Facile Route to Achieve Self-Supported Cu(OH)$_2$/Ni$_3$S$_2$ Composite Electrode on Copper Foam for Enhanced Capacitive Energy Storage Performance

Sa Lv 1*, Peiyu Geng 1, Yaodan Chi 1, Huan Wang 1, Xuefeng Chu 1, Gongda Chen 2*, Wenshi Shang 1, Chao Wang 1, Jia Yang 1, Zhifei Cheng 1 and Xiaotian Yang 1*

Abstract: Herein, a Cu(OH)$_2$/Ni$_3$S$_2$ 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 Ni$_3$S$_2$ was achieved by potentiostatic deposition. The Cu(OH)$_2$ acts as a skeleton, providing support for Ni$_3$S$_2$ 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)$_2$/Ni$_3$S$_2$ 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

1. Introduction

Ni-based transition metal sulfides, including NiS, Ni$_3$S$_2$, and NiS$_2$ 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@Ni$_3$S$_2$ 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 Ni$_3$S$_2$ 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 Ni$_3$S$_2$/NiCo$_2$O$_4$ 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 Ni$_3$S$_2$...
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$_3$S$_2$, 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 Cu(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, Cu(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 Cu(OH)$_2$-based electrode materials derived from copper foam have typical advantages. In general, the process of constructing Cu(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 (NH$_4$)$_2$S$_2$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, Cu(OH)$_2$/Ni$_3$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 Cu(OH)$_2$ nanostructures on copper substrate, and then the further coating of Ni$_3$S$_2$ was completed by potentiostatic deposition. Copper foam functions as a substrate and the only copper source. The Cu(OH)$_2$/Ni$_3$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 cm $\times$ 1.5 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 (NiCl$_2$·6H$_2$O), and thiourea (CH$_4$N$_2$S).

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

The direct growth of Cu(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$_3$S$_2$ potentiostatic deposition was carried out for 1200 s at $-1.1$ V versus SCE by the same system as above, except the Cu(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 CH$_4$N$_2$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 K$\alpha$ radiation with $\lambda = 1.5406$ Å, Shimadzu Co., Ltd, Kyoto, Japan), field-emission scanning electron microscopy (FE-SEM
Firstly, galvanostatic deposition was applied to deposit Cu(OH)$_2$ and Ni$_3$S$_2$ supported by copper foam (Figure 1). This proves that galvanostatic deposition realizes the formation of a Cu(OH)$_2$/Ni$_3$S$_2$ composite on 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) planes of orthorhombic Cu(OH)$_2$ (JCPDS No. 13-0420) [14,18]. This proves that galvanostatic deposition realizes the formation of a relatively high purity of the Cu(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) planes of orthorhombic Cu(OH)$_2$ (JCPDS No. 13-0420) [14,18]. This proves that galvanostatic deposition realizes the formation of a relatively high purity of the Cu(OH)$_2$ phase on the surface of copper substrate.
crystalline planes of Ni$_3$S$_2$ (JCPDS card No. 44-1418) [4,24] further confirms the formation of Cu(OH)$_2$/Ni$_3$S$_2$ composite.

The X-ray photoelectron spectroscopy (XPS) full spectrum of the Cu(OH)$_2$/Ni$_3$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 Ni 2p$_{1/2}$ and 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 Cu 2p$_{1/2}$ and 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].
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].

CV and GCD tests were conducted to assess the pseudocapacitance performances of the Cu(OH)$_2$/Ni$_3$S$_2$ electrode. Figure 5a depicts the CV curves of the Cu(OH)$_2$/Ni$_3$S$_2$, Ni$_3$S$_2$, 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)$_2$/Ni$_3$S$_2$ represents the maximum specific capacitance [32]. Moreover, the CV curve of Cu(OH)$_2$/Ni$_3$S$_2$ displays a pair of redox couples, which can be identified as Ni$^{2+}$/Ni$^{3+}$ attributing to the pseudocapacitive reaction [33]:

$$\text{Ni}_3\text{S}_2 + 3\text{OH}^- \leftrightarrow \text{Ni}_3\text{S}_2(\text{OH})_3 + 3\text{e}^-$$  \hspace{1cm} (1)

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)$_2$/Ni$_3$S$_2$ composite exhibits a longer discharge time than Ni$_3$S$_2$ and Cu(OH)$_2$, indicating the largest specific capacitance of the Cu(OH)$_2$/Ni$_3$S$_2$ composite. The enhanced pseudocapacitance performance of the Cu(OH)$_2$/Ni$_3$S$_2$ composite is ascribed to the synergy between Ni$_3$S$_2$ and Cu(OH)$_2$. Although the capacitance characteristic of a single component is relatively weak, the electrochemical performance of Ni$_3$S$_2$ is significantly enhanced upon introduction of Cu(OH)$_2$ (Figure 5c). Without the support of the Cu(OH)$_2$ component, the bent Ni$_3$S$_2$ 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 Ni$_3$S$_2$, and thus more abundant electrochemical active sites are generated.
of redox couples, which can be identified as Ni$_2^+/Ni_3^+$ attributing to the synergistic reaction [33]:

$$3 Ni + 3 e^- + 3 OH^- \leftrightarrow Ni_3S_2$$

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)$_2$/Ni$_3$S$_2$, Ni$_3$S$_2$, and Cu(OH)$_2$ electrode.

In addition, the amount of Ni$_3$S$_2$ 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 Ni$_3$S$_2$. When the electrodeposition reaches 10 min (S-10), as seen in Figure 7c,d, in addition to the gradually increasing amount of Ni$_3$S$_2$, scattered Ni$_3$S$_2$ 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 Ni$_3$S$_2$ 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 Ni$_3$S$_2$ particles due to the excessive continued deposition of Ni$_3$S$_2$, 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 Ni$_3$S$_2$. 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 Ni$_3$S$_2$, 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$_3$S$_2$, 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 $\Omega$ cm$^{-2}$.

Figure 7. FE-SEM images of the Cu(OH)$_2$/Ni$_3$S$_2$ composite grown on copper foam with different potentiostatic deposition times of Ni$_3$S$_2$: (a,b) S-1; (c,d) S-10; (e,f) S-20; and (g,h) S-40.
The electrochemical behavior of the above four samples was investigated to explore the optimal deposition time of Ni$_3$S$_2$. 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 Ni$_3$S$_2$, 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$_3$S$_2$, 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 Ω cm$^{-2}$.

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 Cu(OH)$_2$/Ni$_3$S$_2$ composite grown on copper foam with different potentiostatic deposition time of Ni$_3$S$_2$.

Based on the above analysis, the areal-specific capacitance of the Cu(OH)$_2$/Ni$_3$S$_2$ electrode gradually increases with the increase of the deposition time of Ni$_3$S$_2$. However, the full play of the electrochemical characteristics of Ni$_3$S$_2$ component is based on the supporting role of Cu(OH)$_2$ nanorods. Therefore, when the deposition time continues to expand to S-40, the disordered accumulation of Ni$_3$S$_2$ begins to destroy Cu(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 Cu(OH)$_2$/Ni$_3$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 Cu(OH)$_2$/Ni$_3$S$_2$ composite electrode reaches 11.43, 10.18, 9.07, 8.58, 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 Ω cm$^{-2}$. In addition, the electrochemical performance data of single component Cu(OH)$_2$ and Ni$_3$S$_2$, including CV curves and GCD curves, are also depicted in Figure 10a–d. The specific capacitance value of Ni$_3$S$_2$ 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$_3$S$_2$; according to the curve, the average $R_{ESR}$ of Ni$_3$S$_2$ could be calculated to be 1.77 Ω cm$^{-2}$, which is significantly higher than that of Cu(OH)$_2$/Ni$_3$S$_2$ composite. From these data, it can be proved that the addition of Cu(OH)$_2$ improves the conductivity of electrode materials and forms more abundant electrochemical active sites for pseudocapacitance reaction.

The specific capacitance retention of the Cu(OH)$_2$/Ni$_3$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 Cu(OH)$_2$/Ni$_3$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 Cu(OH)$_2$/Ni$_3$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 Cu(OH)$_2$, (c) CV curves, (d) GCD curves, (e) specific capacitances, and (f) voltage drops at different current densities of Ni$_3$S$_2$.

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

<table>
<thead>
<tr>
<th>Electrode Material</th>
<th>Substrate</th>
<th>Current Density (mA cm$^{-2}$)</th>
<th>Specific Capacitance (F cm$^{-2}$)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(OH)$_2$</td>
<td>copper foam</td>
<td>2</td>
<td>2.15</td>
<td>[14]</td>
</tr>
<tr>
<td>Cu(OH)$_2$</td>
<td>nanoporous copper</td>
<td>3</td>
<td>0.78</td>
<td>[37]</td>
</tr>
<tr>
<td>Ni$_3$S$_2$</td>
<td>nickel foam</td>
<td>1</td>
<td>2.52</td>
<td>[36]</td>
</tr>
<tr>
<td>Cu(OH)$_2$/Ni$_3$S$_2$</td>
<td>copper foam</td>
<td>2</td>
<td>4.85</td>
<td>[21]</td>
</tr>
<tr>
<td>Cu(OH)$_2$@Co(OH)$_2$</td>
<td>copper foam</td>
<td>4</td>
<td>0.43</td>
<td>[26]</td>
</tr>
<tr>
<td>Cu(OH)$_2$@Ni$_3$(OH)$_2$CO$_3$</td>
<td>copper foam</td>
<td>1</td>
<td>1.09</td>
<td>[39]</td>
</tr>
<tr>
<td>Ni$_3$S$_2$@ppy</td>
<td>nickel foam</td>
<td>2</td>
<td>3.15</td>
<td>[12]</td>
</tr>
<tr>
<td>Ni$_3$S$_2$@CoS$_8$</td>
<td>nickel foam</td>
<td>2</td>
<td>9.79</td>
<td>[33]</td>
</tr>
<tr>
<td>Ni$_3$S$_2$@Mn(OH)$_2$</td>
<td>nickel foam</td>
<td>1</td>
<td>6.43</td>
<td>[40]</td>
</tr>
<tr>
<td>Cu(OH)$_2$/Ni$_3$S$_2$</td>
<td>copper foam</td>
<td>2</td>
<td>11.43</td>
<td>this work</td>
</tr>
</tbody>
</table>
In our reaction system, the excellent pseudocapacitance performance of the optimized Cu(OH)$_2$/Ni$_3$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 Cu(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$_3$S$_2$, 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 Cu(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 Cu(OH)$_2$/Ni$_3$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].

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

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

Self-supported Cu(OH)$_2$/Ni$_3$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 Cu(OH)$_2$ on its surface. Furthermore, the Cu(OH)$_2$ nanorods array acting as a backbone supported the ordered assembly of the Ni$_3$S$_2$ nanostructure, endowing the product enhanced electrochemical activity and stability. Benefiting from the joint contribution of the above factors, the Cu(OH)$_2$/Ni$_3$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 Cu(OH)$_2$-based high performance pseudocapacitive electrode materials to meet the various situation of practical energy storage applications.

Author Contributions: Conceptualization, P.G.; methodology, J.Y. and Z.C.; software, C.W.; validation, W.S.; formal analysis, X.C. and G.C.; investigation, S.L.; writing—original draft, S.L.; writing—review and editing, H.W. and P.G.; supervision, Y.C. and X.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by The Scientific and Technology Development Project of Jilin Province, China (Grant Nos. 20210203098SF and 20210203164SF).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References


10. Xing, Z.C.; Chu, Q.X.; Ren, X.B.; Ge, C.J.; Qusti, A.H.; Asiri, A.M.; Al-Youbi, A.O.; Sun, X.P. Ni$_3$S$_2$ coated ZnO array for high-performance supercapacitors. J. Power Sources 2014, 245, 463–467. [CrossRef]

11. Yang, P.; Feng, L.; Wang, S.H.; Shi, J.J.; Xing, H.L. Construction of core-shell Ni@Ni$_3$S$_2$@NiCo$_2$O$_4$ nanoflakes as advanced electrodes for high-performance hybrid supercapacitors. J. Phys. Chem. Solids 2021, 155, 110110. [CrossRef]

13. Wang, Y.; Liu, J.C.; Liao, Y.F.; Wu, C.L.; Chen, Y.G. Hetero-structured V-Ni$_3$S$_2$@NiOOH core-shell nanorods from an electrochemical anodization for water splitting. J. Alloys Compd. 2021, 856, 158219. [CrossRef]
18. Wang, H.N.; Yan, G.W.; Cao, X.Y.; Liu, Y.; Zhong, Y.X.; Cui, L.; Liu, J.Q. Hierarchical Cu(OH)$_2$@MnO$_2$ core-shell nanorods array in situ generated on three-dimensional copper foam for high-performance supercapacitors. J. Colloid Interface Sci. 2020, 563, 394–404. [CrossRef]
31. Sajjad, M.; Khan, Y. Rational design of self-supported Ni$_3$S$_2$ nanoparticles as a battery type electrode material for high-voltage (1.8 V) symmetric supercapacitor applications. Curr. EngComm 2021, 23, 2869–2879. [CrossRef]
32. Lin, Y.F.; Chen, X.Y.; Chang, P.; Liu, Z.L.; Ren, G.H.; Tao, J.G. Hierarchical design of Ni$_3$S$_2$@Co$_3$S$_4$ nanotubes for supercapacitors with long cycle-life and high energy density. J. Alloys Compd. 2022, 900, 163503. [CrossRef]
34. Savita, L.P.; Shrikant, S.R.; Babasaheb, R.S. Cu(OH)$_2$@Cd(OH)$_2$ core-shell nanostructure: Synthesis to supercapacitor application. Thin Solid Films 2019, 692, 137584.
38. Shen, M.; Liu, J.L.; Liu, T.C.; Yang, C.M.; He, Y.X.; Li, Z.L.; Li, J.H.; Qian, D. Oxidant-assisted direct-sulfidization of nickel foam toward a self-supported hierarchical Ni$_3$S$_2$@Ni electrode for asymmetric all-solid-state supercapacitors. *J. Power Sources* **2019**, *448*, 227408–227416. [CrossRef]


