Electronic Supplementary Information

Surface modification of rice husk-derived hard carbon by grafting porous carbon nanosheets for high-performance supercapacitors

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1. Experimental Section

*Synthesis of PCNS/RHCs:* Rice husks were obtained from the suburb of Maanshan City in China. The coal tar pitch (CTP) with a softening point of 110 °C was provided by Maanshan Iron & Steel Co. Ltd. of China. Other chemicals were purchased from Aladdin, and used as received. For a typical run, rice husks were put into a box furnace and heated to 500 °C for 1 h in Ar atmosphere. The product was washed by 0.5 M NaOH solution and distilled water to remove silicon dioxide. The rice husk-derived carbon (RHC) was obtained after the above mentioned product was dried at 110 °C. Subsequently, the mixtures of RHC (1.0 g), CTP (1.0 g), nano-MgO (8.0 g) and KOH (X g) were ground and transferred to a corundum boat, which was put into a tube furnace and heated to 300 °C at 5 °C min⁻¹ for 1 h, then heated to 950 °C for 1 h. The products were washed with 2 M HCl solution and distilled water to remove the inorganic impurities, and dried at 110 °C for 24 h before use. The obtained materials are named as PCNS/RHCₙ, where X refers to the mass of KOH. For comparison, the mixtures with RHC (2.0 g), nano-MgO (8.0 g) and KOH (8.0 g) without the presence of CTP were also heated to 950 °C for 1 h in Ar atmosphere, and the product was washed by 2 M HCl solution and distilled water to remove the inorganic impurities and dried at 110 °C for 24 h. The obtained material is denoted as RHC₉₅₀. Additionally, the mixtures with CTP (2.0 g), nano-MgO (8.0 g) and KOH (8.0 g) without the presence of RHC were also heated to 950 °C for 1 h in Ar atmosphere, and the product was washed by 2 M HCl solution and distilled water to remove the
inorganic impurities and dried at 110 °C for 24 h. The obtained material is denoted as PCNS$_{950}$.

**Characterization:** The Zeta potentials of MgO, CTP and RHC were tested in the deionized water by Nano-ZS90, Malvern. The microstructures of PCNS/RHCs were analyzed by field emission scanning electron microscopy (FESEM, Hitachi, S4800), transmission electron microscopy (TEM, JEOL-2100). The crystallographic structures of PCNS/RHCs were examined by X-ray diffraction (XRD, Philips X, CuKa Radiation, $\lambda=0.15406$ nm). Raman spectroscopy analysis was performed with JYLab-RamHR800, excited by a 532 nm laser, and X-ray photoelectron spectroscopy (XPS) was obtained by Thermo ESCALAB250, USA. Fourier transform infrared (FT-IR) spectra were recorded with Thermo-Scientific Nicolet 6700 spectrophotometer. The conductivity of PCNS/RHC$_8$ was measured by a four-wire method using a source measure unit (Keithley 6430). The pore structure of the sample was studied by nitrogen adsorption-desorption technique at $-196$ °C in an adsorption apparatus (Micrometrics, ASAP2010). The $S_{BET}$ was calculated at a relative pressure from 0.05 to 0.20.

**Electrochemical measurements:** Active material (PCNS/RHCs) and polytetrafluoroethylene with the mass ratio of 90:10 were mixed together by adding some deionized water and a few drops of ethanol, followed by evaporation of solvent. Then the mixture was rolled into carbon sheet, which was dried at 110 °C under vacuum in drying oven for 2 h and punched into round films with diameter of 12 mm and mass loading of ca. 2 mg cm$^{-2}$. The as-prepared round films were used as
electrodes after being pressed on nickel foam for the electrochemical measurement in 6 M KOH electrolyte.

The electrochemical measurements were carried out in two-electrode system on an electrochemical workstation (CHI760C, Shanghai, China). The charge-discharge performance of supercapacitors was measured on a supercapacitance test system (SCTs, Arbin Instruments, USA). The electrochemical impedance spectroscopy (EIS) measurement was performed with an amplitude of 5 mV over a frequency range from 100 kHz to 0.001 Hz using a Solartron impedance analyzer (Solartron Analytical, SI 1260, UK) with a Solartron potentiostat (SI 1287).

The gravimetric specific capacitance of the electrodes, \( C \) (F g\(^{-1}\)), is calculated according to galvanostatic charge-discharge (GCD) curve based on Eq. (1).

\[
C = \frac{4I}{m \Delta V/\Delta t}
\]  

(1)

where \( I \) is the discharge current (A), \( \Delta V/\Delta t \) is the average slope of the discharge curve after the voltage drop (V s\(^{-1}\)), and \( m \) is the total mass of active materials in two electrodes (g).

The energy density \( E \) (Wh kg\(^{-1}\)) and power density \( P \) (W kg\(^{-1}\)) based on the total mass of active materials in supercapacitors, are calculated according to Eqs. (2) and (3).

\[
E = \frac{1}{2 \times 4 \times 3.6} CV^2
\]

(2)

\[
P = \frac{E}{\Delta t}
\]

(3)
where $V$ is the usable voltage after voltage drop (V) and $\Delta t$ is the discharge time (s).
2. Supplementary Figures and Tables
Fig. S1 FESEM and TEM images of MgO particles.
**Fig. S2** FESEM images of intermediate product of PCNS/RHC$_8$ at 500 °C: (a, b) Unwashed samples; (c, d) Samples washed by acid and distilled water.
Fig. S3 TEM images of PCNS/RHC₈.
Fig. S4 (a) N$_2$ adsorption-desorption isotherms of PCNS$_{950}$, RHC$_{950}$ and PCNS/RHC$_8$; (b) Pore size distribution of PCNS$_{950}$, RHC$_{950}$ and PCNS/RHC$_8$; (c) Cumulative surface area of PCNS/RHC$_8$ and RHC$_{950}$; (d) Cumulative pore volume of PCNS/RHC$_8$ and RHC$_{950}$. 
**Fig. S5** FT-IR spectra of PCNS/RHC composites.
Fig. S6 (a) CV curves of PCNS/RHCs at 5 mV s⁻¹; (b) CV curves of PCNS/RHCs at 100 mV s⁻¹.
Fig. S7 (a) CV curves of RHC$_{950}$ at different scan rates; (b) Specific capacitances of RHC$_{950}$ at different current densities; (c) Nyquist plot of RHC$_{950}$; (d) Bode plot of RHC$_{950}$ electrodes.
Fig. S8 The equivalent circuit of Randle’s model.

$R_S$: equivalent series resistance. \( \text{CPE}_{DL} \): double layer capacitance. \( \text{CPE}_L \): pseudocapacitance. $R_{CT}$: charge transfer resistance. $W_0$: Warburg element. $R_L$: leakage resistance.
**Table S1** The Zeta potential of raw materials.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Zeta potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHC</td>
<td>–21.2</td>
</tr>
<tr>
<td>CTP</td>
<td>–28.8</td>
</tr>
<tr>
<td>MgO</td>
<td>21.5</td>
</tr>
</tbody>
</table>
**Table S2** The contents of C, O, N elements and oxygen-containing functional groups in PCNS/RHCs.

<table>
<thead>
<tr>
<th>Samples</th>
<th>C1s (%)</th>
<th>O1s (%)</th>
<th>N1s (%)</th>
<th>O1s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C=O (%)</td>
</tr>
<tr>
<td>PCNS/RHC&lt;sub&gt;4&lt;/sub&gt;</td>
<td>95.06</td>
<td>3.32</td>
<td>1.62</td>
<td>1.36</td>
</tr>
<tr>
<td>PCNS/RHC&lt;sub&gt;6&lt;/sub&gt;</td>
<td>91.93</td>
<td>6.70</td>
<td>1.37</td>
<td>2.21</td>
</tr>
<tr>
<td>PCNS/RHC&lt;sub&gt;8&lt;/sub&gt;</td>
<td>88.28</td>
<td>10.71</td>
<td>1.01</td>
<td>2.37</td>
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</table>
Table S3 Fitted equivalent circuit elements of PCNS/RHC₈ and RHC₉₅₀.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Rs (Ohm)</th>
<th>Rct (Ohm)</th>
<th>CPE₁DL</th>
<th>W (S s⁰.⁵)</th>
<th>CPE₂L</th>
</tr>
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<tbody>
<tr>
<td>PCNS/RHC₈</td>
<td>0.43</td>
<td>0.62</td>
<td>0.32</td>
<td>1.5*10⁻¹⁶</td>
<td>0.0006</td>
</tr>
<tr>
<td>RHC₉₅₀</td>
<td>6.20</td>
<td>87.13</td>
<td>0.0054</td>
<td>3.8*10⁻⁴</td>
<td>0.0016</td>
</tr>
</tbody>
</table>