Electronic Supporting Information

Preparation of Two-Dimensional Assembled Ni-Mn-C Ternary Composite for High-Performance All-Solid-State Flexible Supercapacitor

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Experimental Section

Synthesis of Ni-MOF crystals
In a typical procedure, 1.3 g NiCl₂•6H₂O and 3 g K₂C₂O₄ were dissolved in 20 mL deionized water (refer to as dispersion A). 1.5 mL ethylenediamine (C₈H₁₈N₂) was added to 1.3 g NiCl₂•6H₂O to form a dispersion B. Then, dispersion B was added dropwisely into dispersion A under stirring. After reaction at ambient condition for 48 h, the formed Ni-MOF crystals were collected by centrifugation followed by washing using methanol several times, and drying in a vacuum oven at 40 °C.

Preparation of Ni(OH)₂-MnO₂/C, MnO₂/C, Ni(OH)₂/C and Ni-MOF-derived porous carbon (NPC) composites
First, the prepared Ni-MOF crystals were annealed under N₂ protection at 300 °C for 1 h, and then 700 °C for another 2 h to obtain the Ni@C composite. After that, 20 mg Ni@C composite and 6 mg potassium permanganate (KMnO₄) were dispersed in 36 mL deionized water. The mixed solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave, and then heated at 150 °C for 24 h. The Ni(OH)₂-MnO₂/C composites were collected and washed with distilled water several times, and then dried in a vacuum oven at 60 °C. Ni-MOF-derived porous carbon (NPC) was obtained by etching Ni@C composite using an aqueous mixture of 3 M FeCl₃ and 3 M HCl at 80 °C for 8 h, followed by washing with deionized water until PH=7, and then drying in a vacuum oven at 60 °C.

The preparation of MnO₂/C composites is similar to that of the Ni(OH)₂-MnO₂/C composites. Briefly, Ni-MOF-derived porous carbon and potassium permanganate (KMnO₄) (mass ratio of 3:1) was dispersed in 36 ml deionized water. The obtained solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave, and then heated at 150 °C for 1 h. The MnO₂/C composites were collected and washed with distilled water several times, and then dried in a vacuum oven at 60 °C.

The Ni(OH)₂/C composite was prepared by mixing 30 mg NPC, 32 mg NiCl₂•6H₂O and 50 mg Urea in 20 mL distilled water. Then the mixed solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave, and heated at 180 °C for 2 h. The Ni(OH)₂/C composites were
collected and washed with distilled water several times, and then dried in a vacuum oven at 60 °C.

Material characterizations

The field emission scanning electron microscope (FESEM, Hitachi SL8010) and transmission electron microscopy (TEM, JEM-100CX II) were used to characterize morphology, microstructure and element compositions of the samples. The structures of the samples were identified by a X-ray powder diffractometer (XRD, PANalytical X'Pert PRO) with Cu Ka radiation (\( \lambda = 1.54056 \, \text{Å} \)) operating at 40 kV and 250 mA, and a Raman spectroscopy (LabRAM HR800 Horiba JobinYvon) with a 531.95 nm laser. The surface chemical states of samples were investigated using a X-ray photoelectron spectroscopy (XPS, Shimadzu Co., Ltd. Hongkong) with a Kratos Axis Ultra-DLD system.

Electrochemical measurements

The Ni(OH)$_2$-MnO$_2$/C composites electrode was fabricated by coating a slurry, which is composed of Ni(OH)$_2$-MnO$_2$/C composites, acetylene black and polyvinylidene difluoride (weight ratio is 8:1:1) dispersed in N-methyl-2-pyrrolidone (NMP), on a carbon paper. Then, the prepared electrodes were dried in a vacuum oven at 80 °C for overnight. Measurements of CV, galvanostatic charge/discharge, electrochemical impedance spectroscopy were carried out on a CHI 760E electrochemistry workstation. The electrochemical measurements of individual working electrodes were performed in 6 M KOH aqueous solution using three-electrode configuration. A platinum foil was used as counter electrode, and an Ag/AgCl was served as reference electrode. The all-solid-state symmetric supercapacitor was constructed by using Ni(OH)$_2$-MnO$_2$/C composites as cathode and anode, and KOH/poly(vinyl alcohol) (PVA) gel as solid electrolyte. The KOH/PVA gel electrolyte was prepared by mixing 0.5 g PVA and 0.5 g KOH in 5 mL distilled water at 80-90 °C to form a homogeneous gel.

The capacitive contribution from surface- and diffusion-controlled processes was analyzed according to Dunn’s method.\(^{47}\) The current response (\( i \)) in a fix potential (\( V \)) were calculated according to the following equation:

\[
i(V) = k_1 V + k_2 V^{1/2}
\]
Where $\nu$ is the sweep rate, $k_1 \nu$ and $k_2 \nu^{1/2}$ presents capacitive effects and diffusion-controlled insertion effects, respectively.
Fig. S1. SEM images of Ni-MOF crystals.

Fig. S2. SEM images of the Ni@C composite derived from Ni-MOF.
**Fig. S3.** TEM image of the Ni(OH)$_2$-MnO$_2$/C composite after a strong sonication to separate the components, and corresponding EDX element mapping images of the region indicated by the red box.

**Fig. S4.** HRTEM image of a MnO$_2$ nanosheet within obtained Ni(OH)$_2$-MnO$_2$/C composite.
Fig. S5. TEM images of a porous carbon structure, which was obtained by the treatment of Ni(OH)$_2$-MnO$_2$/C composite in 1 M HCl for 8 h to completely remove Ni(OH)$_2$, MnO$_2$ and Ni.

Fig. S6. Raman spectra of the Ni(OH)$_2$-MnO$_2$/C and Ni@C composites. * indicates the peak which can be assigned to M-O (M = Ni, Mn) stretching vibrations from Ni(OH)$_2$ and/or MnO$_2$. 
Fig. S7. Nyquist plot of the obtained Ni(OH)$_2$-MnO$_2$/C composite.
Fig. S8. (A) SEM images of the MnO$_2$/C composite. (B) Raman spectra of the MnO$_2$/C composite and Ni-MOF-derived porous carbon (NPC). # indicates the peak corresponding to Mn-O stretching vibrations from MnO$_2$. (C) SEM images of the Ni(OH)$_2$/C composite. (D) XRD pattern of the Ni(OH)$_2$/C composite (the (002) peak is from graphitic carbon). (E) CV curves of the Ni(OH)$_2$-MnO$_2$/C, Ni(OH)$_2$/C, MnO$_2$/C and NPC at a scan rate of 100 mV/s. (F) Rate performance of the Ni(OH)$_2$/C composite at different current densities.
Table S1. The electrochemical performance contribution of each component to the total performance of Ni(OH)$_2$-MnO$_2$/C composite.

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight percentage (%)</th>
<th>Performance contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPC</td>
<td>16</td>
<td>1.7</td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>18</td>
<td>7.2</td>
</tr>
<tr>
<td>Ni(OH)$_2$</td>
<td>66</td>
<td>91.1</td>
</tr>
</tbody>
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Based on the weight percentage of each component of Ni(OH)$_2$-MnO$_2$/C composite obtained from inductively coupled plasma-mass spectrometry (ICP-MS) measurements and corresponding result of electrochemical characterization, the performance contribution of each component can be roughly obtained, which indicates Ni(OH)$_2$ plays an essential role.

Fig. S9. Electrochemical measurements of the fabricated all-solid-state supercapacitors device based on obtained Ni(OH)$_2$-MnO$_2$/C composite. (A) Charge/discharge curves at different current densities. (B) Specific capacitances at different current densities.
Fig. S10. Nyquist plot of the fabricated all-solid-state supercapacitors device based on obtained Ni(OH)$_2$-MnO$_2$/C composite, which shows an equivalent series resistance of 0.71 Ω.