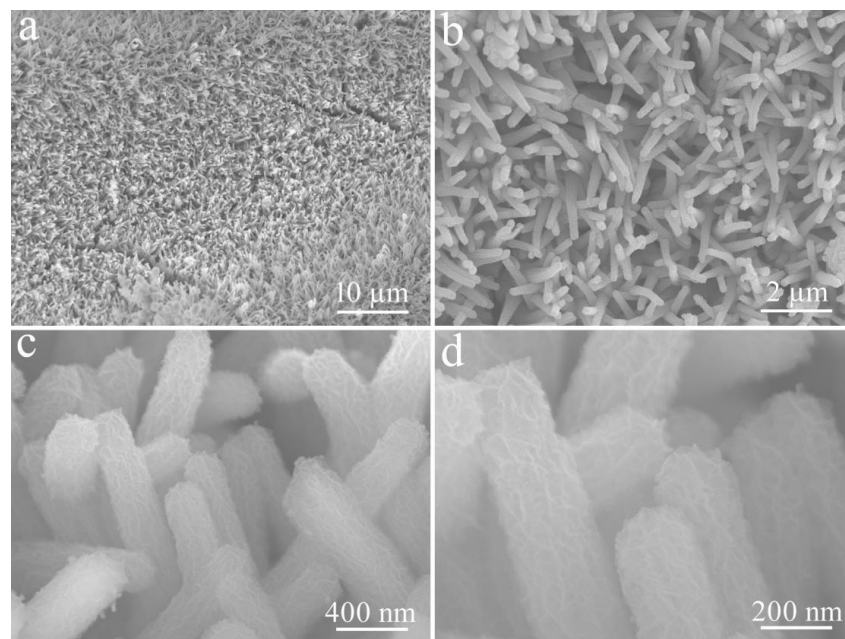


Figure 3. (a,b) Low-magnification and (c,d) high-magnification FE-SEM images of $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ composite.

The X-ray photoelectron spectroscopy (XPS) full spectrum of the $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ composite is displayed in Figure 4b, which proves the existence of Ni, Cu, O, and S elements. In Figure 4c, two primary peaks at 873.80 and 856.10 eV are assigned to $\text{Ni } 2p_{1/2}$ and $\text{Ni } 2p_{3/2}$, with the separation energy of 17.7 eV, indicating the presence of Ni^{2+} and Ni^{3+} [25]. In addition, the corresponding satellite peaks are at 879.70 and 861.70 eV. Figure 4d presents the Cu 2p spectrum; the two prominent peaks at 954.5 and 934.7 eV come from $\text{Cu } 2p_{1/2}$ and $\text{Cu } 2p_{3/2}$, respectively, and the two additional small peaks at 952.45 and 932.5 eV belong to metal copper, which comes from the exposed copper foam substrate [26,27]. In

addition, three accompanying satellite peaks are located at 963.0, 944.2, and 941.9 eV. As for the O 1s spectrum in Figure 4e, the deconvoluted O 1s spectrum situated at 531.7 and 530.9 eV are marked to the oxygen of Cu(OH)₂ and hydroxyl group [26,28]. The S 2p spectrum in Figure 4f depicts two peaks at 162.6 and 161.4 eV, corresponding to S 2p_{1/2} and S 2p_{3/2}, respectively, which can be associated with S^{2−}. Another weak peak of S–O at 168.15 eV is assigned to the oxygen of the hydroxyl group bonded to sulfur, as previously reported [13,29–31].

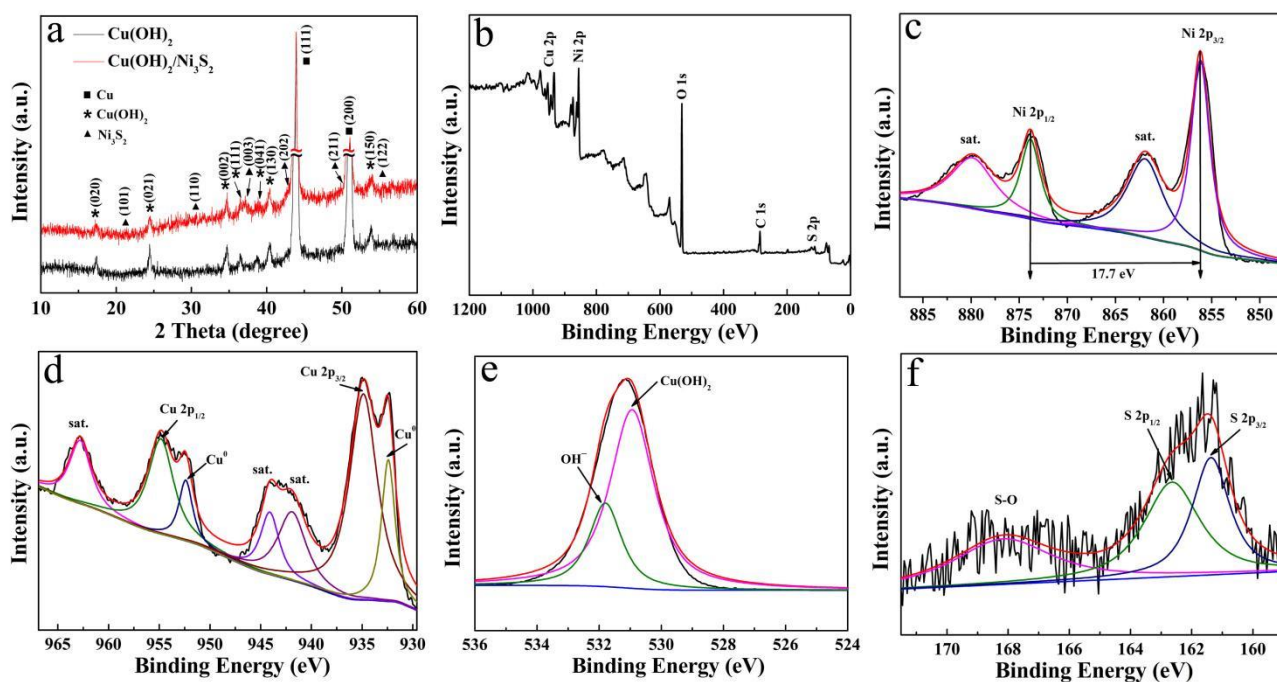
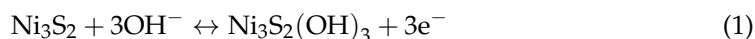


Figure 4. XRD patterns of Cu(OH)₂ and Cu(OH)₂/Ni₃S₂ (a). XPS spectra of Cu(OH)₂/Ni₃S₂: survey scan (b), Ni 2p (c), Cu 2p (d), O 1s (e), and S 2p (f).

CV and GCD tests were conducted to assess the pseudocapacitance performances of the Cu(OH)₂/Ni₃S₂ electrode. Figure 5a depicts the CV curves of the Cu(OH)₂/Ni₃S₂, Ni₃S₂, and Cu(OH)₂ electrodes at the scan rate of 10 mV s^{−1}. The specific capacitances are proportional to the integral area of CV curves, and thus the Cu(OH)₂/Ni₃S₂ represents the maximum specific capacitance [32]. Moreover, the CV curve of Cu(OH)₂/Ni₃S₂ displays a pair of redox couples, which can be identified as Ni²⁺/Ni³⁺ attributing to the pseudocapacitive reaction [33]:



The GCD curves of the three electrodes with the current density of 2 mA cm^{−2} are shown in Figure 5b. Among them, the Cu(OH)₂/Ni₃S₂ composite exhibits a longer discharge time than Ni₃S₂ and Cu(OH)₂, indicating the largest specific capacitance of the Cu(OH)₂/Ni₃S₂ composite. The enhanced pseudocapacitance performance of the Cu(OH)₂/Ni₃S₂ composite is ascribed to the synergy between Ni₃S₂ and Cu(OH)₂. Although the capacitance characteristic of a single component is relatively weak, the electrochemical performance of Ni₃S₂ is significantly enhanced upon introduction of Cu(OH)₂ (Figure 5c). Without the support of the Cu(OH)₂ component, the bent Ni₃S₂ nanoflakes are irregularly interlinked and scattered on the copper substrate, as displayed in Figure 6. Consequently, the Cu(OH)₂ nanorods provide support for the uniform deposition of Ni₃S₂, and thus more abundant electrochemical active sites are generated.

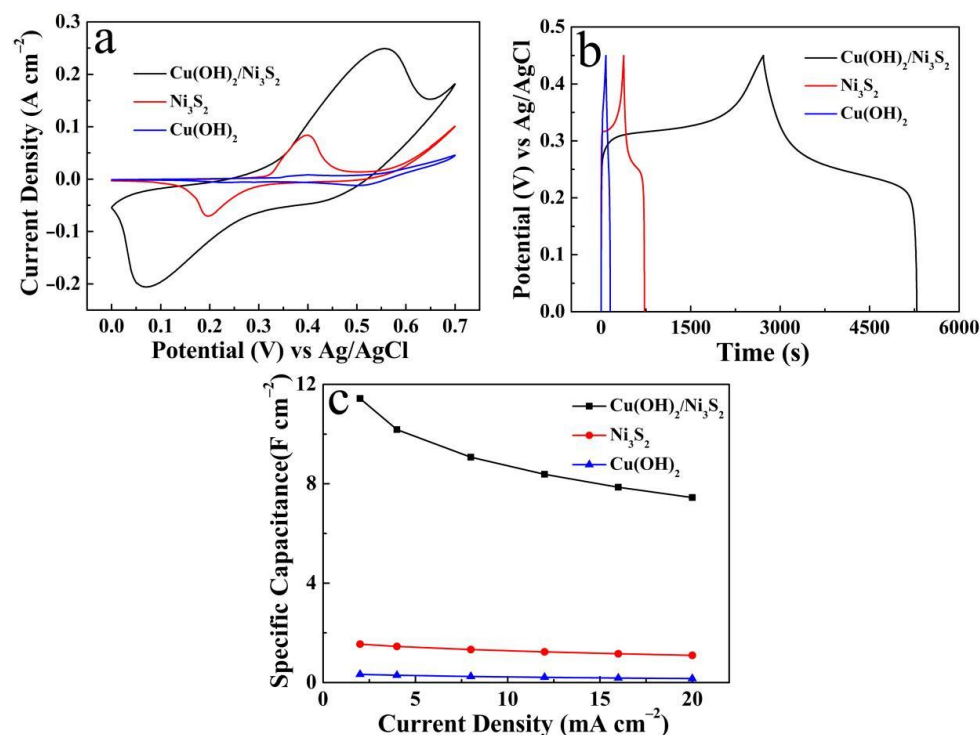


Figure 5. (a) CV curves at 10 mV s⁻¹; (b) GCD curves and (c) specific capacitance at different current densities of the Cu(OH)₂/Ni₃S₂, Ni₃S₂, and Cu(OH)₂ electrode.

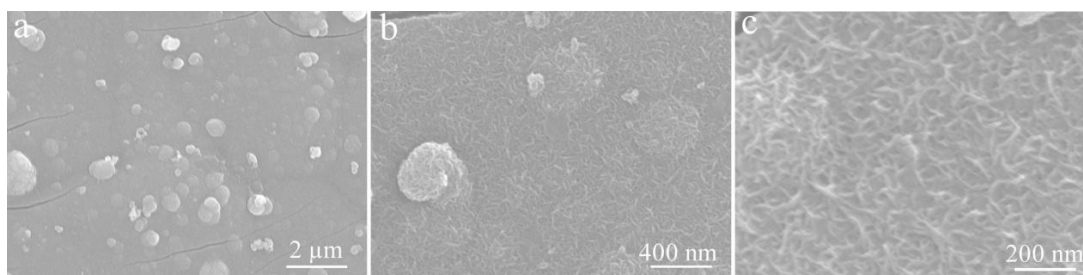


Figure 6. (a) Low-magnification and (b,c) high-magnification FE-SEM images of single Ni₃S₂ deposited on the copper foam.

In addition, the amount of Ni₃S₂ gradually increases with the deposition time. At the early stage of potentiostatic deposition (1 min, labeled as S-1, Figure 7a,b), the Cu(OH)₂ retains the original nanorod morphology with sharp tips, and the surface is rough due to the deposition of a thin layer of Ni₃S₂. When the electrodeposition reaches 10 min (S-10), as seen in Figure 7c,d, in addition to the gradually increasing amount of Ni₃S₂, scattered Ni₃S₂ particles are visible on the surface of the Cu(OH)₂ nanorods, and the sharp tips gradually fade away. When the electrodeposition is extended to 20 min (S-20), the high-density Ni₃S₂ nanosheets are uniformly covered on the surface of the Cu(OH)₂ nanorods arrays (Figure 7e,f). The electrodeposition of up to 40 min results in the disordered aggregation of Ni₃S₂ particles due to the excessive continued deposition of Ni₃S₂, and the Cu(OH)₂ nanorods structure is partially obscured, as shown in Figure 7g,h.

The electrochemical behavior of the above four samples was investigated to explore the optimal deposition time of Ni₃S₂. Figure 8a compares the CV curves of the four samples at 10 mV s⁻¹. Following the rule that the specific capacitance is proportional to the enclosed area of the CV curves, it is concluded that the longer the deposition time of Ni₃S₂, the higher the specific capacitance of the sample [32]. Figure 8b records the GCD curves with the current density of 2 mA cm⁻², which confirms the same conclusion as the CV test. That is, the areal specific capacitance value follows the order as S-40 > S-20 > S-10 > S-1 (Figure 8c).

However, it is to be noted that, with the gradual increase of the electrodeposition time of Ni_3S_2 , the coulomb efficiency reaches the maximum of 94.55 % at S-20 and then decreases significantly. The detailed data, including the charge/discharge time and corresponding specific capacitance of the four samples at 2 mA cm^{-2} , are recorded in the form of an inserted table in Figure 8d. In addition, Figure 8e displays the average R_{ESR} line chart of the four samples and the calculation formula. The parameters involved in the formula are derived from the four small figures on the left, which describe the voltage drop at different current densities of the corresponding four samples. Additionally, S-20 shows the lowest R_{ESR} value with $1.28 \Omega \text{ cm}^{-2}$.

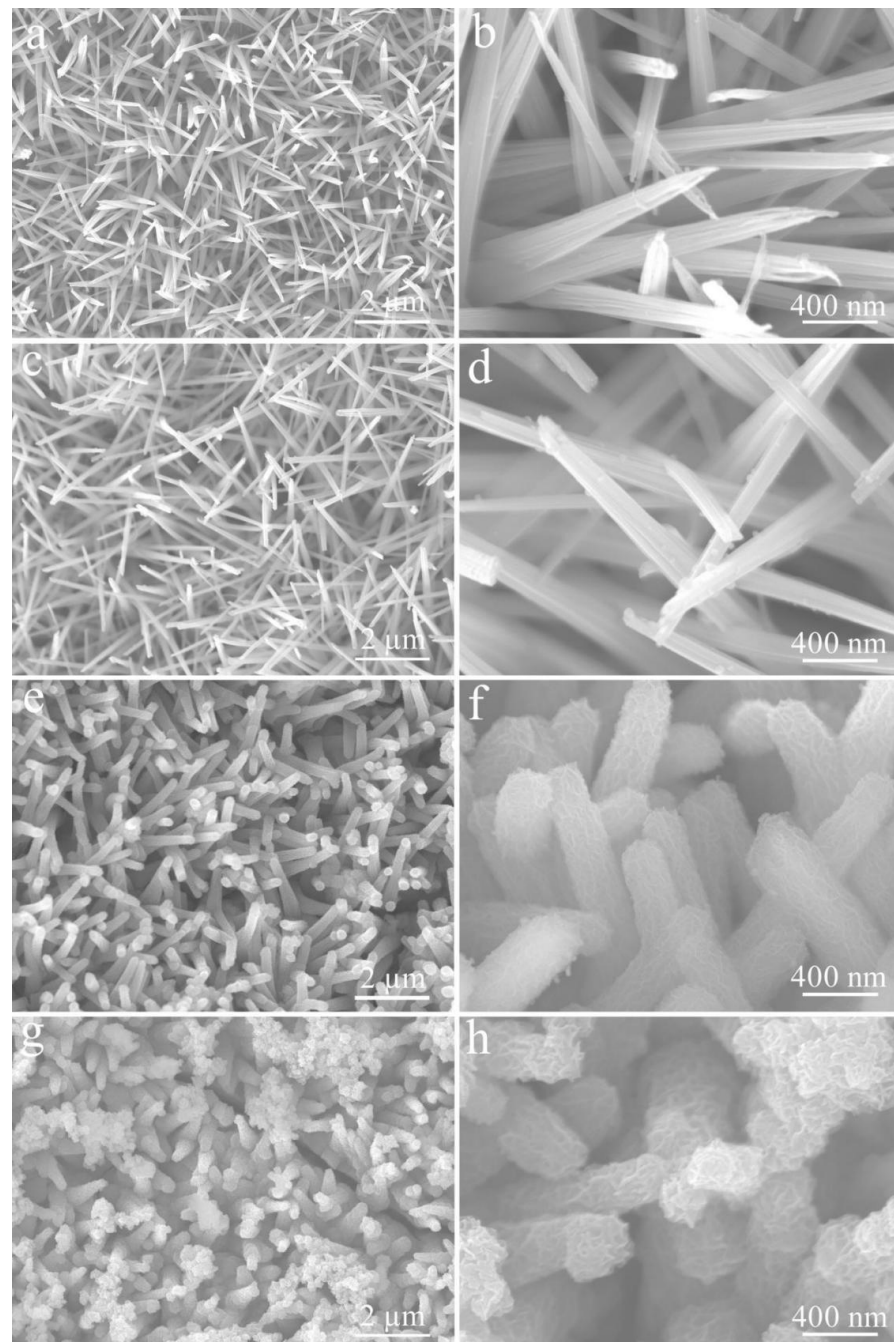


Figure 7. FE-SEM images of the $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ composite grown on copper foam with different potentiostatic deposition times of Ni_3S_2 : (a,b) S-1; (c,d) S-10; (e,f) S-20; and (g,h) S-40.

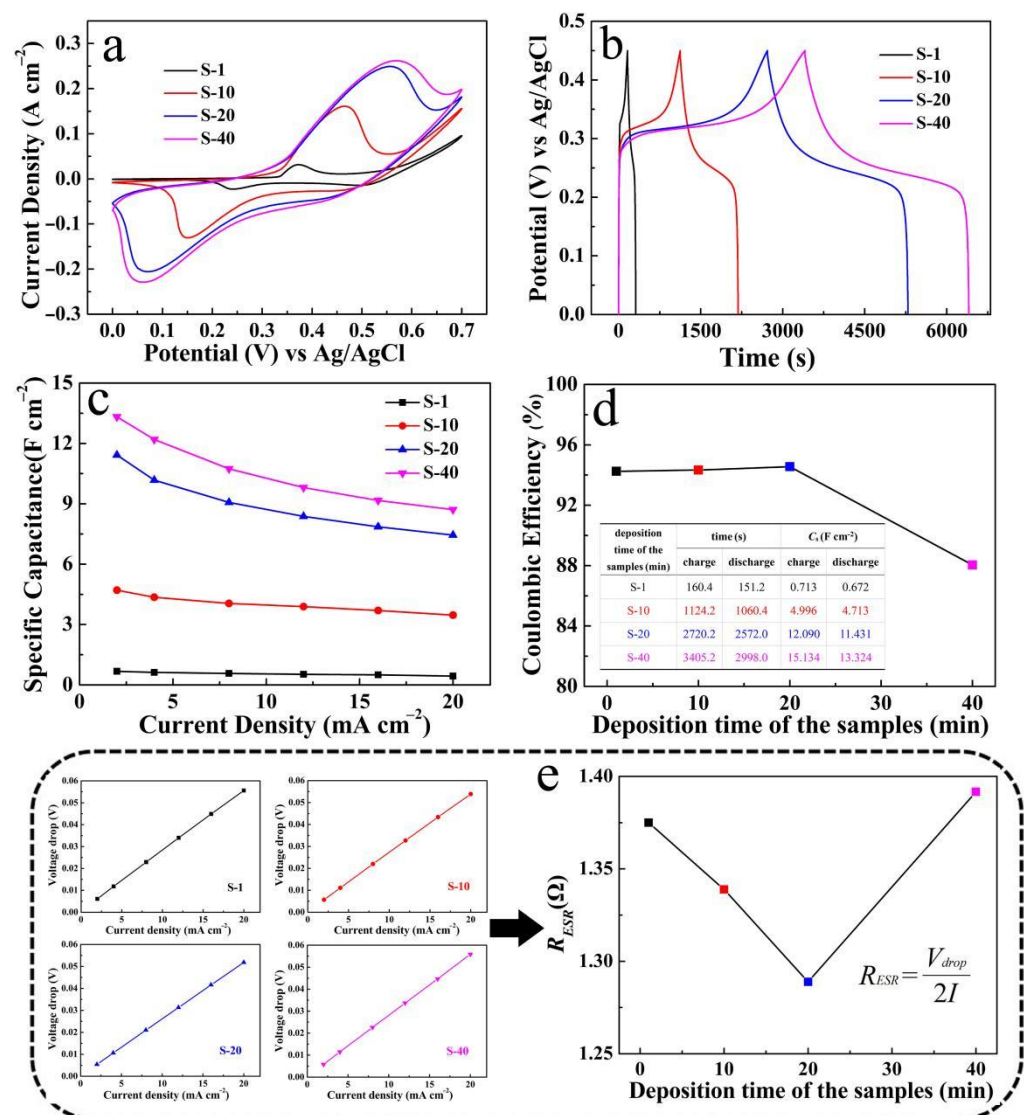


Figure 8. (a) CV curves, (b) GCD curves, (c) specific capacitances at different current densities, (d) coulombic efficiency, and (e) average R_{ESR} of the $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ composite grown on copper foam with different potentiostatic deposition time of Ni_3S_2 .

Based on the above analysis, the areal-specific capacitance of the $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ electrode gradually increases with the increase of the deposition time of Ni_3S_2 . However, the full play of the electrochemical characteristics of Ni_3S_2 component is based on the supporting role of $\text{Cu}(\text{OH})_2$ nanorods. Therefore, when the deposition time continues to expand to S-40, the disordered accumulation of Ni_3S_2 begins to destroy $\text{Cu}(\text{OH})_2$ nanorods (Figure 7g,h). The accumulation is bound to hinder the transmission of ions/electrons and significantly reduce the coulombic efficiency and average R_{ESR} . Therefore, the preparation parameter of S-20 is selected for further study.

Figure 9a reveals the CV curves of the $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ electrode (S-20) at various scan rates. A pair of broad redox peaks illustrates that capacitance primarily arises from the pseudocapacitive reactions process. With the increase of scan rate, the integral area surrounded by the CV curves increases gradually, while the specific capacitance gradually decreases, because the active sites inside the electrode are not able to undergo sufficient electrochemical reaction with the electrolyte at a large scan rate [34,35]. The GCD curves at different current densities are recorded in Figure 9b; the smaller the current density, the longer the discharge time required, but the larger the corresponding specific capacitance [36]. The trend can be seen in Figure 9c according to the calculation formula of specific capacitance [11]. The

specific capacitance of the $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ composite electrode reaches 11.43, 10.18, 9.07, 8.38, 7.86, and 7.45 F cm^{-2} when the current density increases from 2 to 20 mA cm^{-2} , respectively. The voltage drop at various current densities are displayed in Figure 9d, and the average R_{ESR} is $1.28 \Omega \text{ cm}^{-2}$. In addition, the electrochemical performance data of single component $\text{Cu}(\text{OH})_2$ and Ni_3S_2 , including CV curves and GCD curves, are also depicted in Figure 10a–d. The specific capacitance value of Ni_3S_2 at different current densities can be obtained in Figure 10e, and it reaches 1.55 F cm^{-2} at 2 mA cm^{-2} . Figure 10f reveals the voltage drop at various current densities of Ni_3S_2 ; according to the curve, the average R_{ESR} of Ni_3S_2 could be calculated to be $1.77 \Omega \text{ cm}^{-2}$, which is significantly higher than that of $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ composite. From these data, it can be proved that the addition of $\text{Cu}(\text{OH})_2$ improves the conductivity of electrode materials and forms more abundant electrochemical active sites for pseudocapacitance reaction.

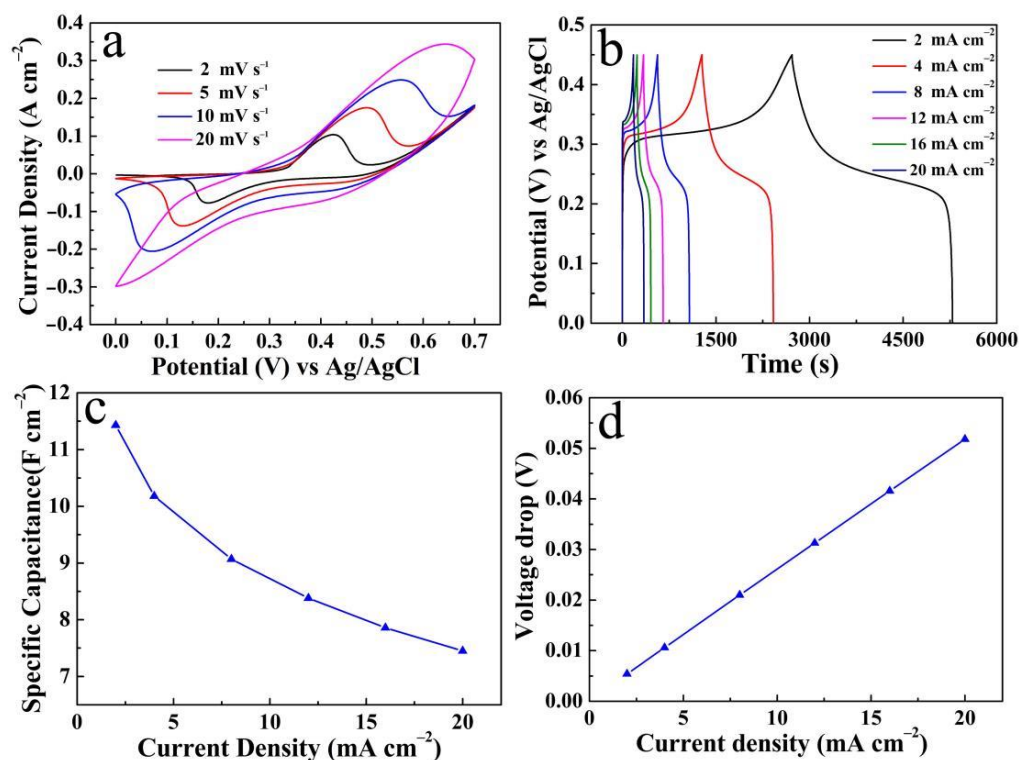


Figure 9. (a) CV curves, (b) GCD curves, (c) specific capacitances, and (d) voltage drops at different current densities of the $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ composite (S-20).

The specific capacitance retention of the $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ electrode is revealed in Figure 11. The specific capacitance reaches 91.67% at the 500th cycle and maintains the initial 83.33% within 5000 cycles. In addition, after the stability test, the morphology of the $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ electrode does not show apparent changes, which proves that the in situ electrodeposition technology is conducive to improving the stability of the electrode material (Figure 12).

A comparison of the specific capacitance of the $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ composite with similar materials in the literature is shown in Table 1. It confirms that the properties of our products are comparable to or even better than that reported in the literature.

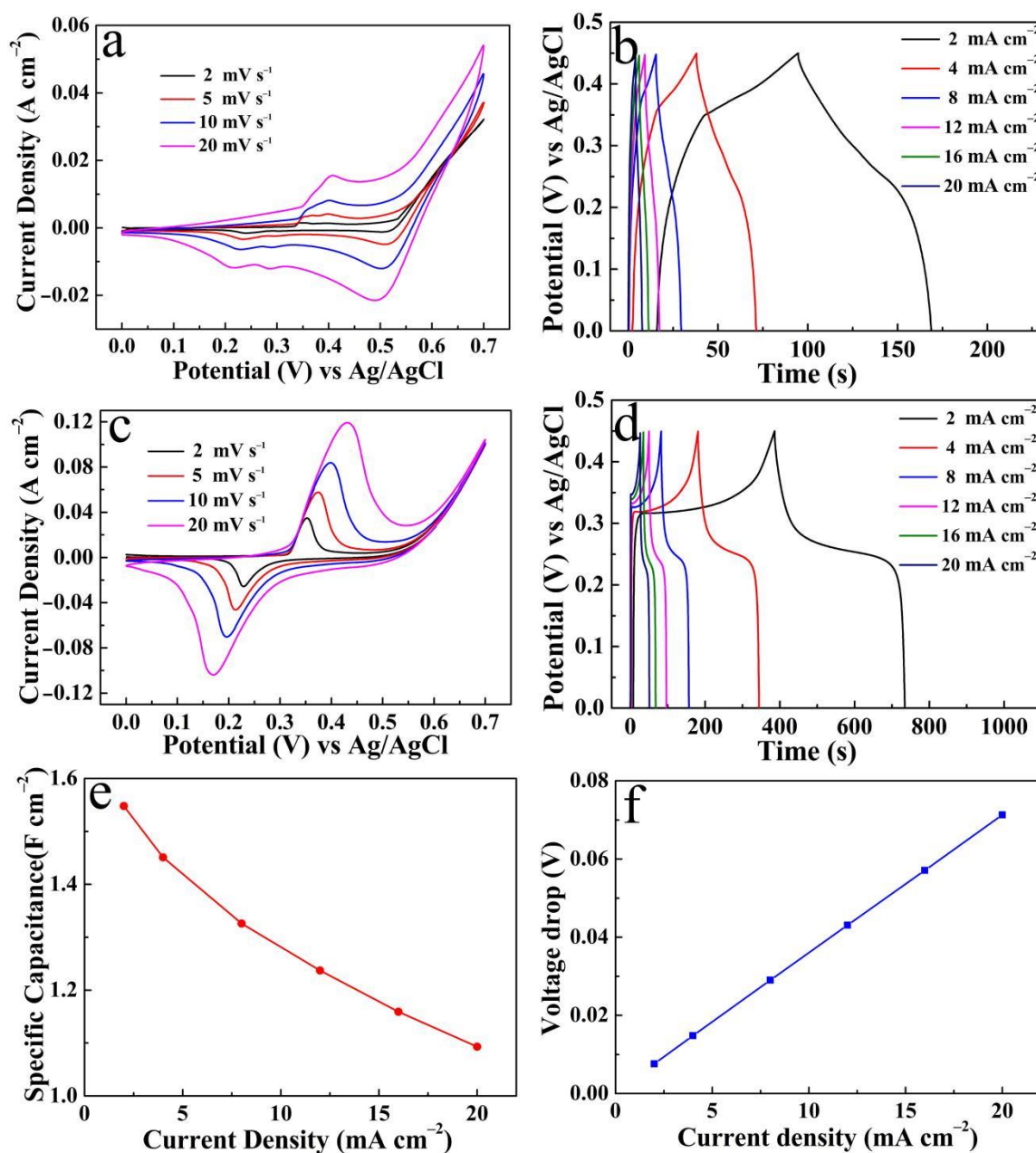


Figure 10. (a) CV curves and (b) GCD curves of $\text{Cu}(\text{OH})_2$, (c) CV curves, (d) GCD curves, (e) specific capacitances, and (f) voltage drops at different current densities of Ni_3S_2 .

Table 1. Comparison of specific capacitance of $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ with similar materials.

Electrode Material	Substrate	Current Density (mA cm^{-2})	Specific Capacitance (F cm^{-2})	Refs.
$\text{Cu}(\text{OH})_2$	copper foam	2	2.15	[14]
$\text{Cu}(\text{OH})_2$	nanoporous copper	3	0.78	[37]
Ni_3S_2	nickel foam	1	2.52	[38]
$\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$	copper foam	2	4.85	[21]
$\text{Cu}(\text{OH})_2@\text{Co}(\text{OH})_2$	copper foam	4	0.43	[26]
$\text{Cu}(\text{OH})_2@\text{Ni}_2(\text{OH})_2\text{CO}_3$	copper foam	1	1.09	[39]
$\text{Ni}_3\text{S}_2@\text{ppy}$	nickel foam	2	3.15	[12]
$\text{Ni}_3\text{S}_2@\text{Co}_9\text{S}_8$	nickel foam	2	9.79	[33]
$\text{Ni}_3\text{S}_2@\text{Mn}(\text{OH})_2$	nickel foam	1	6.43	[40]
$\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$	copper foam	2	11.43	this work

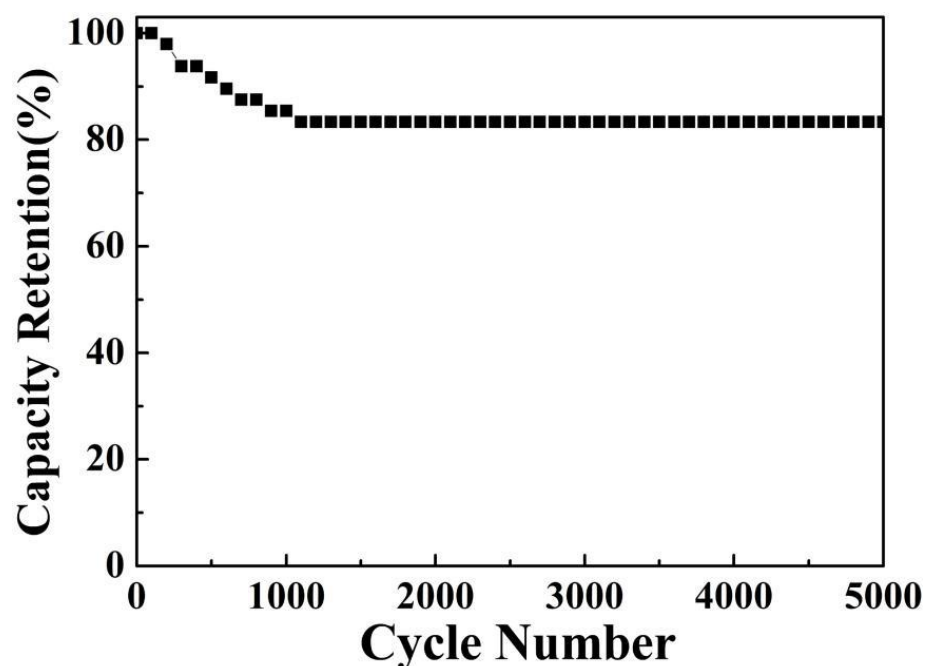


Figure 11. Cycling performance of the $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ electrode.

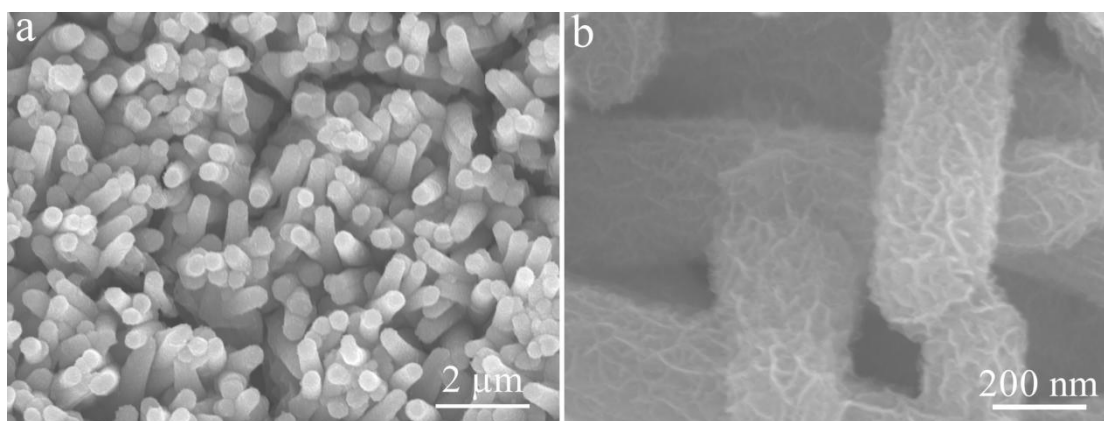


Figure 12. (a) Low-magnification and (b) high-magnification FE-SEM images of the $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ composite after the electrochemical test.

In our reaction system, the excellent pseudocapacitance performance of the optimized $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ electrode mainly comes from the following three aspects: (1) Copper foam was taken as the electrode substrate owing to its high electrical conductivity and metal activity, which can be utilized as the copper source to directly form $\text{Cu}(\text{OH})_2$ at room temperature [14]. Such in situ growth with the substrate as the spontaneous source is bound to be more conducive to reducing the contact resistance and forming a stable interfacial contact between the electrode material and the substrate [17]; (2) Ni_3S_2 , as an electrode material, exhibits better electrochemical activity than their corresponding oxides because of the lower electronegativity of sulfur [41]. In particular, the potentiostatic deposition supported by $\text{Cu}(\text{OH})_2$ nanorod arrays can form abundant electrochemical active sites, so as to achieve ultra-high areal specific capacitance [42]; (3) The hierarchical structure of the $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ electrode constructed by the stepwise electrode deposition facilitates the ions/electrons transmission and is also beneficial to mobilize the synergy of different component [36,43].

4. Conclusions

Self-supported $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ composite electrodes have been prepared on copper substrate by combining galvanostatic and potentiostatic deposition. The in situ electrodeposition technology provided a facile route to synthesis such a hierarchical structure. The copper foam as both electrode substrate and spontaneous source reduced the contact resistance and allowed the uniform and dense growth of $\text{Cu}(\text{OH})_2$ on its surface. Furthermore, the $\text{Cu}(\text{OH})_2$ nanorods array acting as a backbone supported the ordered assembly of the Ni_3S_2 nanostructure, endowing the product enhanced electrochemical activity and stability. Benefiting from the joint contribution of the above factors, the $\text{Cu}(\text{OH})_2/\text{Ni}_3\text{S}_2$ composite demonstrated a prominent specific capacitance of 11.43 F cm^{-2} at 2 mA cm^{-2} , a high coulombic efficiency of 94.55%, and remarkable cyclic behavior (83.33% capacitance retention after 5000 cycles). Moreover, the hierarchical electrodeposition construction strategy can be extended to design other $\text{Cu}(\text{OH})_2$ -based high performance pseudocapacitive electrode materials to meet the various situation of practical energy storage applications.

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