



Article Hierarchical Design of Co(OH)₂/Ni₃S₂ Heterostructure on Nickel Foam for Energy Storage

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Abstract: In this study, we rationally designed a facile stepwise route and successfully synthesized a $Co(OH)_2/Ni_3S_2$ heterostructure supported on nickel foam (NF) as a binder-free electrode for energy storage. Galvanostatic deposition was first applied to produce uniform $Co(OH)_2$ nanoflakes on NF. Then, Ni_3S_2 was applied to its surface by potentiostatic deposition to form a $Co(OH)_2/Ni_3S_2$ heterostructure at room temperature. The added $Co(OH)_2$ not only functions as a practical electrochemically active component but also provides support for the growth of Ni_3S_2 , and the deposition amount of Ni_3S_2 is controlled by adjusting the electrodeposition duration of Ni_3S_2 . Then, the electrochemical behaviors of the $Co(OH)_2/Ni_3S_2$ composite can be optimized. A maximum areal specific capacitance (Cs) of 5.73 F cm⁻² at 2 mA cm⁻² was achieved, and the coulombic efficiency was as high as 94.14%. A capacitance retention of 84.38% was measured after 5000 charge–discharge cycles.

Keywords: hybrid nanomaterials; nickel foam; electrodeposition; electrochemical energy storage

1. Introduction

As the core factor determining the performance of energy storage devices, electrode materials have garnered significant attention [1,2]. Taking supercapacitors as an example, from the perspective of the energy storage mechanism, electrode materials can be divided into two categories: electric double-layer and pseudocapacitance electrode materials [3]. As is known, the latter has been proved to reflect higher specific capacitance (Cs) because the active sites on the surface and near-surface regions of electrode materials can participate in the pseudocapacitive reaction [4]. Therefore, metal-oxide-type electrode materials represented by Ni(OH)₂ and Co(OH)₂ have attracted the particular attention of researchers, including NiO and Co_3O_4 obtained by calcinating them and their derivatives nickel sulfide and cobalt sulfide [5,6]. Therefore, in addition to improving traditional preparation routes, such as the hydrothermal method, coprecipitation technology and the electrodeposition process, extensive research has focused on improving the overall electrochemical properties of the materials by regulating the components of electrode materials and optimizing the structure design [7,8]. For example, Satpathy et al. designed a $Cu(OH)_2$ nanobelt/ $Co(OH)_2$ nanosheet heterostructure through chemical etching and electrodeposition on copper foil. $Cu(OH)_2$ was selected as the component because of its high electrical conductivity, which can also provide abundant available space for the subsequent deposition of Co(OH)2; this hybrid hydroxide as a binder-free electrode exhibits remarkably higher Cs than single Co(OH)₂ [9]. Using similar strategies, our research group prepared a Cu(OH)₂/Ni₃S₂ electrode on copper foam, which achieved a high Cs of 4.85 F cm⁻² at 2 mA cm⁻² [10]. The choice of the Ni_3S_2 component is based on the fact that the sulfur in Ni_3S_2 has a lower electronegativity than the oxygen in the corresponding hydroxide (oxide). Thus, it reflects



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the advantages of better electrochemical activity and stability [11-13]. However, the common problem of the above two examples is that Cu(OH)₂ mainly acts as a bridge between the substrate and another component. As a component, Cu(OH)₂ has little contribution to the overall electrochemical performance. Finding a candidate to ensure that it can replace the role of Cu(OH)₂ and has outstanding pseudocapacitance reaction characteristics has been regarded as the main direction of exploration. Co(OH)₂ has become one of the candidates because of its high theoretical Cs and typical flake structure [14,15]. In addition to providing sufficient support for the growth of other components, these flake structures are intertwined with each other, which facilitates the diffusion of electrolyte ions and promotes the efficient contact between the electrolyte and electrode material [16].

Inspired by the above discussion, we designed and constructed a $Co(OH)_2/Ni_3S_2$ heterostructure on nickel foam, which not only gives full play to the energy storage characteristics of each component but also makes full use of the skeleton support function of $Co(OH)_2$ flakes, which provide sufficient exposed active sites from the perspective of structural design [12,17]. As for the specific preparation route, a three-electrode system was adopted to perform two-step electrodeposition according to previous reports with some modifications; that is, Co(OH)₂ nanoflakes were first grown on nickel foam by galvanostatic deposition, and then Ni_3S_2 was coated on the surface of $Co(OH)_2$ by potentiostatic deposition. An electrodeposition process is a viable option for achieving in situ growth and developing a binder-free electrode. Moreover, its operation process is time-saving, safe and straightforward. In particular, the loading amount of deposited active electrode material can be controlled by adjusting the experimental parameters [18]. In our reaction system, the optimal reaction conditions were identified by adjusting the deposition duration of Ni_3S_2 and thus delivered the best electrochemical properties of the $Co(OH)_2/Ni_3S_2$ heterostructure. The present work provides new insight for selecting composite components and structural designs.

2. Materials and Methods

2.1. Materials

Nickel foam (NF, 110 PPI, 1.5 mm thick) was cut into $1 \text{ cm} \times 1.5 \text{ cm}$ pieces and then used as a substrate after soaking in hydrochloric acid, acetone, ethanol and water. The reagents involved in the experiment include Co(NO₃)₂·6H₂O, NiCl₂·6H₂O, CH₄N₂S and NaOH.

2.2. Electrodeposition of $Co(OH)_2/Ni_3S_2$ Heterostructure on NF

 $Co(OH)_2$ was first deposited on NF by galvanostatic deposition at 0.02 A for 10 min. The division of labor of the three-electrode system is as follows: NF (working electrode), saturated calomel electrode (SCE, reference electrode) and a Pt foil (counter electrode). A 0.1 M Co(NO₃)₂ solution was used as the electrolyte.

 Ni_3S_2 was then deposited on the surface of Co(OH)₂ by potentiostatic deposition at -1.1 V for 20 min. A similar three-electrode system was adopted, except that the working electrode was Co(OH)₂/NF obtained in the previous step. The electrolyte was a mixed solution of NiCl₂ (0.05 M) and CH₄N₂S (0.5 M). For comparison, the potentiostatic deposition of Ni₃S₂ was carried out for different durations, including 1 min (labeled as S-1), 10 min (S-10), 20 min (S-20) and 40 min (S-40).

2.3. Characterization

The products were examined by X-ray diffraction (XRD Cu K α radiation with λ = 1.5406 Å), scanning electron microscopy (FE-SEM JSM-7610F) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). The energy storage properties were evaluated, including cyclic voltammetry (CV, 0–0.7 V vs. Ag/AgCl), galvanostatic charge–discharge (GCD) and cycling performance through a CHI 760E electrochemical workstation in 2 M NaOH solution. The three-electrode test system consisted of Co(OH)₂/Ni₃S₂/NF (working), Ag/AgCl (reference) and a Pt foil (counter) electrode.

3. Results

Scheme 1 depicts the synthesis route of the Cu(OH)₂/Ni₃S₂ heterostructure. The first step is to achieve the in situ growth of Co(OH)₂ on NF through galvanostatic deposition in a three-electrode system. Figure S1 reveals a typical FE-SEM image of pristine NF. As the electrode substrate, its specific 3D porous structure provides sufficient support for the growth of electrode materials, and silver-gray 3D NF is covered by dense bluish-green Co(OH)₂ nanoflakes. In the second step, the surface of Co(OH)₂ turns black due to the deposition of Ni₃S₂, which is performed by potentiostatic deposition in a similar three-electrode system. Thus, the obtained Co(OH)₂/Ni₃S₂ composite can be directly used as an electrode for electrochemical performance testing because it is grown on the NF substrate directly, which avoids the complex process of preparing the electrode by adding a binder and conductive agent.



Scheme 1. The synthesis route of Co(OH)₂/Ni₃S₂ heterostructure.

Figure 1a shows the XRD spectrum of the sample generated by the first step of galvanostatic deposition, in which the two prominent well-defined peaks marked with circles come from the NF substrate (JCPDS No. 01-1258). The peaks marked with squares correspond to the (100), (102), (105), (108) and (110) planes of the hexagonal phase of α -Co(OH)₂ (JCPDS No. 46-0605) [19]. Figure 1b is a low-magnification SEM image of the corresponding Co(OH)₂. As can be seen from this figure, dense Co(OH)₂ evenly covers the surface of the NF substrate. High-magnification images confirmed that these Co(OH)₂ are irregular nanoflake structures with a smooth surface. These curved, silk-ribbon-like nanoflakes are interlaced with a thickness of ca. 10 nm (Figure 1c,d).

The XRD spectrum of the sample after the second step of potentiostatic deposition is shown in Figure 2a. Except for the square (NF substrate) and circular (Co(OH)₂) peaks, the diffraction peaks marked with an asterisk are attributed to the (100), (003), (021) and (122) crystalline planes of Ni₃S₂ (JCPDS card No. 44-1418), which confirms the formation of Ni₃S₂ on the surface of Co(OH)₂ [12]. The SEM image in Figure 2b also confirms that these intertwined Co(OH)₂ nanoflakes became significantly thicker due to the coating of Ni₃S₂. Figure 2c,d are corresponding enlarged images; it should be noted that the coated Ni₃S₂ also has the shape of curved nanoflakes with a thickness of ca. 5 nm. They are also intertwined with each other to form a network on the surface of Co(OH)₂.

Figure 3 presents the XPS spectra of the $Co(OH)_2/Ni_3S_2$ electrode. It is confirmed from the full spectrum that the sample contains Co, Ni, O and S elements (Figure 3a). The calibration is based on the C 1s peak at 284.8 eV (Figure 3b). As for the Co 2p spectrum in Figure 3c, two intense feature peaks situated at 798 and 781.3 eV correspond to Co $2p_{1/2}$ and Co $2p_{3/2}$. They all have corresponding satellite peaks located at 803.7 and 786.85 eV, which are indexed to the characteristic signatures of Co(OH)₂ [15,20,21]. The Ni 2p spectrum is exhibited in Figure 3d. Two prominent peaks positioned at 874.26 and 856.60 eV can be assigned to Ni $2p_{1/2}$ and Ni $2p_{3/2}$ and a spin-orbit splitting of 17.7 eV, which confirms the existence of Ni²⁺ and Ni³⁺. The peaks at 880 and 861.7 eV are their satellite peaks [22,23]. In the O 1s spectrum (Figure 3e), the peak at 531.4 eV comes from hydroxyl oxygen in Co(OH)₂ [14]. Figure 3f records the spectrum of S 2p, in which the intense main peak is composed of S $2p_{1/2}$ and S $2p_{3/2}$ at 163.3 and 162.1 eV, respectively, which arise from S²⁻ [12]. In addition, a broad peak appears at 168.10 eV, which is ascribed to the S-O bond, and the oxygen comes from the hydroxyl groups produced by the hydrolysis of thiourea, as previously reported [24,25].



Figure 1. (a) XRD pattern and (b-d) FE-SEM images of Co(OH)₂ nanoflakes formed on NF.



Figure 2. (a) XRD pattern and (b–d) FE-SEM images of Co(OH)₂/Ni₃S₂ heterostructure at different magnifications.



Figure 3. XPS spectra of (a) survey scan; (b) C 1s; (c) Co 2p; (d) Ni 2p; (e) O 1s; (f) S 2p of $Co(OH)_2/Ni_3S_2$ electrode.

In order to verify the effectiveness of the composite structure design, we compared the electrochemical behavior of $Co(OH)_2/Ni_3S_2$, Ni_3S_2 and $Co(OH)_2$ electrodes. Figure 4a presents the CV curves of the four electrodes at a scan rate of 10 mV s⁻¹. A solution of 2 M NaOH was used as the electrolyte. Its function is to provide OH⁻ for a reversible pseudocapacitance reaction with electrode materials, which also reflects the energy storage mechanism of pseudocapacitance materials. According to the rule, the larger the critical area of the CV curve, the higher the Cs [26]. It is evident that the Cs of the $Co(OH)_2/Ni_3S_2$ electrode is significantly greater than the other three, and NF has almost no capacitance characteristics. The pseudocapacitive reactions involved are as follows [19,27]:

$$Ni_{3}S_{2} + 3OH^{-} \leftrightarrow Ni_{3}S_{2}(OH)_{3} + 3e^{-}$$
(1)

$$Co(OH)_2 + OH \leftrightarrow CoOOH + H_2O + e^-$$
 (2)

$$CoOOH + OH^{-} \leftrightarrow CoO_{2} + H_{2}O + e^{-}$$
(3)

The above inference can also be confirmed from the GCD curve (2 mA cm⁻²) in Figure 4b on the premise of the same discharge current density: the longer the discharge time, the greater the Cs of the electrode [28]. Figure 4c also lists the Cs of the four electrodes at current densities of 2–60 mA cm⁻², which fully confirms that the Cs of the Co(OH)₂/Ni₃S₂ electrode was significantly enhanced compared with any single component. In fact, theoretically speaking, the more OH⁻ that the electrolyte can provide, that is, the greater the electrolyte concentration, the more electrochemical active sites participating in the pseudocapacitance reaction, and the greater the Cs of the product. Therefore, the GCD curves of Co(OH)₂/Ni₃S₂ gradually increases; therefore, Figure S2b shows a significantly enhanced trend of Cs. However, in our reaction system, we focus on comparing the difference in Cs between composite components and single components under the same test conditions. Therefore, we chose the 2 M NaOH electrolyte as an example for the electrochemical test and analysis.

In order to further evaluate the electrochemical properties of the composites and give full play to the supporting role of $Co(OH)_2$ and its synergistic effect with Ni_3S_2 , we systematically investigated the impact of the loading amount of Ni_3S_2 on the morphology and structure of the composite. When the deposition duration is 1 min, as shown in Figure 5a, the SEM image of the $Co(OH)_2/Ni_3S_2$ composite at low magnification does not show a noticeable difference from pure $Co(OH)_2$, which is also a curved flake structure. From

the enlarged image in Figure 5b, it is found that the surface of these $Co(OH)_2$ nanoflakes becomes rough due to the scattering of a large number of linear Ni_3S_2 particles. When the deposition reaches 10 min, it is evident from Figure 5c that these $Co(OH)_2$ nanoflakes become thicker. After magnification, it is confirmed that these wrapped large amounts of Ni_3S_2 also begin to form a curved nanoflake structure, and the size is much smaller than that of $Co(OH)_2$ (Figure 5d). As the deposition increases to 20 min, these nanoflakes gradually increase and become dense (Figure 5e), which is described in detail in Figure 2. When it extends to 40 min, the continuous excessive aggregation of Ni_3S_2 leads to disorderly accumulation and the destruction of the partial structures of $Co(OH)_2$ (Figure 5f).



Figure 4. Performance comparison of $Co(OH)_2/Ni_3S_2$, Ni_3S_2 , $Co(OH)_2$ and NF electrodes: (a) CV curves, (b) GCD curves and (c) Cs at different current densities.

Figure 6 compares the pseudocapacitance characteristics of the above four samples in 2 M NaOH solution. As seen in the CV curves in Figure 6a, the integral areas of the samples show an increasing trend with the increase in the potentiostatic deposition duration, except for S-40 because the necessary site of S-40 is almost the same as that of S-20. This trend is also reflected in Figure 6b. In order to distinguish these results in detail, Figure 6c lists the Cs values of four samples at current densities of 2–60 mA cm⁻² according to the formula calculation [29]. The conclusion is that the Cs value is in the order of S-20 > S-10 > S-1 under the same current density. As for S-40, the Cs value is slightly greater than that of S-20 between 2 and 8 mA cm⁻², while when the current density reaches 12 mA cm⁻², the Cs value of S-40 is lower than that of S-20. Meanwhile, the rate capability of the four samples was deduced based on the sets of data [30]. S-20 is the largest, and its discharge Cs is still maintained at 52.53% when the current density increases from 2 to 60 mA cm⁻². Figure 6d presents the voltage drop curves at current densities of 2–60 mA cm⁻² of the four samples and the corresponding derived average $R_{\rm ESR}$. The minimum $R_{\rm ESR}$ is S-20 with 1.35 Ω cm⁻² according to the formula used [29].

According to the comparison and analysis of the above data, in addition to being the active component of the composite electrode, $Co(OH)_2$ also provides support for the deposition of Ni₃S₂. At the same time, in general, the larger the loading amount of Ni₃S₂, the more active sites provided, and therefore, the more extensive the areal Cs [28], such as S-20 > S-10 > S-1. However, with the excessive aggregation of Ni₃S₂, the nanoflake structure of Co(OH)₂ is completely covered or even destroyed (Figure 5f). These disorderly stacked Ni₃S₂ particles easily fall off in the charge–discharge process, resulting in decreases in Cs and rate capability, such as S-40. Additionally, excessive accumulation is bound to hinder the movement of ions and increase the average R_{ESR} [15]. Therefore, based on the relatively superior energy storage characteristics of S-20, it was further tested and systematically investigated.



Figure 5. FE-SEM images of Ni₃S₂ electrodeposited on Co(OH)₂/NF for different potentiostatic deposition durations: (**a**,**b**) S-1, (**c**,**d**) S-10, (**e**) S-20 and (**f**) S-40.

Figure 7a shows the CV curves of the sample (S-20) in the scan rate range of 2–50 mV s⁻¹. With the increase in the scan rate, the redox peaks move to a broader potential window, and the area surrounded by the CV curve gradually increases, but the corresponding Cs gradually decreases [9]. This is because the internal electrochemical active sites do not have enough time to fully react with the OH⁻ in the electrolyte at high scan rates [15]. Figure 7b shows the GCD curves of the sample in the current density range of 2–60 mA cm⁻². According to the formula, the lower the current density, the higher the discharge time and Cs [29]. At the same time, when the current density is 2 mA cm⁻², the coulombic efficiency reaches 94.14% [31]. The calculated values of Cs are displayed in Figure 7c, which decrease from 5.73 to 3.01 F cm⁻², corresponding to current density increases from 2 to 60 mA cm⁻²; that is, the Cs value can still be maintained at 52.53% of the initial value when the current density increases from 2 to 60 mA cm⁻²; that is, the Voltage drop curve at different current densities, and thus, the calculated average R_{ESR} is 1.35 Ω cm⁻²; these results are described in Figure 6c.



Figure 6. Performance comparison of S-1, S-10, S-20 and S-40: (a) CV curves, (b) GCD curves, (c) Cs at different current densities and corresponding rate capabilities and (d) voltage drops at different current densities and corresponding average R_{ESR} .



Figure 7. (a) CV curves, (b) GCD curves, (c) Cs and (d) voltage drops at different current densities of $Co(OH)_2/Ni_3S_2$ heterostructure (S-20).

As for single-component Co(OH)₂ and Ni₃S₂ electrodes, their CV curves at scan rates of 2–50 mV s⁻¹, GCD curves at current densities of 2–60 mA cm⁻² and the corresponding Cs are also presented in Figure 8.



Figure 8. CV curves, GCD curves and Cs at different current densities of $Co(OH)_2$ (**a**,**c**,**e**) and Ni_3S_2 (**b**,**d**,**f**).

The Cs retention of the $Co(OH)_2/Ni_3S_2$ electrode is presented in Figure 9. It can be observed that Cs reaches 90.63% at the 600th cycle and maintains the initial 84.38% within 5000 cycles.



Figure 9. Cycling performance of the Co(OH)₂/Ni₃S₂ electrode.

Electrode Materials	Electrode Substrate	Electrolyte	Current Density (mA cm ⁻²)	Cs (F cm ⁻²)	Literature
Co(OH) ₂ /CoOOH/ Co ₃ O ₄ /Cu(OH) ₂	Cu foam	1 M KOH	1	1.94	[32]
$Co(OH)_2/Co_9S_8$	NiFe skeleton	3 M KOH	10	5.28	[33]
$Co_9S_8@Co(OH)_2$	Ni foam	3 M KOH	1.5	5.62	[13]
Co ₃ S ₄ -Ni ₃ S ₂	Ni foam	6 M KOH	2	2.83	[34]
Ni_3S_2/rGO	Ni foam	2 M KOH	2	1.96	[27]
Ni ₃ S ₂ /CoFeLDH	Ni foam	1 M KOH	2	5.08	[35]
$Cu(OH)_2/Ni_3S_2$	Cu foam	2 M NaOH	2	4.85	[10]
NiCoLDH@Ni ₃ S ₂	Ni foam	3 M KOH	3	4.95	[36]
$Co(OH)_2/Ni_3S_2$	Ni foam	2 M NaOH	2	5.73	Present work

Table 1. Comparison of Cs of $Cu(OH)_2/Ni_3S_2$ with reported in the literatures.

Table 1 shows several composite electrode materials reported in the recent literature with $Co(OH)_2$ or Ni_3S_2 as components and their Cs. By comparison, the prepared Co(OH)₂/Ni₃S₂ shows comparable or even more prominent properties than those previously reported. This is attributed to the selection of composite components and their preparation strategies, which are mainly reflected in the following aspects: $(1) Co(OH)_2$ and Ni_3S_2 are regarded as the most promising electrode materials owing to their low cost, abundance and high theoretical Cs [22]. At the same time, it can be inferred that in our reaction system, both $Co(OH)_2$ and Ni_3S_2 participate in the pseudocapacitive reaction as active components. In particular, the nanoflake structures of $Co(OH)_2$ and Ni_3S_2 are favorable for fast pseudocapacitive reactions due to the reduced charge transportation pathways [12]. Meanwhile, these nanoflakes interweave with each other to form a network, which provides more channels for charge transportation. Therefore, the $Co(OH)_2/Ni_3S_2$ heterostructure can deliver a robust synergistic effect, which is bound to improve the overall properties of the composite [18]. (2) The addition of $Co(OH)_2$ also acts as a bridge between the electrode substrate and Ni₃S₂, which provides support for the deposition of Ni_3S_2 to form more abundant electrochemical active sites [18,37]. Meanwhile, the $Co(OH)_2$ nanoflakes can effectively alleviate the collapse of the structure in the charge-discharge process [12]. (3) This in situ electrodeposition technology reflects the advantages of a short preparation cycle, easy regulation of the amount of deposited active substances, good stability, direct acquisition of the binder-free electrode to be measured and reduction in contact resistance [38].

4. Conclusions

In summary, we successfully synthesized a hierarchical $Co(OH)_2/Ni_3S_2$ heterostructure on the NF substrate through the combination of galvanostatic and potentiostatic deposition. The introduction of $Co(OH)_2$, as an electrochemically active component, provides support for the deposition of Ni_3S_2 . Then, the optimal deposition amount of Ni_3S_2 is achieved by adjusting the deposition duration of Ni_3S_2 . The $Co(OH)_2/Ni_3S_2$ heterostructures thus obtained exhibited promising electrochemical characteristics with a high areal *Cs* of 5.73 F cm⁻² at 2 mA cm⁻², which remained 3.01 F cm⁻² at 60 mA cm⁻². The coulombic efficiency is excellent, reaching 94.14%, and the long-term cycle reversibility maintains the initial 84.38% within 5000 cycles. Furthermore, the present work provides some new inspiration for designing and developing efficient $Co(OH)_2$ - or Co_3O_4 -based composite electrode materials for energy storage.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr10071255/s1. Figure S1: FE-SEM image of pristine NF; Figure S2: (a) GCD curves at 2 mA cm⁻² and (b) Cs of $Co(OH)_2/Ni_3S_2$ heterostructure at different NaOH concentrations.

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