Electronic Supplementary Information

Low-cost and high energy density asymmetric supercapacitors based on polyaniline nanotubes and MoO$_3$ nanobelts

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Experimental details

Materials: Aniline monomer (AN, Shanghai Chemical Works, China) was distilled under reduced pressure. D-tartaric acid (D-TA, Shanghai Chemical Works, China), ammonium persulfate (APS, Tianjin Damao Chemical Co., China) and sodium molybdate (Na$_2$MoO$_4$·2H$_2$O, Tianjing Chemical Co., China), solutions were prepared using deionized water. All other chemical reagents were in analytical grade.

Synthesis of PANI nanotubes: The PANI nanotubes were fabricated similar to our previous reported literature.[51] In a typical process, aniline monomer (2 mmol) and D-tartaric acid (1 mmol) were dissolved in 10 mL of deionized water with magnetic stirring for 20 min at room temperature. After that, the resulting solution was cooled to 0-5 °C in an ice bath and an aqueous solution of ammonium persulfate (2 mmol in 5 mL of deionized water) cooled in advance was added drop-by-drop into the above solution. The reaction was carried out with magnetic stirring below 5 °C for 10 h. The resulting precipitate was washed several times with deionized water and ethanol, respectively. Finally, the product was dried at 60 °C for 12 h to obtain a dark green powder.

Synthesis of MoO$_3$ nanobelts: In a typical process, 4.84 g Na$_2$MoO$_4$·2H$_2$O was dissolved in 10 ml
deionized water. Then 16 ml 4 M HClO₄ was added dropwise to the molybdate solution under constant stirring. Finally, this solution was transferred into a 100 ml Teflon-lined stainless steel autoclave and heated at 140 °C for 24 h. After cooled to room temperature naturally, the resulting precipitates of MoO₃ were collected by filtration, washed with distilled water and absolute ethanol for several times to remove the residue of reactants, and then dried in vacuum at 60 °C for 12 h.

**Materials Characterization**

The morphologies of the as-prepared products were examined with field emission scanning electron microscopy (FE-SEM, JSM-6701F Japan) at an accelerating voltage of 5.0 kV. The structure of the PANI samples was characterized by a transmission electron microscopy (TEM, JEM-2010 Japan). X-ray diffraction (XRD) of samples was performed on a diffractometer (D/Max-2400, Rigaku) advance instrument using Cu Kα radiation (λ =1.5418 Å) at 40 kV, 100 mA. The 2θ range used in the measurements was from 5 to 80°.

**Three-electrode fabrication**

For conventional three-electrode system, the glassy carbon electrode with a diameter of 5 mm was used as the working electrode. The working electrodes were fabricated similar to the literature.[82] Typically, 4 mg of electrode material was ultrasonically dispersed in 0.4 mL of 0.25 wt% Nafion (DuPont, USA). The above suspension of 8 μL using a pipet gun was dropped onto the glassy carbon electrode and dried at room temperature. The three-electrode system was tested in 1 M H₂SO₄ aqueous solutions, platinum electrode serves as the counter electrode, and standard calomel electrode (SCE) as the reference electrode, respectively.

**Two-electrode cell fabrication**

The capacitive performance of asymmetric supercapacitors was investigated using a two-electrode testing cell. The working electrode was prepared by mixing the electroactive material with polyvinylidene fluoride (PVDF) and commercial carbon black (8:1:1) in N-methyl-2-pyrrolidone (NMP) until homogeneous slurry. The slurry was coated on carbon plate (99.99%, 3 mm) with a working area of 1.0 cm² and the electrodes were dried at 120 °C for 12 h. To construct an ASC, the loading mass ratio of active materials (PANI//MoO₃) was estimated to be 0.89 from
the specific capacitance calculated from their galvanostatic charge/discharge curves. The PANI
positive electrode and MoO$_3$ negative electrode were pressed together and separated by a thin
polypropylene film. The electrochemical measurements of the ASCs were carried out in a two
electrode cell at room temperature in 1 M H$_2$SO$_4$ electrolyte.

**Electrochemical measurements**

The electrochemical properties of the samples were investigated by cyclic voltammetry (CV)
and galvanostatic charge/discharge measurements in three-electrode cell and two-electrode
configuration using a CHI 660D electrochemical workstation. The cycle-life stability was
performed using computer controlled cycling equipment (LAND CT2001A, Wuhan China).
Electrochemical impedance spectroscopy (EIS) measurements were performed with the Autolab
PGSTAT 128N equipped (Eco-chemie, Netherland) with FRA module, the frequency ranging
from 10 mHz to 100 kHz and an impedance amplitude of ±5 mV at open circuit potential.

The gravimetric capacitance from galvanostatic charge/discharge was calculated by using the
formula of $C_s=4I\Delta t/(m\Delta V)$ for the two-electrode cells, while, $C_s^* = I\Delta t/(m\Delta V)$ for the three-
electrode system, where $I$ is the constant current (A) and $m$ is the mass (g) of electrode material
(For the two-electrode cells, $m$ is the total mass of positive and negative electrodes), $\Delta t$ the
discharge time and $\Delta V$ the voltage change during the discharge process.

The specific energy density ($E$, Wh kg$^{-1}$) and power density ($P$, W kg$^{-1}$) for a supercapacitor cell
can be calculated using the following equations: $E=1/2CV^2$ and $P=E/t$, where $C$ is the specific
capacitance of supercapacitor cell, $V$ is voltage change during the discharge process after IR drop
in V-t curve, and $t$ is the discharge time.
Figure S1. Nyquist plots of PANI and MoO$_3$ electrodes for three-electrode system and its expanded high frequency region (inset).

Figure S2. Comparative CV curves of PANI and MoO$_3$ electrodes performed in three electrode cell in 1 M H$_2$SO$_4$ electrolyte at a scan rate of 100 mV s$^{-1}$
**Figure S3.** Nyquist plots of PANI//MoO$_3$ asymmetric supercapacitors for two-electrode system (the inset of modeled equivalent circuit of electrochemical impedance spectroscopy).
<table>
<thead>
<tr>
<th>ASCs structure</th>
<th>Electrolyte</th>
<th>Operation voltage (V)</th>
<th>Energy density (Wh kg(^{-1}))</th>
<th>Power density (W kg(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GrMnO(_2)/GrMoO(_3)</td>
<td>Na(_2)SO(_4)</td>
<td>2.0</td>
<td>42.6</td>
<td>276</td>
<td>[S3]</td>
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<td>CNT/MnO(_2)/CNT/In(_2)O(_3)</td>
<td>Na(_2)SO(_4)</td>
<td>2.0</td>
<td>25.5</td>
<td>50.3K</td>
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<td>RGO-RuO(_2)/RGO-PANI</td>
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<td>26.3</td>
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<td>41.1</td>
<td>400</td>
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<tr>
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<td>43.5</td>
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<td>PbO(_2)/AC</td>
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<td>PANI//MoO(_3)</td>
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References