Co-doped amorphous NiMoS$_4$ modified with rGO for high-rate and long-cycle stability of hybrid supercapacitor

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1. Experimental section

1.1 Materials

(NH$_4$)$_2$S solution (16–20%), NH$_3$·H$_2$O (30–33%), (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, Co(NO$_3$)$_2$·6H$_2$O, concentrated H$_2$SO$_4$ (95–98%), KMnO$_4$, KOH and polytetrafluoroethylene (PTFE) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Needle Coke (carbon content ≥ 98% and ash content ≤ 0.8%) was purchased from Jinzhou Petrochemical Co., Ltd (China). All reagents and solvents were of analytical grade and used as received.

1.2 Preparation of GO

Graphite oxide (GO) is prepared by a modified Hummers method.

1.3 Preparation of (NH$_4$)$_2$MoS$_4$

The preparation method of (NH$_4$)$_2$MoS$_4$ has been improved on the basis of the work of our group$^1$. 19.6 g of (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O were dissolved in 50 mL of ammonia water, and the pH of the ammonia water was adjusted to 9 using NH$_3$·H$_2$O. The solution was stirred in a water bath at 65 °C for 1 h after...
340 mL of (NH$_4$)$_2$S solution was added. Following this, the solution was crystallized in an ice-water bath at 0 °C for 1 h. The resulting material was washed with deionized water and vacuum-dried for 12 h at 60 °C to give (NH$_4$)$_2$MoS$_4$.

1.4 Preparation of Ni$_{1-x}$Co$_x$MoS$_4$/rGO composite

The preparation process taking Ni$_{0.7}$Co$_{0.3}$MoS$_4$/rGO as an example is as follows: 0.13 g of (NH$_4$)$_2$MoS$_4$ was dissolved in 20 mL of deionized water in a 60 °C water bath. At the same time, 0.102 g of Ni(NO$_3$)$_2$·6H$_2$O and 0.044 g of Co(NO$_3$)$_2$·6H$_2$O were added to 40 mL of GO dispersion with 16 mg dispersed in it, stirred at a constant speed for 10 min, and then sonicated for 20 min. Then the cooled (NH$_4$)$_2$MoS$_4$ solution was slowly added dropwise to the above dispersion, stirred at a constant speed for 30 min, and reacted at 120 °C for 12 h. The samples were centrifuged three times with deionized water and then freeze-dried to obtain a black powder sample. A series of Ni$_{1-x}$Co$_x$MoS$_4$/rGO (x=0, 0.3, 0.5, 0.7 and 1) composites were prepared by adjusting the molar ratio of nickel-cobalt metal salts. For comparison, NiMoS$_4$ and Ni$_{0.7}$Co$_{0.3}$MoS$_4$ were prepared under the same conditions without adding GO.

1.5 Preparation of needle coke oxide (NCO)

1 g of the needle coke (NC) was slowly added to a beaker containing 25 mL of concentrated H$_2$SO$_4$ under ice-water bath, and stirred for 1 h. Then 3 g of KMnO$_4$ was slowly added in an ice-water bath andkept stirring for 12 h at room temperature. After that, 60 mL of deionized water was slowly added to the above mixture, stirring for 12 h at 60 °C. Finally, the product was rinsed to neutrality with deionized water and dried at 60 °C in oven, named as NCO.

1.6 Materials characterization

The crystalline phase was investigated by powder X-ray diffraction (XRD, Bruker D8 Advance with Cu K$_\alpha$ radiation, $\lambda = 0.15418$ nm). The specific surface area was obtained from the N$_2$ adsorption-
desorption isotherms and calculated by the Brunauer-Emmett-Teller method (BET, ASAP2460). The chemical species and structure of samples were examined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) and Fourier transform infrared spectroscopy (FT-IR, Nicolet Avatar 370). The morphology of samples was observed by field-emission scanning electron microscopy (FESEM, Zeiss Supra 55) equipped with an energy dispersive spectrometer (EDS) and transmission electron microscopy (TEM, JEOL JEM-2100).

1.7 Electrochemical measurements

Electrochemical studies were conducted using three-electrode and two-electrode systems. Acetylene black and polytetrafluoroethylene (PTFE) were used as the conductive component and binder, respectively. The active material, acetylene black, and PTFE were uniformly mixed in an 8:1:1 mass ratio, and the resulting slurry was uniformly coated on a porous NF substrate with a 1 cm×1 cm area. The mass of the active ingredient is approximately 1.2 mg. As the electrolyte, a KOH solution of 6 mol L⁻¹ was used. The platinum rod and the Hg/HgO electrode serve as the counter and reference electrodes in the three-electrode test, respectively. For the two-electrode test, a CR2032 battery box was used, and glass fiber filter paper was used as a separator to construct a two-electrode symmetrical button capacitor. The cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) tests of the samples were performed using the CHI 760E electrochemical workstation of Shanghai Chenhua Company. All electrochemical tests were performed at room temperature.

The specific capacitance \( C \) (C·g⁻¹) of the three-electrode system was calculated using the equation:\(^1\)

\[
C = \frac{I \Delta t}{m}
\]  
where \( m \) is the weight of the active material, \( \Delta t \) is the discharge duration, \( I \) is the discharge current.

The following equations are used to compute the power density \( P \) (W·kg⁻¹) and energy density \( E \) (Wh·kg⁻¹) of the HSC:\(^2\)

\[
E = \frac{C A V}{7.2}
\]  

\[\text{Equation 1}\]

\[\text{Equation 2}\]
\[ \frac{3600E}{\Delta t} \]

where \( C \) represents the specific capacitance of the HSC (C·g⁻¹), and \( \Delta V \) and \( \Delta t \) are equivalent to those in equations (1).

Fig. S1 XRD spectra of NiMoS₄ and standard card

Fig. S2 The EDS spectra of Ni₀.7Co₀.3MoS₄/rGO (the inset shows the Ni, Co, Mo and S elemental mappings).
Fig. S3 (a) Amplified Raman spectra of GO, RGO and Ni$_{0.7}$Co$_{0.3}$MoS$_4$/rGO from 2450 cm$^{-1}$ to 3000 cm$^{-1}$, (b) Amplified Raman spectra of NiMoS$_4$ and Ni$_{0.7}$Co$_{0.3}$MoS$_4$/rGO from 500 cm$^{-1}$ to 1000 cm$^{-1}$.

Fig. S4 FT-IR spectra of NiMoS$_4$, NiMoS$_4$/rGO and Ni$_{0.7}$Co$_{0.3}$MoS$_4$/rGO

Fig. S4 clearly shows that rGO has weak absorption bands at 1630, 1403, 1150 and 1098 cm$^{-1}$, which is caused by functional groups such as -OH, -O and -OOH on the surface. In addition, the tensile vibration peaks of Ni-S and Mo-S appeared at 760 and 631 cm$^{-1}$ respectively. With the introduction of Co, the Ni-S and Mo-S peak intensities of the Ni$_{0.7}$Co$_{0.3}$MoS$_4$/rGO curve are also weakened. These results indicate that NiMoS$_4$ and Ni$_{0.7}$Co$_{0.3}$MoS$_4$/rGO were successfully prepared.
Fig. S5 (a) XPS survey spectrum of NiMoS$_4$/rGO. Core XPS spectrum of (b) C 1s, (c) Ni 2p, (d) Mo 3d and (e) S 2p XPS spectra of NiMoS$_4$/rGO.

The Ni 2p spectrum of NiCoMoS$_4$/rGO can be fitted into the satellite peaks (862.7 and 882.0 eV), corresponding to Ni$^{3+}$ (879.7 and 857.1 eV) and Ni$^{2+}$ (875.4 and 853.8 eV) characteristic peaks. The above data can prove that compared with NiMoS$_4$/rGO, the Ni characteristic peaks of Ni$_{0.7}$Co$_{0.3}$MoS$_4$/rGO generally have obvious red shift.

Fig. S6 CV (a) and GCD (b) curves of Ni$_{0.7}$Co$_{0.3}$MoS$_4$ and Ni$_{0.7}$Co$_{0.3}$MoS$_4$/rGO.
Fig. S7 GCD curves of NCO in different current density.

Table S1 Comparison of electrochemical performance of Ni\textsubscript{0.7}Co\textsubscript{0.3}MoS\textsubscript{4}/rGO (three-electrode system) with reported transition metal-based sulfides electrode in literatures

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Specific capacity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni\textsubscript{0.7}Co\textsubscript{0.3}MoS\textsubscript{4}/rGO</td>
<td>509.8 C·g\textsuperscript{-1} at 1 A·g\textsuperscript{-1}</td>
<td>This work</td>
</tr>
<tr>
<td>Amorphous CoMoS\textsubscript{4}</td>
<td>396.6 C·g\textsuperscript{-1} at 1 A·g\textsuperscript{-1}</td>
<td>6</td>
</tr>
<tr>
<td>Amorphous structured NiMoS\textsubscript{4}-rGO</td>
<td>500 C·g\textsuperscript{-1} at 1 A·g\textsuperscript{-1}</td>
<td>7</td>
</tr>
<tr>
<td>NiCo\textsubscript{2}S\textsubscript{4} nanotube</td>
<td>397 C·g\textsuperscript{-1} at 1 A·g\textsuperscript{-1}</td>
<td>8</td>
</tr>
<tr>
<td>NiCo\textsubscript{2}O\textsubscript{4} flowerlike nanostructure</td>
<td>361.9 C·g\textsuperscript{-1} at 1 A·g\textsuperscript{-1}</td>
<td>9</td>
</tr>
<tr>
<td>NiCo\textsubscript{2}S\textsubscript{4}@MnO\textsubscript{2} heterostructure</td>
<td>286.4 C·g\textsuperscript{-1} at 1 A·g\textsuperscript{-1}</td>
<td>10</td>
</tr>
<tr>
<td>NiCo\textsubscript{2}S\textsubscript{4} cubic octahedron</td>
<td>334 C·g\textsuperscript{-1} at 1 A·g\textsuperscript{-1}</td>
<td>11</td>
</tr>
<tr>
<td>rGO\textsubscript{100}-CNT\textsubscript{50}-Co\textsubscript{3}S\textsubscript{4}</td>
<td>488.6 C·g\textsuperscript{-1} at 1 A·g\textsuperscript{-1}</td>
<td>12</td>
</tr>
<tr>
<td>Ni\textsubscript{2}S\textsubscript{3}-MoS\textsubscript{2} nano flower</td>
<td>490.8 C·g\textsuperscript{-1} at 1 A·g\textsuperscript{-1}</td>
<td>13</td>
</tr>
<tr>
<td>MOF-derived Co\textsubscript{9}S\textsubscript{8}/carbon</td>
<td>367 C·g\textsuperscript{-1} at 1 A·g\textsuperscript{-1}</td>
<td>14</td>
</tr>
<tr>
<td>Co\textsubscript{3}O\textsubscript{4}-rGO</td>
<td>330 C·g\textsuperscript{-1} at 0.5 A·g\textsuperscript{-1}</td>
<td>15</td>
</tr>
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</table>
Table S2 Rate performance of NiMoS$_4$/rGO, Ni$_{0.7}$Co$_{0.3}$MoS$_4$/rGO, Ni$_{0.5}$Co$_{0.5}$MoS$_4$/rGO, Ni$_{0.3}$Co$_{0.7}$MoS$_4$/rGO and CoMoS$_4$/rGO

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Capacitance in 1 A·g$^{-1}$ (C·g$^{-1}$)</th>
<th>Capacitance in 20 A·g$^{-1}$ (C·g$^{-1}$)</th>
<th>Capacitance retention (%)</th>
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<tr>
<td>NiMoS$_4$/rGO</td>
<td>114.1</td>
<td>36</td>
<td>31</td>
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<tr>
<td>Ni$<em>{0.7}$Co$</em>{0.3}$MoS$_4$/rGO</td>
<td>509.8</td>
<td>260.3</td>
<td>51</td>
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<tr>
<td>Ni$<em>{0.5}$Co$</em>{0.5}$MoS$_4$/rGO</td>
<td>312</td>
<td>76.8</td>
<td>24.6</td>
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<tr>
<td>Ni$<em>{0.3}$Co$</em>{0.7}$MoS$_4$/rGO</td>
<td>140</td>
<td>34.6</td>
<td>24.7</td>
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<tr>
<td>CoMoS$_4$/rGO</td>
<td>370</td>
<td>23.8</td>
<td>6.4</td>
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</table>

Reference


