Supplementary Information for

Microwave-assisted hydrolysis of crystalline cellulose catalyzed by biomass char sulfonic acids

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Titration method of every functional group over BC-SO$_3$H samples$^1$

The measurement of the total functional groups (-SO$_3$H, -COOH and -OH groups): a sodium hydroxide aqueous solution (0.01 mol L$^{-1}$, 20 mL) was added to a catalyst (0.050 g). The mixture was stirred for 60 min at room temperature under ultrasonic vibration. After centrifugal separation, the supernatant solution was titrated by a hydrochloric acid (0.01 mol L$^{-1}$) aqueous solution using phenolphthalein as an indicative.

The contents of -SO$_3$H plus -COOH groups: a sodium bicarbonate aqueous solution (0.01mol L$^{-1}$, 20 mL) was added to a catalyst (0.050 g). The mixture was stirred for 60 min at room temperature under ultrasonic vibration. After centrifugal separation, the supernatant solution was titrated by a hydrochloric acid (0.01mol L$^{-1}$) aqueous solution using phenolphthalein as an indicative.

The content of -SO$_3$H group: a sodium chloride aqueous solution (0.01mol L$^{-1}$, 20 mL) was added to a catalyst (0.050 g). The mixture was stirred for 60 min at room temperature under ultrasonic vibration. After centrifugal separation, the supernatant solution was titrated by a sodium hydroxide (0.01 mol L$^{-1}$) aqueous solution using phenolphthalein as an indicative.

According to the above titration results, the content of -OH groups = the content of the total functional groups – the content of -SO$_3$H plus -COOH
groups; the content of -COOH groups = the content of -SO$_3$H plus -COOH

groups – the content of -SO$_3$H groups. The calculated results are listed in
Table S1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SO$_3$H</th>
<th>COOH</th>
<th>OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC-SO$_3$H-1</td>
<td>1.8750</td>
<td>0.1769</td>
<td>2.5930</td>
</tr>
<tr>
<td>BC-SO$_3$H-2</td>
<td>1.9886</td>
<td>0.1321</td>
<td>3.4317</td>
</tr>
<tr>
<td>BC-SO$_3$H-3</td>
<td>1.1357</td>
<td>0.2927</td>
<td>1.9818</td>
</tr>
</tbody>
</table>

**Characterization of BC-SO$_3$H**

The powder X-ray diffraction (XRD) and the fourier transform infrared

spectrum (FT-IR) of the BC-SO$_3$H samples were recorded on a Y-2000
diffractometer and Nicolet Avatar 370 FT-IR spectrometer (using KBr
pellets), respectively. The thermogravimetric analysis (TGA) was carried
out in flowing air (10 ml min$^{-1}$) at a heating rate of 10 K min$^{-1}$ on
NETZSCH-STA 409PC. The specific surface area was measured by
nitrogen volumetric adsorption-desorption method at 77 K on a
Micromeritics TriStar 3000 apparatus. The X-ray photoelectron
spectroscopy (XPS) was measured on Kratos XSAM 800-type
photoelectron spectrometer by using the Mg Ka line as the excitation
As shown in Fig. S1, the XRD pattern of a typical BC-SO$_3$H-1 sample exhibited a broad but weak diffraction peak at 2$\theta$ angles of 10$^\circ$–35$^\circ$ which is attributed to amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion.$^2$
Figure S2. FT-IR spectra of bamboo char material (a) and bamboo char sulfonic acid BC-SO$_3$H-1 (b)

Figure 2 is the FTIR spectra for the carbonized (a) and sulfonated (b, BC-SO$_3$H-1) materials from bamboo, wherein the carbonized material exhibited some characteristic bands, consisting of the polycyclic aromatics in 1400-1600 cm$^{-1}$ region, the Ar-OH stretching vibration at 1594 cm$^{-1}$ and the C=O stretching vibration at 1713 cm$^{-1}$. The sulfonated material (BC-SO$_3$H-1) showed a distinguished absorption band at 1032 cm$^{-1}$ that is assigned to the stretching vibration of S=O bond, as a result of inducing the SO$_3$H groups into bamboo charred material.
Figure S3. XPS spectra of the BC-SO$_3$H-1

The XPS spectrum for the BC-SO$_3$H-1 exhibited a single S$_{2p}$ peak at 168 eV, which is assigned to SO$_3$H groups.$^5$ This indicated that all S atoms in the BC-SO$_3$H-1 are contained in SO$_3$H groups.
Figure S4. TG and DTG curves of the BC-SO$_3$H-1 (A), BC-SO$_3$H-2 (B), BC-SO$_3$H-3 (C) under air atmosphere

In all TGA curves, the weight losses below 150°C apparently resulted
from evaporation of adsorbed water. Under air, the decomposition behavior of -SO\(_3\)H groups in various BC-SO\(_3\)H samples was nearly the same,\(^6\) most weight loss taking place at 210-240 °C by 10 °C/ min heating.

**References**


