Electronic Supporting Information

From Tofu to N-doped Porous Carbon Nanobelts through Molten salts assisted “stripping and cutting” technique: A universal synthesis for high energy density asymmetric supercapacitor

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Experiment

\textit{Synthesis of 1D CNB materials:}

In this work, the pretreatment of fresh tofu is according to our previously reported, which was first frozen completely by using liquid nitrogen and then freeze dried for 48 h to obtained a powder, and used as a nitrogen containing precursor for the following carbonization process. Briefly, the tofu powder and ZnCl\textsubscript{2} salt with a weight ratio of 1:10 were homogeneous mixed by a ball mill and then transferred to a tube furnace and heated under Ar atmosphere. In order to evaluate the morphology transformation, the calcination temperature were set as 400, 600 and 800 °C, and kept for 0.5, 1, 2 and 4 h.

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After natural cooling to ambient temperature, then the products were first washed with 0.1 mol L\(^{-1}\) HCl solution and dispersion in sufficient amount of water to dissolve the salts. The obtained activated carbon was collected through filtration and further dried in vacuum at 80 °C for 24 h.

**Synthesis of MnO\(_2\)-CNB:**

MnO\(_2\)-CNB composite was synthesized by in-situ hydrothermal deposition method. 0.1 g of CNB was added into (0.04 mol, 90 mL) KMnO\(_4\) solution. Subsequently, the mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated up to 120 °C for 1 h. Then, the autoclave was taken out and naturally cooled down to room temperature. The as-synthesized sample was washed by deionized water and ethanol for several times and then dried in vacuum at 80 °C for 24 h.

**Materials Characterization**

The morphology and structure of the as-prepared samples were investigated by field emission scanning electron microscopy (Hitachi, SU-8000F), transmission electron microscopy (TEM, JEM-2010FEF), and X-ray diffraction (Rigaku TTR III) with Cu Kα radiation. The surface elemental composition was determined by X-ray photoelectron spectroscopy with Al Kα radiation (XPS, Thermo ESCALAB 250). Thermogravimetric analysis (TGA) is conducted on a Netzsch STA 449C analyzer and the sample is heated from room temperature to 800 °C at a heating rate of 5 °C min\(^{-1}\) under N\(_2\) atmosphere. N\(_2\) adsorption/desorption measurements were characterized by N\(_2\) adsorption at 77 K on an ASAP 2020 (Micrometritics, USA). All samples were degassed at 150 °C under vacuum for 10 h before the measurements. The specific
surface area was calculated by the modified Brunauer-Emmet-Teller (BET) method using the adsorption branch of nitrogen isotherm.

**Electrochemical measurements**

The working electrode was prepared as follows: resultant sample, carbon black and poly(tetrafluoroethylene) with a mass ratio of 85:10:5 in ethanol to form a slurry. Then the slurry was coated onto the nickel foam current collector to form the working electrode. The mass loading of active materials is ca. 3 mg cm$^{-2}$. The prepared electrode (1 cm$^2$ nominal planar area) acted as the working electrode, a platinum foil (1 cm×2 cm) served as the counter electrode, and Hg/HgO was used as the reference electrode. The cyclic voltammetrys (CVs), galvanostatic charging-discharging (GCD) tests and electrochemical impedance spectroscopy (EIS) were performed using a computerized potentiostat (Autolab PGSTAT302, Eco Chemie) Electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an AC voltage with 5 mV amplitude in a frequency range from 0.01 Hz to 100 kHz at the open circuit potential. The specific capacitance of the electrodes can be calculated from the charge/discharge curves according to the following equation:

\[ C_g = \frac{I \times \Delta t}{m \times \Delta V} \]  

(1-1)

where $C_g$ (F g$^{-1}$) is specific capacitance based on the mass of the active materials, $I$ (A) is the constant charge/discharge current, $\Delta t$ (s) is the discharge time, $\Delta V$ (V) is the discharge voltage excluding the IR drop. In the three-electrode set-up, $m$ (mg) is the mass loading of active material in a single electrode, in the two-electrode system, $m$ (mg) represents the total mass loading of active materials on both electrodes.
The energy density \( E \) and power density \( P \) of symmetric and asymmetric capacitors were calculated as the following equation:

\[
E = \frac{1}{2} CV^2 \quad \text{(1-2)}
\]

\[
P = \frac{E}{\Delta t} \quad \text{(1-3)}
\]

where \( C \) (F g\(^{-1}\)) represents the specific capacitance of the supercapacitor measured from the Eq. (1), \( V \) (V) refers to the discharge potential range that is exclusive of the IR drop, \( \Delta t \) (s) is the discharge time, \( E \) (Wh kg\(^{-1}\)) is the energy density, and \( P \) (W kg\(^{-1}\)) is the power density.

**Figure S1.** TG curves of Tofu powder
Figure S2. (a) The diagram image of ZnCl$_2$ recycling process. The electrochemical performance of CNB prepared by using the recycled ZnCl$_2$: (b) CV curves at different scan rates; (c) the GCD curves at different current densities; (d) the comparison of the specific capacitance with CNB sample prepared using fresh ZnCl$_2$.

Figure S3. SEM image of the tofu direct carbonization, showing a dense structure.
with SSA of 51 m² g⁻¹.

**Figure S4.** The SEM images of CNB-400-2 (a), CNB-600-2 (b) and CNB-800-2 (c), respectively.

**Figure S5.** XRD patterns of the resultant CNB samples

**Figure S6.** Raman patterns of the resultant CNB samples
**Figure S7.** $N_2$ adsorption/desorption isotherms of the resultant CNB samples

**Figure S8.** Pore-size distribution of the resultant CNB samples
Figure S9. CV and GCD curves of CNB-400-2 (a), CNB-800-2 (b), CNB-600-0.5 (c), CNB-600-1(d) and CNB-600-4, respectively.
Figure S10. Capacitances of samples at different current densities.

Figure S11. EIS spectra of CNB-400-2, CNB-800-2, CNB-600-0.5, CNB-600-1 and CNB-600-4, respectively.

Figure S12. XRD patterns of MnO$_2$-CNB composite.
Figure S13. The N\textsubscript{2} adsorption-desorption isotherms MnO\textsubscript{2}-CNB composite.

Figure S14. Pore size distribution curves calculated from the adsorption isotherms using the quenched solid density functional theory (QSDFT) method of MnO\textsubscript{2}-CNB composite.
Figure S15. The high-resolution N1s spectrum of MnO$_2$-CNB composite.

Table S1: The amount of minerals in the tofu derived carbon

<table>
<thead>
<tr>
<th>Element</th>
<th>Na</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNB without HCl washing</td>
<td>2.83 wt.%</td>
<td>2.23 wt.%</td>
<td>4.2 wt.%</td>
<td>1.48 wt.%</td>
</tr>
<tr>
<td>CNB with HCl washing</td>
<td>0.57 wt.%</td>
<td>0 wt.%</td>
<td>0.66 wt.%</td>
<td>0.0076 wt.%</td>
</tr>
</tbody>
</table>

In order to distinguish the amount of minerals in the tofu derived carbon, we have performed an ICP test for the as-obtained CNB-600-2 before and after the HCl washing, and the results are presented as the followed Table S1. Obviously, the CNB sample without HCl washing contains Ca, Mg, K and Mg in minute amounts. As we know, the melting points of CaSO$_4$ and MgSO$_4$ are 1450 and 1124 °C, respectively, which are higher than the carbonization temperature (600 °C). Therefore, these Ca and Mg salts have already been acted as pore-forming agent to create pores in the synthesis of CNB. After the HCl washing, the amount of Ca and Mg are almost none, which will show few effect on the electrochemical performance of CNB.

Table S2: Physical properties of the as-prepared carbon materials.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{BET}$[a] [m$^2$ g$^{-1}$]</th>
<th>$V_{mic}$[b] [cm$^3$ g$^{-1}$]</th>
<th>$V_{mes}$ [cm$^3$ g$^{-1}$]</th>
<th>$I_D/I_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNB-400-2</td>
<td>458</td>
<td>0.302</td>
<td>0.133</td>
<td>0.169</td>
</tr>
<tr>
<td>CNB-800-2</td>
<td>684</td>
<td>1.156</td>
<td>0.006</td>
<td>1.150</td>
</tr>
<tr>
<td>CNB-600-0.5</td>
<td>1069</td>
<td>1.146</td>
<td>0.232</td>
<td>0.914</td>
</tr>
<tr>
<td>CNB-600-1</td>
<td>1121</td>
<td>1.349</td>
<td>0.172</td>
<td>1.177</td>
</tr>
<tr>
<td>CNB-600-4</td>
<td>938</td>
<td>1.304</td>
<td>0.140</td>
<td>1.164</td>
</tr>
</tbody>
</table>

[a] Specific surface area based on Brunauer-Emmett-Teller equation. [b] The total pore volume was determined from the nitrogen adsorption at a relative pressure of 0.99. [c] Specific surface area of micropores obtained from t-plot method.

Table S3: Comparison of the synthesis process of the carbon materials from biomass
<table>
<thead>
<tr>
<th>Materials</th>
<th>Activating agent</th>
<th>Temperature/Duration</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flour</td>
<td>KOH</td>
<td>2h @ 700°C</td>
<td>[1]</td>
</tr>
<tr>
<td>Dried fungus</td>
<td>KOH</td>
<td>6 h @ 120 °C /1 h @ 800°C</td>
<td>[2]</td>
</tr>
<tr>
<td>Silk</td>
<td>FeCl3/ZnCl2</td>
<td>1h @ 900°C</td>
<td>[3]</td>
</tr>
<tr>
<td>Shiitake mushroom</td>
<td>H3PO4/KOH</td>
<td>2 h @ 500 °C /2 h @ 800°C</td>
<td>[4]</td>
</tr>
<tr>
<td>Watermelon</td>
<td>No activation</td>
<td>12 h @ 180 °C /1 h @ 600°C</td>
<td>[5]</td>
</tr>
<tr>
<td>Silk proteins</td>
<td>H3PO4</td>
<td>3h @ 800°C</td>
<td>[6]</td>
</tr>
<tr>
<td>Yogurt</td>
<td>KOH</td>
<td>24 h @ 180 °C /2 h@800°C</td>
<td>[7]</td>
</tr>
<tr>
<td>Graphene/silk fibroin</td>
<td>KOH</td>
<td>3 h @ 700°C</td>
<td>[8]</td>
</tr>
<tr>
<td>Glucose@silica template</td>
<td>ZnCl2</td>
<td>2h @ 1000°C</td>
<td>[9]</td>
</tr>
<tr>
<td>COF-5</td>
<td>ZnCl2</td>
<td>3 h @ 700°C</td>
<td>[10]</td>
</tr>
<tr>
<td>Tofu</td>
<td>ZnCl2</td>
<td>2h @ 600°C</td>
<td>This work</td>
</tr>
</tbody>
</table>

8. Wang, Y., et al., *Graphene/silk fibroin based carbon nanocomposites for high performance*