Facile Synthesis of Ultrathin CuCo$_2$S$_4$ Nanosheets for High-Performance Supercapacitors

Liang Chen, Yinze Zuo, Yu Zhang and Yanmin Gao*

School of Materials Science and Engineering, Jiangsu University of Science and Technology, Jiangsu, Zhenjiang 212003, China
*E-mail: gymjust@126.com

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Two-dimensional (2D) structural CuCo$_2$S$_4$ exhibits great potential for applications in the renewable energy and catalysis fields. However, the fabrication of CuCo$_2$S$_4$ nanosheets remains a great challenge, and studies focussed on CuCo$_2$S$_4$ nanosheets used for supercapacitors are seldom reported. In this work, for the first time, polyvinylpyrrolidone (PVP) was used to level the sulfurization rate and reactivity of Cu and Co ions in a glycerol solution. As a result, the crystallographic growth direction of CuCo$_2$S$_4$ was controlled to be a sheet. Furthermore, the obtained CuCo$_2$S$_4$ nanosheets mainly exhibited an ultrathin thickness of approximately 15 nm. From the electrochemical measurements, the specific capacitance of the CuCo$_2$S$_4$ nanosheet was 1742 F g$^{-1}$ at a current density of 10 A g$^{-1}$. The capacitance retention was 93.4% at 10 A g$^{-1}$ for 2000 cycles. In addition, the CuCo$_2$S$_4$ nanosheet/rGO asymmetric supercapacitor exhibited an energy density of approximately 45.6 Wh kg$^{-1}$ at a power density of 748.2 W kg$^{-1}$. After 5000 cycles at a current density of 10 A g$^{-1}$, the capacitance retention was 91.7%.

Keywords: supercapacitors, CuCo$_2$S$_4$ nanosheet, polyvinylpyrrolidone, glycerol, solvothermal method

1. INTRODUCTION

Rapid fossil fuel consumption and serious environmental pollution have seriously hampered the development of science, technology and society [1, 2]. To solve this problem, as a promising energy conversion device, supercapacitors (SCs) have gained great attention due to their superior electrochemical properties such as high-power output, fast recharging rate and excellent cycling stability [3-5]. Active electrode materials, such as carbonaceous materials [6, 7], transition metal oxides [8, 9] and conductive polymers [10, 11], have been intensively investigated for their application as SCs. To date, SCs have been widely used in hybrid vehicles, industrial equipment and electricity systems. However, their energy density is obviously lower than that of rechargeable batteries.
exploit the further application of SCs, massive studies have been devoted to improving their energy density [12-15].

Recently, it has been confirmed that transition metal sulfides possess the ability to undergo a reversible redox reaction in alkaline electrolytes. The present correlative studies mainly focus on the binary metal sulfides such as MnS, CoS, NiS and MoS$_2$, which exhibit greater conductivity and higher energy density than transition metal oxides [16-19]. To develop novel electrode materials, the ternary metal sulfides receive extensive attention due to their synergistic effects with two metal ions and the crystal structure. Specifically, the spinel structural CuCo$_2$S$_4$ exhibits an ultrahigh specific capacitance and cycling stability as a pseudocapacitive material. Seyyed and co-workers synthesized CuCo$_2$S$_4$ hollow nanoneedle arrays on a Ni foam, which revealed a specific capacitance of 2163 F g$^{-1}$ at a current density of 6 mA cm$^{-2}$ [20]. Zhu and co-workers synthesized mesoporous CuCo$_2$S$_4$, which exhibited a specific capacitance of 752 F g$^{-1}$ at a current density of 2 A g$^{-1}$ [21]. Wang and co-workers synthesized sphere-like CuCo$_2$S$_4$ nanostructure on a Ti wire, which showed 53.5 mF cm$^{-2}$ at a current density of 0.17 mA cm$^{-2}$ [22].

Clearly, the morphology of CuCo$_2$S$_4$ has a huge impact on its electrochemical performance. However, there have been few studies focused on CuCo$_2$S$_4$ nanosheets, and the CuCo$_2$S$_4$ nanosheets used as an active material for SCs have not been previously reported. Since the sulfurization rate and reactivity of Cu and Co ions are seriously influenced by the distinct affinity for elemental S, it is difficult to obtain pure CuCo$_2$S$_4$ nanosheets. To achieve the purpose, the reactivity of Cu and Co ions should be levelled. Therefore, the ligands in the Cu and Co precursors are vital. In this work, for the first time, polyvinylpyrrolidone (PVP) was used to synthesize CuCo$_2$S$_4$ nanosheets in a glycerol solution. According to the results of characterization, the CuCo$_2$S$_4$ thus obtained mainly exposed an ultrathin thickness of approximately 15 nm. As a comparison, the CuCo$_2$S$_4$ synthesized without PVP exhibited a morphology of agglomerated nanospheres. From the electrochemical measurements, the CuCo$_2$S$_4$ nanosheets exhibited better performance. The specific capacitance of the CuCo$_2$S$_4$ nanosheets was 1742 F g$^{-1}$ at a current density of 10 A g$^{-1}$. The capacitance retention was 93.4% at 10 A g$^{-1}$ for 2000 cycles. In addition, the CuCo$_2$S$_4$ nanosheet//rGO asymmetric supercapacitor exhibited superior performance for practical applications.

2. EXPERIMENT

2.1. Synthesis of the CuCo$_2$S$_4$ nanosheets and nanospheres

First, 1 mmol of C$_4$H$_6$CuO$_4$•H$_2$O, 2 mmol of C$_4$H$_6$CoO$_4$•4H$_2$O and 4 mmol of CS(NH$_2$)$_2$ were dissolved in 20 ml of glycerol, and then the solution was stirred at 100 °C for 5 h. Next, 0.1 g of polyvinylpyrrolidone (PVP-K30) was dissolved in 5 ml of glycerol and injected into the above solution. Subsequently, the mixture was transferred into a 100 ml Teflon-lined stainless-steel autoclave and heated at 200 °C for 1 h. After cooling to room temperature, the resultant was separated by centrifugation and washed with deionized water. Finally, the CuCo$_2$S$_4$ nanosheets were dried in a vacuum oven at 60 °C.
As a comparison, CuCo$_2$S$_4$ nanospheres were synthesized by the similar preparation process. The only difference was that no polyvinylpyrrolidone was injected into the solution.

### 2.2. Materials characterization

X-ray powder diffraction (XRD) was carried out on a D8 Advance diffractometer (Bruker, Germany) with Cu Ka radiation ($\lambda = 0.15406$ nm). The Raman spectra were recorded with an InVia Raman microscope (Renishaw, UK). The surface morphology and elemental distribution were observed by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) using a ZEISS Merlin Compact spectroscope (ZEISS, Germany). The microstructure was examined by transmission electron microscopy (TEM) using a JEM-2100F (JEM, Japan). The X-ray photoelectron spectroscopy (XPS) spectra were recorded by an ESCALAB 250Xi (ThermoFisher Scientific, America).

### 2.3. Electrochemical characterization

Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements were recorded with an Autolab-AUT86742. These measurements were carried out in a three-electrode system using 6 M KOH as the electrolyte. A platinum plate and saturated calomel electrode was used as the counter and reference electrodes, respectively.

The working electrode was fabricated by coating active electrode material onto pure nickel foam. The active electrode material was a mixture of CuCo$_2$S$_4$, super P and polyvinylidene fluoride (PVDF) with a mass ratio of 8:1:1. Then, the electrode was pressed at 10 MPa for 30 s and dried in a vacuum at 100 °C for 24 h. Finally, the specific capacitance of the CuCo$_2$S$_4$ nanosphere and nanosheet electrode was calculated by the following equation:

$$C_{sp} = \frac{I \times \Delta t}{m \times \Delta V}$$

where $C_{sp}$, $I$, $\Delta t$, $m$ and $\Delta V$ are the specific capacitance (F g$^{-1}$), discharge current (A), discharge time (s), mass of the active material (g) and potential window (V), respectively.

The CuCo$_2$S$_4$ nanosheet/rGO asymmetric supercapacitor was fabricated using the CuCo$_2$S$_4$ nanosheet electrode as a positive electrode and rGO as a negative electrode. The mass ratio of CuCo$_2$S$_4$ nanosheets and rGO can be calculated by the following equation:

$$\frac{m_+}{m_-} = \frac{C_{5-} \times \Delta V_-}{C_{5+} \times \Delta V_+}$$

where $m$ is the mass (g), $C_s$ is the specific capacitance (F g$^{-1}$) and the $\Delta V$ is the potential window (V) of each electrode. As a result, the mass ratio of is approximately 0.2.

The energy density and power density of this asymmetric supercapacitor were calculated by the following equation:

$$E_m = \frac{C_{sp} \times \Delta V^2}{2 \times 3600}$$

$$P_m = \frac{E_m \times 3600}{t_{dis}}$$
where $E_m$ and $P_m$ are the energy density (Wh kg$^{-1}$) and power density (W kg$^{-1}$), respectively. $\Delta V$ is the potential window (V) and $t_{dis}$ is the discharge time(s).

3. RESULTS AND DISCUSSION

3.1. Morphological analysis

Fig. 1a shows the morphology of the CuCo$_2$S$_4$ nanospheres, which have an average size of 1 $\mu$m. A detailed image is illustrated in Fig. 1b, which reveals that these nanospheres are comprised of numerous nanosheets. Fig. 1c shows the morphology of the CuCo$_2$S$_4$ nanosheets, and a detailed image is illustrated in Fig. 1d. Clearly, these CuCo$_2$S$_4$ nanosheets show an average diameter of 500 nm and a thickness of approximately 15 nm. To further investigate the microstructure, a TEM image of the CuCo$_2$S$_4$ nanosheet was captured and is shown in Fig. 1e. In addition, Fig. 1f shows an HR-TEM image of CuCo$_2$S$_4$ nanosheets with an interplanar distance of 0.29 nm corresponding to the (1 1 3) plane of CuCo$_2$S$_4$.

These morphological results indicate that the crystallographic growth direction of CuCo$_2$S$_4$ was controlled to be a sheet during the incipient reaction. This finding is attributed to the ligand effect of the hydroxyl in the glycerol solution, which levelled the sulfurization rates and reactivity of Cu and Co ions. However, during the crystal growth process, the ligand effect of glycerol was not enough. These nanosheets became agglomerate nanospheres.
Although similar studies were reported that use an alcohol group, nitroxyl or amidogen, to synthesize sheet electrode active materials [23-25], this is the first investigation of the use of PVP as the active agent to synthesize CuCo$_2$S$_4$. As a result, the CuCo$_2$S$_4$ synthesized in a solution with PVP appeared as nanosheets.

### 3.2. Structural characterization and elemental composition

To further investigate the structure of the CuCo$_2$S$_4$ nanosheets and nanospheres, XRD patterns were captured and are shown in Fig. 2a. The apparent peaks at 2θ = 26.6°, 31.3°, 38.0°, 47.0°, 49.9° and 54.8° correspond to the (0 2 2), (1 1 3), (0 0 4), (2 2 4), (1 1 5) and (0 4 4) planes of CuCo$_2$S$_4$ (JCPDS card No. 42-1450), respectively. In addition, the CuCo$_2$S$_4$ nanosheets exhibit a higher crystallinity than that of the CuCo$_2$S$_4$ nanospheres. These structures correspond to a uniform sheet morphology for the CuCo$_2$S$_4$ nanosheets and an agglomerate morphology for the CuCo$_2$S$_4$ nanospheres.

The Raman spectra are shown in Fig. 2b and three main peaks are obviously observed. The Raman peak at 473 cm$^{-1}$ is assigned to the Cu-S bond [26, 27]. The other two peaks at 514 cm$^{-1}$ and...
680 cm\(^{-1}\) are assigned to the Co-S bond [28]. The higher peak intensity of the CuCo\(_2\)S\(_4\) nanosheets demonstrates a higher crystallinity, and the blueshift of the CuCo\(_2\)S\(_4\) nanospheres corresponds to a disordered structure containing more residual stress.

The EDS analysis of CuCo\(_2\)S\(_4\) nanosheets is shown in Fig. 3a and the EDS mapping demonstrates the homogeneous elemental distribution of Cu, Co and S. To investigate the oxidation of Cu, Co and S, an XPS survey was performed and is shown in detail. Fig. 3b illustrates the fine spectrum of Cu 2p. The binding energies at 951.8 and 931.8 eV are assigned to the spin–orbit doublets for the 2p\(_{1/2}\) and 2p\(_{3/2}\) peaks of Cu\(^{+}\), and the binding energies at 954.1 and 932.4 eV are assigned to the 2p\(_{1/2}\) and 2p\(_{3/2}\) peaks of Cu\(^{2+}\), respectively [29]. Fine spectrum of Co 2p is shown in Fig. 3c, and the binding energies at 795.7 and 778.9 eV are assigned to the spin–orbit doublets for the 2p\(_{1/2}\) and 2p\(_{3/2}\) peaks of Co\(^{2+}\), respectively. The binding energies at 793.4 and 778.2 eV are assigned to the 2p\(_{1/2}\) and 2p\(_{3/2}\) peaks of Co\(^{3+}\), respectively [30]. In addition, the satellite peaks of Co\(^{2+}\) exist at 801.2 and 780.9 eV. For the fine spectrum of S 2p shown in Fig. 3d, the binding energies at 161.7 and 161.0 eV are attributed to the spin–orbit doublets for 2p\(_{1/2}\) and 2p\(_{3/2}\) peaks of S\(^2-\) ions, respectively. In addition, the satellite peak of S\(^2-\) exists at 168.6 eV [31]. Furthermore, the binding energy at 162.8 eV is assigned to S bound to Cu [32].

\[\text{Figure 3. (a) EDS analysis of the CuCo}_2\text{S}_4\text{ nanosheets; and the XPS fine spectra of (b) Cu 2p, (c) Co 2p and (d) S 2p.}\]

3.3. Electrochemical measurements with a three-electrode system

The electrochemical properties of the CuCo\(_2\)S\(_4\) nanosphere and nanosheet electrode were estimated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical
impedance spectroscopy (EIS) measurements with a three-electrode system. Fig. 4a illustrates the CV curves of the CuCo$_2$S$_4$ nanosphere electrode at different scan rates from 5 to 50 mV s$^{-1}$ with a potential window from -0.2 to 0.4 V. Clearly, a pair of redox peaks can obviously be observed in these curves, and this is the typical characteristic of pseudocapacitive SCs. Fig. 4b illustrates the CV curves of the CuCo$_2$S$_4$ nanosheet electrode, which exhibits a similar shape as the CuCo$_2$S$_4$ nanosphere electrode. However, the CuCo$_2$S$_4$ nanosheet electrode reveals the higher peak current density at the same scan rate. To investigate the electrochemical reaction mechanism, the anodic and cathodic peak current densities against the scan rates are shown in Fig. 4c. The linear relationship between peak current densities and the square root of scan rates demonstrates the typical charge transfer process of the pseudocapacitive SCs [33, 34]. Fig. 4d illustrates the CV curves of the CuCo$_2$S$_4$ nanosphere and nanosheet electrodes at the same scan rate of 5 mV s$^{-1}$. Since the integral area of CV curve can be used to estimate the specific capacitance, naturally, the CuCo$_2$S$_4$ nanosheet electrode reveals the higher specific capacitance.

**Figure 4.** (a) CV curves of the CuCo$_2$S$_4$ nanosphere electrode, (b) CV curves of the CuCo$_2$S$_4$ nanosheet electrode, (c) peak current densities against the square root of scan rates (A and C represent the anodic and cathodic peak current density, respectively), and (d) CV curves of the CuCo$_2$S$_4$ nanosphere and nanosheet electrodes at the same scan rate of 5 mV s$^{-1}$.

Galvanostatic charge-discharge (GCD) measurements were carried out at various current densities from 10 to 50 A g$^{-1}$. The GCD curves of the CuCo$_2$S$_4$ nanosphere and nanosheet electrodes are illustrated in Fig. 5a and 5b, respectively. Corresponding to the results of CV curves, the nonlinear shape of GCD curves is attributed to the reversible redox reaction of CuCo$_2$S$_4$ with OH$^-$. The specific capacitances of these two electrodes are shown in Fig. 5c. At discharge current densities of 10, 20, 30, 40 and 50 A g$^{-1}$, the specific capacitances of the CuCo$_2$S$_4$ nanosphere electrode are 1138, 909, 796,
698 and 636 F g⁻¹, respectively. On the other hand, the specific capacitances of the CuCo₂S₄ nanosheet electrode at the same discharge current densities are 1742, 1618, 1516, 1433 and 1372 F g⁻¹. Literally, the CuCo₂S₄ nanosheet electrode reveals higher specific capacitances. Furthermore, the capacitance retention of the CuCo₂S₄ nanosheet electrode from 10 to 50 A g⁻¹ is 78.8%, which is higher than that of the CuCo₂S₄ nanosheet electrode (59.9%). It is well known that charge transfer into the interior active material is limited at high-rate GCD measurement [35, 36]. Obviously, the CuCo₂S₄ nanosheet with ultrathin thickness is more suitable for rapid charge transfer.

![GCD curves](image1)

**Figure 5.** GCD curves of the CuCo₂S₄ (a) nanosphere and (b) nanosheet electrodes; (c) specific capacitance at different current densities; EIS curves of the CuCo₂S₄ (d) nanosphere (e) and nanosheet electrodes; and (f) cycling stability.

To further investigate the charge transfer kinetics at the interface of the electrode and electrolyte, electrochemical impedance spectroscopy (EIS) data were collected. Fig. 5d illustrates the EIS curve of the CuCo₂S₄ nanosphere electrode, and the equivalent circuit fits well with the raw data.
Reasonably, the equivalent circuit contains the impedance from the electrolyte solution ($R_s$), the adhesives ($R_{ad}$) and the reaction resistance ($R_{re}$) of CuCo$_2$S$_4$ with OH$^-$ [37]. In addition, the roughness of the working electrode causes an extra influence ($R_{ro}$). As shown in Fig. 5e, although the CuCo$_2$S$_4$ nanosheet electrode reveals the same equivalent circuit, the charge transfer resistance is lower than that of the CuCo$_2$S$_4$ nanosphere electrode, which is illustrated in the inset.

To estimate the cycling stability of the CuCo$_2$S$_4$ nanosphere and nanosheet electrodes, continuous GCD measurements were performed at a current density of 10 A g$^{-1}$. After 2000 cycles, the capacitance retention of the CuCo$_2$S$_4$ nanosheet electrode is 93.4%, which is higher than that of the CuCo$_2$S$_4$ nanosphere electrode (86.8%).

In view of these above characterization and electrochemical measurements, CuCo$_2$S$_4$ nanosheets exhibit better performance than the nanospheres. The main reason is that the CuCo$_2$S$_4$ nanosheets with an ultrathin thickness facilitate charge transfer into the interior active material and provide a larger contact area with electrolyte than that of the CuCo$_2$S$_4$ nanospheres. In addition, the higher crystallinity and more ordered morphology ensure the stability of the CuCo$_2$S$_4$ nanosheet electrode during electrochemical measurements. Compared with the recent studies, as shown in Table 1, the CuCo$_2$S$_4$ nanosheets exhibit the better performance than other correlative studies focused on morphology.

Table 1. Comparative representation of the specific capacity of recently reported correlative studies.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Specific capacitance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_7$S$_4$ nanowires</td>
<td>400 F g$^{-1}$ at 10 mV s$^{-1}$</td>
<td>[38]</td>
</tr>
<tr>
<td>MnCo$_2$S$_4$ nanoneedle</td>
<td>1402 F g$^{-1}$ at 1 A g$^{-1}$</td>
<td>[39]</td>
</tr>
<tr>
<td>Multilayer NiCo$_2$S$_4$@MnO$_2$</td>
<td>1338 F g$^{-1}$ at 2 A g$^{-1}$</td>
<td>[40]</td>
</tr>
<tr>
<td>Mesoporous CuCo$_2$S$_4$</td>
<td>752 F g$^{-1}$ at 2 A g$^{-1}$</td>
<td>[21]</td>
</tr>
<tr>
<td>Sphere-like CuCo$_2$S$_4$@Ti wire</td>
<td>53.5 mF cm$^{-2}$ at 0.17 mA cm$^{-2}$</td>
<td>[22]</td>
</tr>
<tr>
<td>CuCo$_2$S$_4$ nanospheres</td>
<td>1138 F g$^{-1}$ at 10 A g$^{-1}$</td>
<td>This work</td>
</tr>
<tr>
<td>CuCo$_2$S$_4$ nanosheets</td>
<td>1742 F g$^{-1}$ at 10 A g$^{-1}$</td>
<td>This work</td>
</tr>
</tbody>
</table>

3.4. Electrochemical measurements of the CuCo$_2$S$_4$ nanosheet/rGO asymmetric supercapacitor

To evaluate the practical energy storage applications of the CuCo$_2$S$_4$ nanosheets, the CuCo$_2$S$_4$ nanosheet electrode was used as a positive electrode, and the rGO was used as a negative electrode to assemble an asymmetric supercapacitor [41, 42]. Fig. 6a shows the CV curves of the CuCo$_2$S$_4$ nanosheet/rGO asymmetric supercapacitor at different scan rates from 10 to 50 mV s$^{-1}$ with a potential window from 0 to 1.6 V. The GCD curves at different current densities from 1 to 20 A g$^{-1}$ are illustrated in Fig. 6b. The linear shape of GCD curves is a typical characteristic of asymmetric supercapacitors. The cycling stability was investigated at a current density of 10 A g$^{-1}$. After 5000 cycles, the capacitance retention was 91.7%. The energy density and power density were calculated...
using GCD curves, and the results were illustrated as a Ragone plot, which is shown in Fig. 6c. At a power density of 748.2 W kg\(^{-1}\), the energy density is 45.6 Wh kg\(^{-1}\). Compared with recent studies, as shown in Table 2, the CuCo\(_2\)S\(_4\) nanosheet/rGO asymmetric supercapacitor reveals a superior practicability.

![Figure 6](image)

**Figure 6.** (a) CV curves and (b) GCD curves of the CuCo\(_2\)S\(_4\) nanosheet//rGO asymmetric supercapacitor; (c) cycling stability at a current density of 10 A g\(^{-1}\), and (d) Ragone plots of the asymmetric supercapacitors.

**Table 2.** Comparative representation of the energy density with recently reported asymmetric supercapacitors.

<table>
<thead>
<tr>
<th>Asymmetric supercapacitor</th>
<th>Energy density</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCo(_2)S(_4) nanonneedle//AC</td>
<td>44.1 Wh kg(^{-1}) at 800 W kg(^{-1})</td>
<td>[20]</td>
</tr>
<tr>
<td>Cu(_7)S(_4) nanowires//carbon fibres</td>
<td>35.0 Wh kg(^{-1}) at 200 W kg(^{-1})</td>
<td>[38]</td>
</tr>
<tr>
<td>MnCo(_2)S(_4) nanonneedle//rGO</td>
<td>43.0 Wh kg(^{-1}) at 801 W kg(^{-1})</td>
<td>[39]</td>
</tr>
<tr>
<td>NiCo(_2)S(_4) nanosheet//AC</td>
<td>25.5 Wh kg(^{-1}) at 334 W kg(^{-1})</td>
<td>[43]</td>
</tr>
<tr>
<td>Co(_9)S(_8) layer//AC</td>
<td>31.4 Wh kg(^{-1}) at 200 W kg(^{-1})</td>
<td>[44]</td>
</tr>
<tr>
<td>CuCo(_2)S(_4) nanosheet//rGO</td>
<td>45.6 Wh kg(^{-1}) at 748 W kg(^{-1})</td>
<td>This work</td>
</tr>
</tbody>
</table>
The superior electrochemical performance of the CuCo$_2$S$_4$ nanosheet/rGO asymmetric supercapacitor is attributed to the following synergies. First, the CuCo$_2$S$_4$ nanosheets ensured an excellent positive electrode with a high specific capacitance and great cycling stability. Furthermore, the appropriate mass ratio of the anode and cathode active materials maintained the charge transfer balance between these two electrodes.

4. CONCLUSIONS

For the first time, polyvinylpyrrolidone (PVP) was used to control the crystallographic growth direction of CuCo$_2$S$_4$ in a glycerol solution. The obtained CuCo$_2$S$_4$ nanosheets mainly exposed an average thickness of approximately 15 nm. From the electrochemical measurements, CuCo$_2$S$_4$ nanosheets facilitated the charge transfer into the interior active material and provided a large contact area with the electrolyte. The specific capacitance of the CuCo$_2$S$_4$ nanosheets was 1742 F g$^{-1}$ at a current density of 10 A g$^{-1}$. The capacitance retention was 93.4% at 10 A g$^{-1}$ for 2000 cycles. In addition, the CuCo$_2$S$_4$ nanosheet/rGO asymmetric supercapacitor exhibited an energy density of approximately 45.6 Wh kg$^{-1}$ at a power density of 748.2 W kg$^{-1}$. After 5000 cycles at a current density of 10 A g$^{-1}$, the capacitance retention was 91.7%.

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References


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