Supplementary Information

Cellulose-based hybrid 2D material aerogel for flexible all-solid-state supercapacitor with high specific capacitance

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Preparation of CNFs suspension

CNFs were prepared according to the literature methodology reported by Isogai, \textsuperscript{51} and described in brief as follows: TEMPO (0.0495 g) and NaBr (0.495 g) were dissolved in deionized water (400 mL) with continuous stirring. Next, hardwood bleached kraft pulps (3 g) were added after the catalysts have been completely dissolved. The oxidation reaction was started by adding the desired amount of the NaClO solution (15 mmol g\textsuperscript{-1} cellulose). Then 0.5 M NaOH was added to maintain the pH of the reaction solution at about 10.00-10.50 at 10\textdegree C until the pH remained essentially constant that indicated the oxidation reaction ended. And then the TEMPO-oxidized cellulose was washed thoroughly with deionized water by filtration for at least 3 times. After that, 2 mg mL\textsuperscript{-1} oxidized cellulose/water slurries were sonicated for 20 min at power of 300 W in an ice bath. Following, transparent CNFs dispersion was prepared by centrifuging at 9800 rpm for 20 min to remove the unfibrilated cellulose. The last the transparent CNFs dispersion was stored at 4\textdegree C before use.

Preparation of MoS\textsubscript{2} powder

The MoS\textsubscript{2} were synthesized via a hydrothermal route and described in brief as follows: 0.24 g Na\textsubscript{2}MoO\textsubscript{4}·2H\textsubscript{2}O was dissolved in 40 mL deionized water. Then 0.60 g L-cysteine was added after the Na\textsubscript{2}MoO\textsubscript{4} has been completely dissolved and the
mixture was diluted with deionized water to 70 mL, and then the solution was violently stirred for about 1 h. Subsequently, the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 200°C for 24 h. After cooling naturally, the black MoS$_2$ composites were collected by filtration, washed with distilled water and absolute ethanol for several times, and then dried in vacuum at 60°C for 24 h.

**Preparation of GO suspension**

The synthesis of dispersions of GO were produced using a modified Hummers’ method$^2$ from graphite powder and described in brief as follows: Graphite powder (5 g) was added into 100 ml beaker containing concentrated H$_2$SO$_4$ (25 ml), K$_2$S$_2$O$_8$ (5 g), P$_2$O$_5$ (5 g) with continuous stirring at 80°C. The resulting mixture was kept at 80°C for 4.5 h in oil bath, then DI water (~1 L) was added to the resulting mixture and left overnight. Pretreated graphite was thoroughly washed with water by filtration to remove all soluble substances and then dried in the oven at 60 °C. Pretreated graphite was added into 1000 ml beaker containing concentrated H$_2$SO$_4$ (230 ml) in ice bath. KMnO$_4$ (30 g) was added slowly to dissolve completely. The resulting mixture was allowed to react at 35 °C for hours, and then 460 ml DI water was slowly added. In the process of adding water, the temperature of the mixture was remained constant. Another 1.4 L DI water was added to the mixed solution with continuous stirring at room temperature for 2 h. Afterward, 25 ml of 30% H$_2$O$_2$ was added to the mixture with continuous stirring at room temperature. The color of the mixed solution becomes golden yellow. The resulting mixture was stand for about 12h and then the supernatant was decanted. The graphite oxide was thoroughly washed with 5% HCl solution and then DI water to remove all soluble substances. 8 mg·ml$^{-1}$ graphite oxide was sonicated for 20 min using an ultrasonic generator at an output powder of 800 W. The graphene oxide solution was centrifuged at 9800 r/m for 5 min to remove the
unexfoliated graphite oxide. The inorganic ions in graphene oxide suspension were removed by dialysis.

**Electrochemical characterization**

The electrochemical performances of all-solid-state flexible supercapacitors were tested by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS, on a CHI 660D, CH Instruments, Inc). All the electrochemical parameters are calculated as follows,

The gravimetric capacitance:

\[ C_g = \frac{4(\int idV)}{(v \times m \times V)} \text{ (CV curves)} \quad \text{or} \quad C_g = \frac{4I \times \Delta t}{(\Delta V \times m)} \text{ (GCD curves)} \]

The area capacitance:

\[ C_s = \frac{\int idV}{(v \times S \times V)} \]

The specific capacitance of supercapacitor devices:

\[ C_{sp} = \frac{I \times \Delta t}{(\Delta V \times m)} \]

\[ E = \frac{1}{2} C_{sp} \times V_{IR}^2 \]

\[ P = V_{IR}^2(4m \times R_{ESR}) \]

Where \( I \) is the applied current, \( \Delta t \) is the discharged time, \( \Delta V \) is the discharged potential, \( m \) is the total mass of two symmetrical electrodes (based on the total mass of MoS\(_2\) and RGO), \( V_{IR} \) is voltage after IR drop, \( v \) is the voltage scan rate, \( V \) is the cell voltage, and \( S \) is the area of the supercapacitor.

For the supercapacitor, the area made accessible to the electrolyte was 2.0 cm\(^2\), corresponding to a mass of 2.0 mg of the active materials (MoS\(_2\) and RGO) per electrode. The areal density of the active materials was calculated to be 1mg cm\(^2\) per electrode.
Photograph

**Fig. S1** Photograph of the CNFs/MoS$_2$/RGO nanohybrid aerogel

**Fig. S2** Demonstration of the flexibility of CNFs/MoS$_2$/RGO nanohybrid aerogel film

**Fig. S3** Photograph of the CNFs/MoS$_2$/RGO all-solid-state flexible supercapacitor

**Fig. S4** SEM images of different weight percentages of MoS$_2$ in the CNFs/MoS$_2$ aerogels, (a) 10%, (b) 20%, (c) 30%, (d) 40%, (e) 50%.
**Fig. S5** SEM image of MoS$_2$/RGO hybrid aerogel without CNFs.

**Fig. S6** Optical images of the aqueous dispersion of CNFs/MoS$_2$/GO, CNFs/MoS$_2$ and CNFs suspension.

**Fig. S7** (a) N$_2$ adsorption/desorption isotherms of CNFs aerogel, pure MoS$_2$, RGO aerogel. The inset is an enlarged view of the N$_2$ adsorption/desorption isotherm of MoS$_2$. (b) BJH pore size distribution curves of CNFs aerogel, pure MoS$_2$, RGO aerogel. (c) The enlarged view of (b). The inset is an enlarged view of the BJH pore size distribution curve of MoS$_2$. 

- Volume adsorption (cm$^3$/g)
- Relative Pressure (P/P$_0$)
- Diameter (nm)
- $\Delta V$ (cm$^3$/g)
**Table S1.** The specific electrode capacitance of some graphene and MoS$_2$-based supercapacitors

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specific capacitance (F g$^{-1}$)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNFs/MoS$_2$/RGO aerogel film</td>
<td>916.42</td>
<td>Our work</td>
</tr>
<tr>
<td>CNF/RGO/MoOxNy aerogel film</td>
<td>680</td>
<td>J. Mater. Chem. A, 2017$^{S3}$</td>
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<tr>
<td>CNFs/RGO/CNT aerogel film</td>
<td>252</td>
<td>ACS Appl. Mater. Interfaces, 2015$^{S4}$</td>
</tr>
<tr>
<td>PANI/MoS$_2$</td>
<td>575</td>
<td>Electrochimica Acta., 2013$^{S6}$</td>
</tr>
<tr>
<td>CNFs/RGO aerogel film</td>
<td>207</td>
<td>J. Mater. Chem. A, 2013$^{S8}$</td>
</tr>
<tr>
<td>RGO aerogel film</td>
<td>172</td>
<td>Adv. Mater., 2012$^{S9}$</td>
</tr>
<tr>
<td>GO</td>
<td>189</td>
<td>Energy Environ. Sci., 2011$^{S11}$</td>
</tr>
<tr>
<td>CNPs/RGO</td>
<td>198</td>
<td>Energy Environ. Sci., 2011$^{S12}$</td>
</tr>
<tr>
<td>RGO/cellulose</td>
<td>120</td>
<td>Adv. Energy Mater., 2011$^{S13}$</td>
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<tr>
<td>RGO aerogel</td>
<td>128</td>
<td>J. Mater. Chem, 2011$^{S14}$</td>
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**Table S2.** The capacitance per geometric area of some flexible or thin-film supercapacitors

<table>
<thead>
<tr>
<th>Materials</th>
<th>Areal capacitance (mF cm$^{-2}$)</th>
<th>Source</th>
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<tr>
<td>CNFs/MoS$_2$/RGO aerogel film</td>
<td>458</td>
<td>Our work</td>
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<tr>
<td>CNFs/RGO/CNT aerogel film</td>
<td>216</td>
<td>ACS Appl. Mater. Interfaces, 2015$^{S4}$</td>
</tr>
<tr>
<td>CNFs/RGO aerogel film</td>
<td>158</td>
<td>J. Mater. Chem. A., 2013$^{S8}$</td>
</tr>
<tr>
<td>Porous RGO film</td>
<td>45.6</td>
<td>Adv. Mater., 2012$^{S15}$</td>
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<tr>
<td>CNTs/bacterial cellulose paper</td>
<td>18.8</td>
<td>ACS Nano., 2012$^{S16}$</td>
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<tr>
<td>SWCNT/cotton paper</td>
<td>34</td>
<td>Nano Res., 2010$^{S17}$</td>
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<tr>
<td>CNT coating on paper</td>
<td>160</td>
<td>PNAS., 2009$^{S18}$</td>
</tr>
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Fig. S8 SEM image of the cross-section of the CNFs/MoS$_2$/RGO aerogel electrode infiltrated with H$_2$SO$_4$/PVA gel electrolyte: (a) before cyclic test, (b) the enlarged view of the red area of (a), (c) after 5000 cyclic test, (d) the enlarged view of the red area of (c).

References


