Three-Dimensional Porous Network Electrodes with Cu(OH)$_2$ Nanosheet/Ni$_3$S$_2$ Nanowire 2D/1D Heterostructures for Remarkably Cycle-Stable Supercapacitors

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ABSTRACT: Developing advanced electrode materials with highly improved charge and mass transfer is critical to obtain high specific capacities and long-term cycle life for energy storage. Herein, three-dimensionally (3D) porous network electrodes with Cu(OH)$_2$ nanosheets/Ni$_3$S$_2$ nanowire 2D/1D heterostructures are rationally fabricated. Different from traditional surface deposition, the 1D/2D heterostructure network is obtained by in situ hydrothermal chemical etching of the surface layer of nickel foam (NF) ligaments. The Cu(OH)$_2$/Ni$_3$S$_2$@NF electrode delivers a high specific capacity (1855 F g$^{-1}$ at 2 mA cm$^{-2}$) together with a remarkable stability. The capacity retention of the electrode is over 110% after 35,000 charge/discharge cycles at 20 mA cm$^{-2}$. The improved performance is attributed to the enhanced electron transfer between 1D Ni$_3$S$_2$ and 2D Cu(OH)$_2$, highly accessible sites of 3D network for electrolyte ions, and strong mechanical bonding and good electrical connection between Cu(OH)$_2$/Ni$_3$S$_2$ active materials and the conductive NF. Especially, the unique 1D/2D heterostructure alleviates structural pulverization during the ion insertion/desertion process. A symmetric device applying the Cu(OH)$_2$/Ni$_3$S$_2$@NF electrode exhibits a remarkable cycling stability with the capacitance retention maintaining over 98% after 30,000 cycles at 50 mA cm$^{-2}$. Therefore, the outstanding performance promises the architectural 1D/2D heterostructure to offer potential applications in future electrochemical energy storage.

1. INTRODUCTION

With the ever-increasing growth of portable devices, the increasing demand for efficient energy supply for electronic devices is becoming more and more impending.1–3 Advanced energy storage systems with expectative battery performance are highly required. To this regard, supercapacitors (SCs) are considered as a competitive one due to their inherent advantages of low cost, high safety, fast charge/discharge, and long usage life.3–8 In spite of this, the relatively low energy density ($\leq$ 10 Wh kg$^{-1}$) together with the unsatisfying long-life cycling stability at too high discharging rates is the main problems with SCs, which severely inhibits their commercial application.9–11 According to the charge storage mechanisms, electrode materials of SCs are divided into electric double-layer capacitors (EDLCs) and pseudocapacitors.6,12–15 The latter stores energy by the adsorption of near-surface ions, and the fast reversible Faradic reactions lead to additional contribution taking place on the electrode materials’ surface. This makes the latter have much higher electrochemical capacities and energy densities than the EDLCs.16–19 Therefore, developing new pseudocapacitive electrode materials is highly expected to break the ceiling of performance limit of SCs.

Among the pseudocapacitive materials available, transitional metal sulfides exhibit more enhanced electrical conductivity than their oxide counterparts and have been regarded as one
The synthetic process of the 1D/2D heterostructure constructed by 1D Ni₃S₂ nanowires and 2D Cu(OH)₂ nanosheets includes two-step hydrothermal processes, which is schematically shown in Figure 1. First, 1D Ni₃S₂ nanowires grow on the ligaments of NF by direct in situ sulfurization etching of the surface of NF’s ligaments. During the process, at 160 °C under a hydrothermal environment, the chemical reaction between the sublimed sulfur (Sₙ) with ethylenediamine leads to H₂S. Then, the generated H₂S reacts with NF to result in the generation of Ni₃S₂. One-dimensional Ni₃S₂ nanowires successfully form on the ligaments of 3D porous NF due to an anisotropic growth during the in situ chemical etching and growth process. The possible reaction equations are as follows:

\[ S_n + 2 \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \rightarrow \text{NH}_2\text{CH}_2\text{CH}_2\text{NH} - S_{n-1} + \text{HNCH}_2\text{CH}_2\text{NH}_2 + H_2S \]  
\[ 2H_2S + 3 \text{Ni} \rightarrow \text{Ni}_3\text{S}_2 + 2 \text{H}_2 \]
In the subsequent synthetic step, Cu(OH)$_2$ nucleates on the surfaces of individual Ni$_3$S$_2$ nanowires after Cu$^{2+}$ ions react with OH$^-$ ions in the alkaline solution. The growth rate of Cu(OH)$_2$ mainly depends on the concentration of Cu$^{2+}$ ions, and the resulting morphology of grown Cu(OH)$_2$ nanostructures can be controllable. When the typical Cu$^{2+}$ concentration is 0.125 M, the Cu(OH)$_2$ nuclei grow up in an anisotropic growth way, and standing 2D Cu(OH)$_2$ nanosheets from surrounding each Ni$_3$S$_2$ nanowire. Simultaneously, the 1D/2D heterostructures are successfully constructed by the newly formed 2D Cu(OH)$_2$ nanosheets covering the 1D Ni$_3$S$_2$ nanowires.

The advantages of 1D/2D heterostructure network structures on 3D porous NF for SCs are suggested as follows. Since Ni$_3$S$_2$ is of high conductivity, the 3D network of Ni$_3$S$_2$ nanowires not only guarantees good electron transfer to Cu(OH)$_2$ nanosheets but also acts as a skeleton to avoid their aggravation. Moreover, the synergistic effect between the grown 2D Cu(OH)$_2$ nanosheets and 1D Ni$_3$S$_2$ nanowires promotes efficient reversible Faradic reactions. In addition, the 1D/2D heterostructures on the NF with lightweight, high porosity, and excellent electrical conductivity ensure large surface areas to offer sufficient exposed surface active sites. Therefore, the NF-supported Cu(OH)$_2$/Ni$_3$S$_2$ networks are able to deliver high capacitance and long-term cycling stability even at high discharging rates.

Figure 2a shows the XRD pattern of Cu(OH)$_2$/Ni$_3$S$_2$@NF (the red one), and the XRD pattern of Ni$_3$S$_2$@NF (the black one) is also presented for comparison. Obviously, three sharp diffraction peaks at 43.9, 51.3 and 75.9° correspond to (111), (200), and (220) planes of NF (JCPDS PDF #04-0850). In addition, other five apparent peaks correspond to Ni$_3$S$_2$ with high crystalline phase (JCPDS PDF #44-1418). It should be noted that the other five diffraction peaks indexing to Cu(OH)$_2$ (JCPDS PDF #13-0240) are also clearly observable for Cu(OH)$_2$/Ni$_3$S$_2$@NF but not for Ni$_3$S$_2$@NF, which confirms that Cu(OH)$_2$ successfully forms in the obtained sample after Cu$^{2+}$ ions react with OH$^-$ ions during the second step hydrothermal synthesis in an alkaline solution.

Figure 2b–d show XPS spectra of the typical Cu(OH)$_2$/Ni$_3$S$_2$@NF, which further check the main elements of Ni, S, and Cu and their chemical states. The high-resolution Ni 2p spectrum (Figure 2b) is deconvoluted into two dominant peaks for Ni 2p$_{3/2}$ (873.1 eV) and Ni 2p$_{1/2}$ (855.7 eV) with two satellite signals (879.5 and 861.4 eV). These match with Ni$^{2+}$ very well. For the S 2p spectrum (Figure 2c), two peaks contributing to S 2p$_{3/2}$ and S 2p$_{1/2}$ components of S$^{2-}$ are found at 163.3 and 162.1 eV, respectively. Another weak peak at 168.0 eV is the satellite peak. These peaks coordinate with S in the Ni$_3$S$_2$ phase, which confirm that Ni$_3$S$_2$ is kept well in the resulting product after the hydrothermal growth of Cu(OH)$_2$. Furthermore, the high-resolution XPS Cu 2p spectrum in Figure 2d displays a peak for Cu 2p$_{3/2}$ (934.5 eV) and a satellite peak (at 942.3 eV), suggesting that the valence state of Cu in the product is +2, which is consistent with Cu(OH)$_2$. Therefore, the XPS analysis also confirms that the resulting product consists of Ni$_3$S$_2$ and Cu(OH)$_2$, which agrees with the XRD results very well.

Figure 3a,c displays the low-magnification SEM images for the Ni$_3$S$_2$@NF and Cu(OH)$_2$/Ni$_3$S$_2$@NF electrodes. It is observed that the three-dimensional porous structure of bare NF is maintained well in the samples. Obviously, more folds are present on the NF skeleton in Cu(OH)$_2$/Ni$_3$S$_2$@NF than those on Ni$_3$S$_2$@NF. From high-magnification SEM images (Figure 3b), a uniform coverage of Ni$_3$S$_2$ nanowires can be seen on the ligaments of the NF surface. After growth of Cu(OH)$_2$, the 3D network of Ni$_3$S$_2$ nanowires (Figure 3d) were kept well; meanwhile, a large number of 2D nanosheets are distributed among the nanowires to construct 1D/2D heterostructures.

The morphology and nanostructure are further observed by using TEM. As it can be observed in Figure 4a, a low-magnification TEM image exhibits that Cu(OH)$_2$/Ni$_3$S$_2$ is separated from the ligaments of NF. It consists of 1D...
nanowires and 2D nanosheets. A TEM image at a higher magnification (Figure 4b) confirms that the Ni$_3$S$_2$ nanowires have an average diameter of about 18 nm, in accordance with the SEM analysis result. On one side of the nanowire, a 2D thin nanosheet grows on it. Therefore, it is obvious that the 1D nanowires and 2D nanosheets constructed the desirable 1D/2D heterostructure. An HRTEM image (Figure 4c) exhibits a series of lattice fringes; a spacing of 0.29 nm belongs to the (110) crystallographic plane of Ni$_3$S$_2$. In the nanosheet area, the interlayer distance of lattice fringes is measured to be 0.26 nm, indexing to the (002) plane of Cu(OH)$_2$. Therefore, the combined results of the TEM and HRTEM images further confirm that the obtained heterostructures are composed of 1D Ni$_3$S$_2$ nanowires and 2D Cu(OH)$_2$ nanosheets.

As is reported, Ni$_3$S$_2$ has the ability of compatibility with electrolyte ions and high conductivity for charge transfer, and thus electrons are free to transfer in a Ni$_3$S$_2$ nanowire. When used in electrochemical energy storage, these properties of Ni$_3$S$_2$ result in reversible redox reactions of Ni$^{2+}$/Ni$^{3+}$ in a 3 M KOH, and the related reaction follows the equation Ni$_3$S$_2$ + 3OH$^{-}$ $\leftrightarrow$ Ni$_3$S$_2$(OH)$_3$ + 3e$^-$.44 The newly grown 2D Cu(OH)$_2$ delivers fast transportation of electrons with an assistance of the 1D Ni$_3$S$_2$ and possesses a high contacting area for OH$^-$ ions transfer due to richin-accessible active sites and exposed surfaces/edges. The related redox reactions for the active material (Cu(OH)$_2$) take place according to the following equation: 2Cu(OH)$_2$ + 2e$^-$$\leftrightarrow$ Cu$_2$O + 2OH$^-$$+$$H_2$O.48 The 1D/2D heterostructures for electrochemical energy storage are shown in Figure 4d. Figure 5a shows N$_2$ adsorption–desorption isotherms of the two electrodes, and an obvious difference is observed. In particular, in the isotherms of the Cu(OH)$_2$/Ni$_3$S$_2$@NF electrode, the slope of the curves rises remarkably with a relative pressure above $\sim$0.95, which is attributed to the nanostructure change induced by the Cu(OH)$_2$ nanosheets. Cu(OH)$_2$/Ni$_3$S$_2$@NF delivers a relatively higher BET specific surface area (42.63 m$^2$ g$^{-1}$) than Ni$_3$S$_2$@NF (21.76 m$^2$ g$^{-1}$), which is attributed to the 3D nanowire network and 2D grown nanosheets. Their pore diameters are distributed in a range of 2–5 nm (Figure 5b), and the Cu(OH)$_2$/Ni$_3$S$_2$@NF electrode has much more pores than the Ni$_3$S$_2$@NF one.

Electrochemical examination of the obtained Cu(OH)$_2$/Ni$_3$S$_2$@NF is conducted by cyclic voltammetry (CV) measurements in an electrochemical potential window ranging from $-0.2$ to 0.8 V in a 3 M KOH electrolyte. Figure 6a,c shows CV curves at different scan rates for the Ni$_3$S$_2$@NF and Cu(OH)$_2$/Ni$_3$S$_2$@NF electrodes, respectively. All of the CV curves have an oxidation peak during the charge stage and a reduction peak in the discharge process. This behavior indicates that the capacities of the two electrodes are mainly from the pseudocapacitance. As shown in Figure 6a, a pair of redox

Figure 3. SEM images at different magnifications of (a, b) Ni$_3$S$_2$@NF and (c, d) Cu(OH)$_2$/Ni$_3$S$_2$@NF. The thin nanosheets in the dashed circles in (d) are Cu(OH)$_2$.

Figure 4. (a, b) TEM images for Cu(OH)$_2$/Ni$_3$S$_2$ separated from the ligaments of NF. (c) HRTEM image for Cu(OH)$_2$/Ni$_3$S$_2$. (d) Charge/discharge mechanism of the 1D/2D heterostructure for SCs in a KOH electrolyte.

Figure 5. (a) Nitrogen adsorption/desorption isotherms and (b) corresponding pore size distribution of Ni$_3$S$_2$@NF and Cu(OH)$_2$/Ni$_3$S$_2$@NF.
peaks located at about 0.05 and 0.3 V with a scan rate of 5 mV s\(^{-1}\) belonging to the reversible Faradic redox reactions of Ni(II)/Ni(III). In the curve of Cu(OH)\(_2\)/Ni\(_3\)S\(_2\)@NF at the same scan rate (see Figure 6c), a pair of redox peaks appeared at about 0.05 and 0.43 V, attributed to the reversible Faradic redox reactions of Ni(II)/Ni(III) and Cu(II)/Cu(I), respectively. Compared with the curves of Ni\(_3\)S\(_2\)@NF, the reduction peak shifts more negatively and simultaneously the oxidation peak shifts more positively in the curves for Cu(OH)\(_2\)/Ni\(_3\)S\(_2\)@NF. This might be due to the fact that the improvement of OH\(^-\) transfer is helped by Cu\(^+/\)Cu\(^{2+}\) and Ni\(^{2+}/\)Ni\(^{3+}\), which demonstrates the specific pseudocapacitive contributions of Ni\(_3\)S\(_2\) and Cu(OH)\(_2\) in the electrode. According to the CV results, the diffusion-controlled process dominates the electrochemical reactions, which is in accordance with the hierarchically 3D nanowire network structure and richness in 1D/2D interfaces promoting the electrolyte diffusion. The electron/ ion transfer of the interfacial redox reactions has a faster kinetics for Cu(OH)\(_2\)/Ni\(_3\)S\(_2\)@NF. Under the same scan rate, the integrated area of CV curves for Cu(OH)\(_2\)/Ni\(_3\)S\(_2\)@NF is larger than that for Ni\(_3\)S\(_2\)@NF, which suggests that the former has a higher electrochemical capacity. The improvement is because the thin Cu(OH)\(_2\) nanosheets strongly give pseudocapacitive contribution by supplying much more much charges.

Furthermore, galvanostatic charge and discharge (GCD) of the two electrodes are performed and the obtained curves are presented in Figure 6b,d. It is observed that two obvious well-defined voltage plateaus corresponding to the Faradic redox reaction appear during the charge/discharge process, in good agreement with the redox peaks. Specific capacitances are obtained according to the discharge curve from the reported equation \(C = I\Delta t/(m\Delta V)\), and the discharge times of the Cu(OH)\(_2\)/Ni\(_3\)S\(_2\)@NF heterostructure are much longer than those of Ni\(_3\)S\(_2\)@NF at the same current densities. The CV and GCD results suggest that Cu(OH)\(_2\)/Ni\(_3\)S\(_2\)@NF has a better electrochemical performance. Specific capacitances of the Ni\(_3\)S\(_2\)@NF and Cu(OH)\(_2\)/Ni\(_3\)S\(_2\)@NF electrodes at various
current densities are presented in Figure 6e. Specific capacitances of the Cu(OH)$_2$/Ni$_3$S$_2$@NF electrode are calculated to be 1855, 1479, 1412, 1371, and 1188 F g$^{-1}$ at 2, 5, 8, 10, and 20 A cm$^{-2}$, respectively. As expected, these values are much higher than those of the Ni$_3$S$_2$@NF electrode (1310, 1015.2, 610.5, 487.6, and 212.6 F g$^{-1}$ at the corresponding current densities). In general, the large specific surface area and porous network structure can enhance the active sites and improve the electrochemical performance. As discussed in Figure 5, the higher BET value of Cu(OH)$_2$/Ni$_3$S$_2$@NF and hierarchical distribution of pores facilitate faster ion transport and assure higher rate performance. The improved electrochemical performance should be attributed to the combined advantages of the 1D/2D heterostructures of Cu(OH)$_2$/Ni$_3$S$_2$. One-dimensional Ni$_3$S$_2$ nanowires grown on the NF surface facilitate the electron transport and boost the electrical conductivity in Cu(OH)$_2$/Ni$_3$S$_2$@NF, meanwhile, 2D ultrathin Cu(OH)$_2$ nanosheets are distributed among the nanowires networks, remarkably increasing the amount of electroactive sites, which is able to efficiently accelerate the process of the ion’s diffusion and diminish the diffusion distance to the interior surfaces in the electrode.

The cycling stability is also another important index for SCs. To further examine the recycling stability of the as-obtained Cu(OH)$_2$/Ni$_3$S$_2$@NF electrode, the cycling performance is performed by GCD tests in a 3 M KOH solution. With a high current density of 20 mA cm$^{-2}$, the specific capacitance of Cu(OH)$_2$/Ni$_3$S$_2$@NF increases by 18.2% in the initial 4800 cycles (the black curve), as shown in Figure 6f. The possible reason is that the Cu(OH)$_2$/Ni$_3$S$_2$@NF electrode is selectively etched in a 3 M KOH alkaline solution and further activated electrochemically in the initial cycling process, which is able to increase the electroactive surface area and to improve their wettability, and these changes encourage the trapped electrolyte ions to diffuse out. Although the capacitance displays slight fluctuations after the initial increase, its specific capacitance still keeps beyond 110% of the initial specific capacitance after 35,000 cycles. This is because the active material with the unique heterostructures had been absolutely contacted with the electrolyte ions after 4800 cycles, and more electrochemical active sites participated in the oxidation–reduction reaction. This is quite common in many other reported works.\cite{52–54} Coulombic efficiency is calculated based on the reported equation $\eta = t_d / t_c \times 100\%$, in which $t_c$ and $t_d$ stand for the charge time and discharge time, respectively.\cite{58} Notably, the Coulombic efficiency of Cu(OH)$_2$/Ni$_3$S$_2$@NF keeps a good stability with a value of 95.6% ± 0.5% and no drastic fluctuation can be observed during the whole cycling measurements (the red curve). This means that there is no significant reduction in the ratio of $t_d$ to $t_c$ during continuous charge–discharge cycles, which is mainly due to the obtained unique nanostructure. Therefore, Cu(OH)$_2$/Ni$_3$S$_2$@NF shows an excellent charge–discharge long-term electrochemical durability for energy storage. The inset of Figure 6f shows an SEM image of the electrode after continuous 35,000 cycles at a high current density of 20 mA cm$^{-2}$. It can be observed that the whole morphology and the intact 3D network structure are remained well after the cycling, which further demonstrates that the Cu(OH)$_2$/Ni$_3$S$_2$@NF electrode has an excellent cyclic stability.

The intrinsic difference of the interfacial redox reaction kinetics between the two electrodes is highly dependent on the internal resistances that can be analyzed by electrochemical impedance spectroscopy (EIS) measurements. Nyquist plots of the two electrodes are shown in Figure 7. The inset picture shows the proposed equivalent circuit applied to gain the electrochemical parameters, where $R_s$ stands for the resistance of the electrolyte solution, $R_{ct}$ denotes the Faradic charge transfer resistance, $C_d$ represents the double-layer capacitance, and $W$ expresses the Warburg impedance, which stands for the electrolyte diffusion. The Nyquist plots of both the electrodes display a small semicircle expressed by an almost vertical line. The Cu(OH)$_2$/Ni$_3$S$_2$@NF electrode displays an $R_{ct}$ value of 1.08 $\Omega$, which is smaller than the Ni$_3$S$_2$@NF electrode ($R_{ct}$ = 1.3 $\Omega$). The smaller internal resistance is owing to the thin Cu(OH)$_2$ nanosheets, which are well separated apart and maintained a space for the electrolyte to reach the surface of the Ni$_3$S$_2$ nanowires. Cu(OH)$_2$/Ni$_3$S$_2$@NF has much more active sites available and a faster ion/charge transport kinetics, and the redox reactions are thus increased.

A two-electrode symmetric device as a coin-type cell is fabricated by assembling two pieces of Cu(OH)$_2$/Ni$_3$S$_2$@NF (1 cm × 1 cm) with the same mass as the positive electrode and the negative electrode, respectively. A schematic configuration of the designed coin-type cell is illustrated in Figure 8a. The GCD curves of the assembled supercapacitor (ASC) examined at 3, 5, 10, 20, and 50 mA cm$^{-2}$ are represented in Figure 8b. It can be clearly seen that all of the GCD curves at varying current densities remain in good symmetry at different cell voltages, suggesting that the device has an outstanding electrochemical reversibility. Based on the GCD curves (Figure 8c), the ASC gives a specific capacitance of 47.6, 34.6, 25.5, 18.1, and 10.4 F g$^{-1}$ at different current densities (3, 5, 10, 20, and 50 mA cm$^{-2}$), respectively. More importantly, an inset digital image shows that the cell is able to deliver the current normally, which promises potential applications.

To further investigate the stable performance for the assembled coin-type cell, the cell is subjected to 30,000 cycles of full-depth charge and discharge at 50 mA cm$^{-2}$ in a 3 M KOH electrolyte. As shown in Figure 8d, although a slight fluctuation is present in the capacitance during the long-time cycling test due to the minor temperature variation, the capacitance retention of the cell still remains more than 98% after this long-term cycling, which can be attributed to the 1D/2D heterostructures. More importantly, two of the assembled ASCs are able to power a mobile phone, as displayed by the
inset digital image in Figure 8d. The excellent performance opens many opportunities for miniaturized electronic devices.

3. CONCLUSIONS

In summary, we demonstrate the fabrication of 1D Ni$_3$S$_2$ nanowire/2D Cu(OH)$_2$ nanosheet heterostructures by two-step hydrothermal reactions. First, the surface layer of NF is sulfidated, leading to an in situ growth of 1D Ni$_3$S$_2$ nanowire networks. In the following hydrothermal process, Cu$^{2+}$ ions react with hydroxide ions to form 2D Cu(OH)$_2$ nanosheets, which cover the 1D Ni$_3$S$_2$ nanowires to construct 1D/2D heterostructures. The Cu(OH)$_2$/Ni$_3$S$_2$@NF electrode demonstrates enhanced electrochemical performance with a superior cyclic performance of more than 110% capacity retention at 20 mA cm$^{-2}$ over 35,000 cycles. Especially, the ASC delivers an outstanding long-life recycling stability, maintaining a capacitance retention of more than 98% at 50 mA cm$^{-2}$ after 30,000 cycles. The improved performance for SCs is owing to the unique architecture supplying a high contacting area between the electrolyte with the active sites, alleviated structural pulverization during the process of the ion insertion and desertion, a good electrical conductivity for increased ions/charge kinetics, and a synergistic effect between 1D Ni$_3$S$_2$ nanowires and 2D Cu(OH)$_2$ nanosheets. This encouraging work provides a new path for developing heterostructures for high-rate and cycle-stable energy storage.

4. EXPERIMENTAL SECTION

4.1. Materials’ Preparation. 4.1.1. Preparation of Ni$_3$S$_2$@NF. A piece of thin NF (2 cm $\times$ 2 cm) was cleaned in a 1 M HCl solution for 10 min under ultrasonic irradiation and then was washed by using deionized water and absolute ethanol few times. Subsequently, the NF was put into a vacuum oven to be dried. Typically, 2 mmol of sublimed sulfur (S$_8$) powders was dissolved in the mixed solution consisting of anhydrous ethylenediamine (16 mL) and absolute ethanol (16 mL) under magnetic stirring. Then, the mixed solution was transferred into a clean and dry Teflon-lined stainless-steel autoclave (50 mL). After that, the pretreated NF was placed in the autoclave with the mixed solution. Subsequently, the autoclave was heat treated in an oven for 6 h with a constant temperature of 160 °C. After cooling to r.t., the obtained Ni$_3$S$_2$@NF product was rinsed by using deionized water and ethanol several times. Finally, the rinsed Ni$_3$S$_2$@NF was dried in a vacuum oven with a constant temperature of 50 °C.

4.1.2. Preparation of Cu(OH)$_2$/Ni$_3$S$_2$ Heterostructures. Typically, 0.8 mmol of CuSO$_4$·5H$_2$O was dissolved into a hexamethylenetetramine solution with the concentration of Cu$^{2+}$ ions being 0.125 M. Then, the as-prepared solution was transferred into a 50 mL clean and dry Teflon-lined stainless-steel autoclave, and Ni$_3$S$_2$@NF was immersed into the solution. After that, the autoclave was thermally treated in a blast dry oven for 5 h with the constant temperature maintained at 90 °C. Subsequently, the product was rinsed with the application of lots of deionized water and ethanol three times and then put into a vacuum oven for drying under 60 °C. Finally, the Cu(OH)$_2$/Ni$_3$S$_2$@NF electrode material was obtained and the loading mass of Cu(OH)$_2$/Ni$_3$S$_2$ was about 4.6 mg cm$^{-2}$.

4.2. Materials’ Characterizations. X-ray diffraction (XRD) were analyzed on a D/Max-RA X-ray diffractometer employing Cu radiation ($K_\alpha = 1.5418$ Å) with a certain scan rate (2° min$^{-1}$). X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo VG Scientific
KAAlpha spectrometer with an Al Kα radiation and a base pressure less than $3 \times 10^{-10}$ mbar. Scanning electron microscopy (SEM) images were investigated on an FE-SEM microscope (JSM-6510) with an acceleration voltage at 10 kV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were observed by using a JEM-2100HR (JEOL) with an accelerating voltage of 200 kV. The measurements of $N_2$ adsorption−desorption isotherms of the electrodes were obtained at 77 K by using a Micromeritics ASAP2020 equipment. The specific surface areas were gained according to the Brunauer−Emmett−Teller (BET) methods, and the pore size distributions were obtained based on the Barrett−Joyner−Halenda (BJH) method.

4.3. Electrochemical Tests. Electrochemical tests of the as-prepared products were conducted on an electrochemical workstation (Metrohm Autolab 302 N). Cyclic voltammetry, galvanostatic charge−discharge, long-term cycle performance, and electrochemical impedance spectroscopy measurements were all taken out through the same workstation. A platinum (Pt) plate, an Ag/AgCl electrode, and the prepared materials (1 cm × 1 cm) played as the counter electrode, the reference electrode, and the work electrode, respectively. In addition, specific capacitances of the electrodes were calculated based on the equation $C = \frac{I\Delta t}{m\Delta V}$, in which $I$ represents the discharge current (A), $\Delta t$ denotes the time of the discharge process (s), $m$ is the loading mass of the active materials (g), and $\Delta V$ stands for the window of the working potential (V). In the EIS measurements, the AC amplitude was kept at 5 mV and the frequency was conducted ranging from 105 to 0.1 Hz.

4.4. Symmetric Supercapacitors. To further estimate the capacitance values of the Cu(OH)$_2$/Ni$_3$S$_2$@NF electrode, an assembled supercapacitor (ASC) was fabricated as a coin-type cell by using the prepared Cu(OH)$_2$/Ni$_3$S$_2$@NF materials as electrodes together with a polyvinylidene fluoride separator in an alkaline electrolyte of the 3 M KOH solution.

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