$NiCo_2S_4/CuCo_2S_4$ Composite Cathode Materials for High-Performance Supercapacitors

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Abstract. Transition metal sulfides are considered as good electrode materials for supercapacitors due to their high specific capacity and good structural stability. However, its poor multiplicative performance and limited cycle life limit its wide application. To solve this problem, we synthesized $NiCo_2S_4/CuCo_2S_4$ bimetallic sulphide nanocomposites by combining $NiCo_2S_4$ with $CuCo_2S_4$ using a two-step hydrothermal method. Compared with $NiCo_2S_4$ and $CuCo_2S_4$ alone, the $NiCo_2S_4/CuCo_2S_4$ nanocomposites have higher specific capacity and better cycling stability as supercapacitor electrodes. The specific capacity value of the $NiCo_2S_4/CuCo_2S_4$ electrodes at 1 A g^{-1} is 830.3 C g^{-1} with a potential window of 0-0.5 V. The $NiCo_2S_4/CuCo_2S_4$ nanocomposites are used as the electrodes in supercapacitors. Ni_3S_4 and activated carbon as cathode and anode, respectively, the hybrid supercapacitor (HSC) assembled with NiCo2S4/CuCo2S4 electrodes has a capacitance value of 129.4 F g^{-1} at 1 A g^{-1} and an energy density of up to 52.9 Wh kg^{-1} at 410 W kg^{-1}. Long-term electrochemical stability tests show that the retention of the electrochemical specific capacity is 54% after 16,000 cycles.

Keywords: $NiCo_2S_4/CuCo_2S_4$, Supercapacitor, Nanocomposite.

1. Introduction

Transition metal sulfides have been shown to be highly promising SC materials due to their excellent thermal stability, theoretical specific capacitance, electrical conductivity, and the availability of more valence states. However, sulfur has a relatively poor multiplicative capacity and limited cycle life [1, 2]. One of the means to solve this problem is to increase the charge transport rate in SC. Among them, the introduction of heterogeneous metals to synthesise bimetallic sulphides as a way to modulate the surface reactivity is an effective way to improve the electrochemical performance, and cobalt-nickel sulphides and cobalt-copper sulphides have attracted a lot of attention due to the fact that the metal ions in them have multiple valence states and can be transformed into each other. According to previous studies, polymetallic sulphide electrode materials have better multiplicity, so it is necessary to prepare polymetallic sulphides to improve the electrochemical performance. Wei.et al. prepared Co-S@Ni hydroxide electrode materials, which can still exhibit 87 % capacitance retention and a high specific capacitance of 2730 F g^{-1} after 10,000 cycles [3]. A special structure of Zn-Co-S/Ni $(OH)_2$ composition multicomponent electrode material was designed and fabricated by Junaid et al. The electrochemical performance of their prepared electrode material Zn-Co-S/$Ni(OH)_2$ hybrid material was 2156 F g^{-1} with an energy density of 74.93 Wh kg^{-1} [4].

In this study, $NiCo_2S_4/CuCo_2S_4$ nanocomposites were successfully synthesised using a two-step hydrothermal method. The electrochemical performance of $NiCo_2S_4/CuCo_2S_4$ electrodes was greatly improved compared to $NiCo_2O_4/Cu_{0.76}Co_{2.24}O_4$ and constituent $NiCo_2S_4$ with $CuCo_2S_4$ before vulcanisation. Subsequently, the AC electrode was then combined to form the $NiCo_2S_4/CuCo_2S_4$//AC HSC and electrochemical tests were conducted on it, which proved that it had high energy density with good cycling stability, and its electrochemical specific capacity retention rate was 54 % after 16,000 cycles, which demonstrated that the introduction of copper and nickel could significantly improve the electrochemical performance of cobalt sulphides.

2. Experimental Section

2.1. Materials

All the reagents in their analytical grades were used without any further treatments. Cobalt acetate tetrahydrate (Co $(CH_3COO)_2 \cdot 4H_2O$, ≥99.0%) were received from Guangdong Chemical Reagent Engineering Technology R&D Center. Nickel acetate tetrahydrate (Ni $(CH_3COO)_2 \cdot 4H_2O$, ≥98.0%) and Copper acetate tetrahydrate (Cu $(CH_3COO)_2 \cdot H_2O$, ≥98.0%) were received from Chengdu Colom Chemicals Co., Ltd. Sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, ≥98.0%) were received from Chengdu Jinshan Chemical Reagent Co., LTD. Urea (≥99.0%) were received from Tianjin Zhiyuan Chemical Reagent C., LTD. Polytetrafluoroethylene (PTFE) and potassium hydroxide (KOH, 99.99%) were received from Aladdin Biochemical Technology Co., Ltd. Nickel foam was procured from Tianjin lvixin Chemical Co., Ltd. Carbon black was procured from Kuraray Co., Ltd.

2.2. Synthesis of $NiCo_2S_4/CuCo_2S_4$

Cu $(CH_3COO)_2 \cdot H_2O$ (0.49 g) and Ni $(CH_3COO)_2 \cdot 4H_2O$ (0.662 g) and Co $(CH_3COO)_2 \cdot 4H_2O$ (0.49 g) were dissolved in 75 mL of deionized water and stirred for 15 minutes. The whole solution was stirred for 20 min after adding urea (0.480 g) and KOH (0.11 g) to the above solution man. Then $C_6H_8O_7$ (0.38 g) was added and stirred for 20 min and then poured into a 100 mL hydrothermal kettle and reacted at 160 °C for 6 h and naturally cooled to room temperature. The prepared precursor was washed with deionized water and anhydrous ethanol alternately three times and dried at 60 °C for 8 h. The prepared precursor (0.16 g) and $Na_2S \cdot 9H_2O$ (2.8 g) were placed into to 75 mL of deionized water with stirring for 20 min and then poured into a 100 mL hydrothermal kettle, reacted at 120 °C for 8 h and naturally cooled to room temperature. The samples were washed three times alternately with anhydrous ethanol and deionized water and dried at 60 °C for 8 h. For comparison, this experiment involved exploring the synergistic improvement of multiple ions and $NiCo_2S_4$ was prepared using the same process as $CuCo_2S_4$ for comparison.

3. Results and Discussion

The XRD spectra of $NiCo_2S_4/CuCo_2S_4$ (CCNS) nanocomposites are shown in Fig. 1(a). The diffraction peaks of the obtained samples are (220), (311), (400), (440) from the granular material $NiCo_2S_4$ (JCPDS card No. 43-1477) and (220), (311), (400), (440) from $CuCo_2S_4$ (JCPDS card No. 42-1450), respectively. No other phases were detected, proving that the composite consists only of $NiCo_2S_4$ and $CuCo_2S_4$. As shown in Figs. 1(b) and (d), the SEM images of the $NiCo_2S_4/CuCo_2S_4$ nanocomposites show that the $NiCo_2S_4/CuCo_2S_4$ nanocomposites are made of nanoparticles stacked in a structure, and it can be seen from the figure that the lattice of $NiCo_2S_4/CuCo_2S_4$ particles is about 0.28 nm, which corresponds to the $CuCo_2S_4$ (113) surface, the lattice of $NiCo_2S_4$ particles is about 0.33 nm, which corresponds to the (220) surface of $NiCo_2S_4$, and it can be seen that the $NiCo_2S_4/CuCo_2S_4$ nanocomposites have certain crystalline nature from Fig. 1(d).

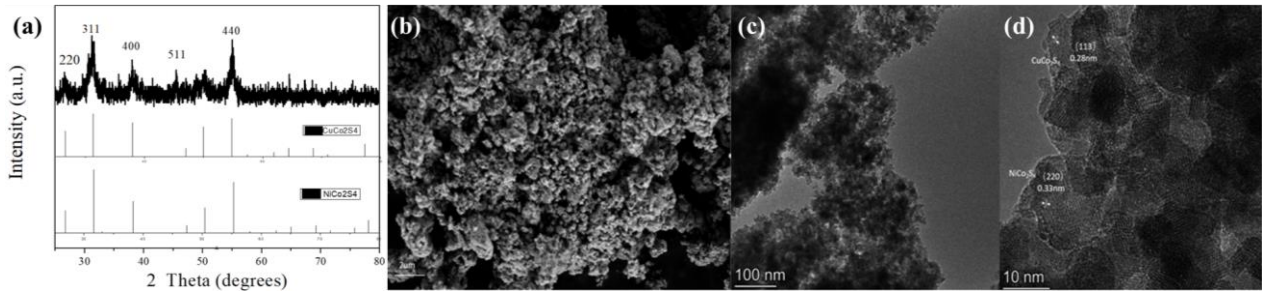

Figure 1. $NiCo_2O_4/CuCo_2O_4$ nanocomposite of (a) XRD spectrum, (b) SEM image, (c) TEM image, (d) HR-TEM image.

The three electrodes of $NiCo_2S_4$, $CuCo_2S_4$ and $NiCo_2S_4/CuCo_2S_4$ nanocomposites were subjected to CV and GCD tests and compared using a three-electrode test system, in which the electrolyte used was an aqueous solution of 2 M KOH, and the results are shown in Fig. 2a, where the three-electrode CV test was carried out for 10 mV s^{-1} according to the images, and the specific capacity of $NiCo_2S_4/CuCo_2S_4$ was the largest among the three electrode materials, and this can be seen that the specific capacity of $NiCo_2S_4/CuCo_2S_4$ was the largest. $CuCo_2S_4$ has the largest area among the three electrode materials, which shows that the specific capacity of $NiCo_2S_4/CuCo_2S_4$ is the largest. The redox peaks of $NiCo_2S_4$, $CuCo_2S_4$ and $NiCo_2S_4/CuCo_2S_4$ electrodes are very obvious, and it can be seen that the redox peaks are shifted to the two ends of the graph, which are asymmetric redox peaks. From the Fig. 2a, it can be seen that the closed area of the CV curve of $NiCo_2S_4/CuCo_2S_4$ is the largest, and it is known that $NiCo_2S_4/CuCo_2S_4$ has a larger specific capacity. Fig. 2b shows the GCD curve, the three electrode materials have obvious charging and discharging platforms, which can be seen to be dominated by the battery type, and at the same time have good symmetry, indicating a high Coulombic efficiency. The EIS of $NiCo_2S_4$, $CuCo_2S_4$ and $NiCo_2S_4/CuCo_2S_4$ electrode materials were determined by using the three-electrode test system as shown in Figs. 2c for the $NiCo_2S_4$, $CuCo_2S_4$ and $NiCo_2S_4/CuCo_2S_4$ nanocomposite electrode materials, where the R_{ct} is large (1.14, 1.08, 0.96 Ω) and small is similar to each other, which indicates that the anisotropy between the crystal interfaces of the composites did not affect their charge transport too much, while the three-electrode test shows that the composite $NiCo_2S_4/CuCo_2S_4$ has the best electrochemical performance. According to Fig. 2d, the peak voltage during the test is proportional to the scan rate, indicating that the $NiCo_2S_4/CuCo_2S_4$ nanocomposites have a good Faraday behavior, and the shape of the CV curve does not change much while the scan rate is gradually increased, which shows that the $NiCo_2S_4/CuCo_2S_4$ nanocomposite electrodes have a good redox stability. According to the GCD curve in Fig. 2e the specific capacity can be calculated for different current densities. The specific capacities of $NiCo_2S_4/CuCo_2S_4$ nanocomposite electrodes at different current densities of 0.5, 2, 4, 6, 8, 10, 15, 20, and 30 A g^{-1} were 902.5, 876.5, 846.5, 809, 785, 722.5, 744.5, 712.5, 700, and 613 C g^{-1}, respectively, with a capacity retention of 69%. The specific capacity decreases with increasing current density because at lower current densities, the ions in the electrolyte are able to sufficiently penetrate the interior and surface of the active material and the Faraday reaction is more adequate. The electrochemical reaction kinetics of the $NiCo_2S_4/CuCo_2S_4$ nanocomposite electrode was analyzed by curve fitting using log v and log i, and the fitted curves were obtained as shown in Fig. 2f. The b value of the electrode was calculated to be 0.53, indicating that the energy storage mechanism of the electrode material is dominated by diffusion control.

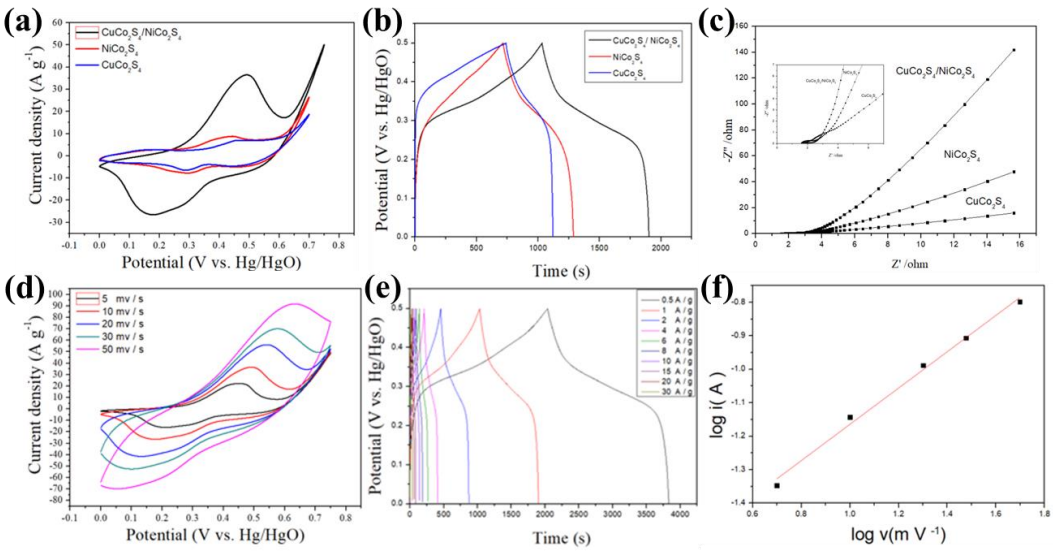

Figure 2. (a) CV, (b) GCD and (c) EIS curve of $NiCo_2S_4$, $CuCo_2S_4$ and $NiCo_2S_4/CuCo_2S_4$. (d) CV, (e) GCD and (f) logarithmic relationship between scan rate v and peak current i of $NiCo_2S_4/CuCo_2S_4$.

For further performance analysis of $NiCo_2S_4/CuCo_2S_4$, $NiCo_2S_4/CuCo_2S_4$ and AC electrodes were assembled into HSC. in with 2 M KOH aqueous solution as the electrolyte of HSC. The CV curves of $NiCo_2S_4/CuCo_2S_4$//AC at a scan rate of 10 mV s^{-1} are shown in Fig. 3a. The potential window of AC is -1 V~0 V, while that of $NiCo_2S_4/CuCo_2S_4$ composite electrode material is 0~0.7 V, but there is a certain polarisation phenomenon, so 0~1.65 V is selected as the potential window of HSC, as shown in Fig. 3b. The Ragone plot of this HSC is shown by Fig. 3c, and the energy density is 52.9 Wh kg^{-1} when the power density of the device is 410 W kg^{-1}. When the device has a power density of 7700 W kg^{-1} and energy density of 30.5 Wh kg^{-1}, its performance is better than that of reported supercapacitors with terpolymer metal sulfide electrode materials. The cyclic stability of $NiCo_2S_4/CuCo_2S_4$//AC device was tested with a constant current density of 6 A g^{-1}. After 16,000 cycles, the test results were shown in Fig. 3d. During the cycle, the specific capacity of $NiCo_2S_4/CuCo_2S_4$ electrode continued to decrease and eventually became stable. Finally, after 16,000 charge and discharge cycles, the specific capacity of the $NiCo_2S_4/CuCo_2S_4$ electrode was able to maintain 52.4% of its initial capacity, and the coulomb efficiency remained above 98% during the process.

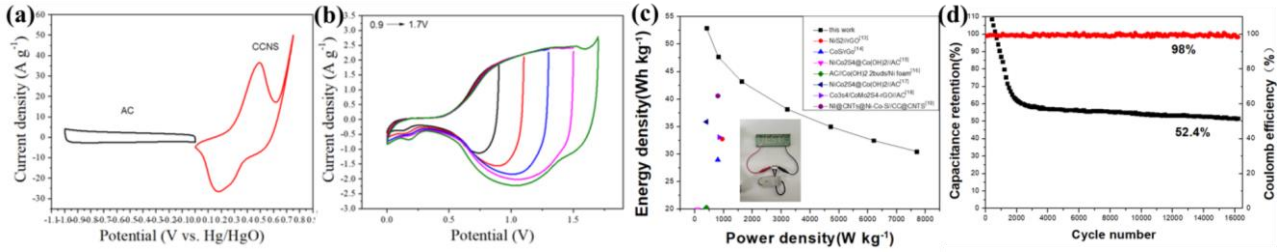

Figure 3. $NiCo_2S_4/CuCo_2S_4$//AC of (a) CV curves at 10 mV s^{-1}, (b) CV curves at various voltage ranges, (c) Ragone plots, and Long Cycle tests.

4. Summary

$NiCo_2S_4/CuCo_2S_4$ nanocomposites were prepared by a two-step hydrothermal method. The specific capacity of the $NiCo_2S_4/CuCo_2S_4$ nanocomposite electrode was 876.5 C g^{-1} at 1 A g^{-1}. Comparing $NiCo_2S_4$ with $CuCo_2S_4$, it has excellent electrochemical properties and the energy density of the assembled $NiCo_2S_4/CuCo_2S_4$//AC HSC was 52.9 Wh kg^{-1} at a power density of 410 Wk g^{-1}. After 16,000 charge/discharge cycles, the $NiCo_2S_4/CuCo_2S_4$ nanocomposites maintained 52.4%, which indicates that the developed $NiCo_2S_4/CuCo_2S_4$ nanocomposites have a good application prospect as electrode materials for energy storage devices.

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