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_3H samples[1]

The measurement of the total functional groups (-SO_3H, -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_3H 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_3H 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_3H plus -COOH groups; the content of -COOH groups = the content of -SO_3H plus -COOH groups – the content of -SO_3H groups. The calculated results are listed in Table S1.

Table S1. The density of every functional group

Sample	The functional groups densities (mmol/g)		
	SO_3H	COOH	OH
BC-SO_3H-1	1.8750	0.1769	2.5930
BC-SO_3H-2	1.9886	0.1321	3.4317
BC-SO_3H-3	1.1357	0.2927	1.9818

Characterization of BC-SO_3H

The powder X-ray diffraction (XRD) and the fourier transform infrared spectrum (FT-IR) of the BC-SO_3H 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 source.

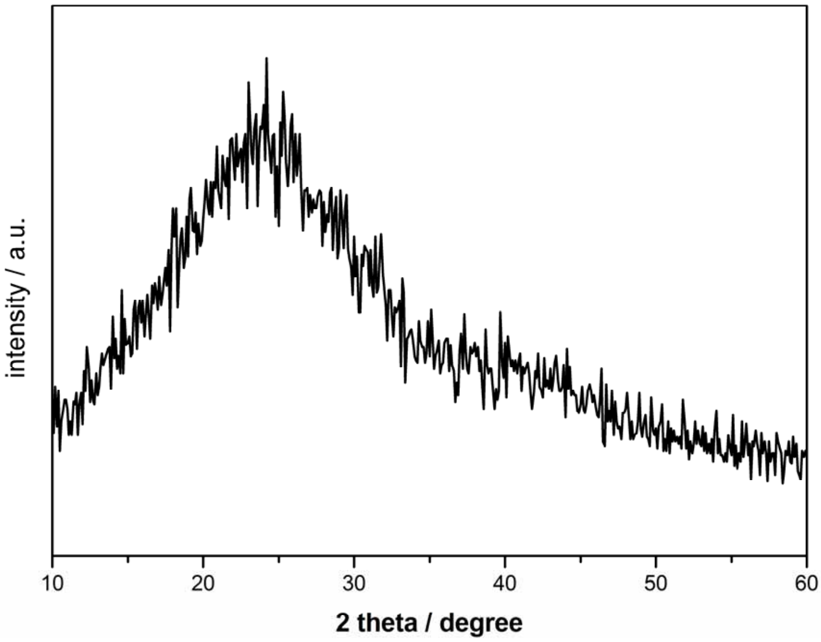


Figure S1. XRD pattern for bamboo char sulfonic acid BC-SO_3H-1

As shown in Fig. S1, The XRD pattern of a typical BC-SO_3H-1 sample exhibited a broad but weak diffraction peak at 2θ angles of 10°–35° which is attributed to amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion.[2]

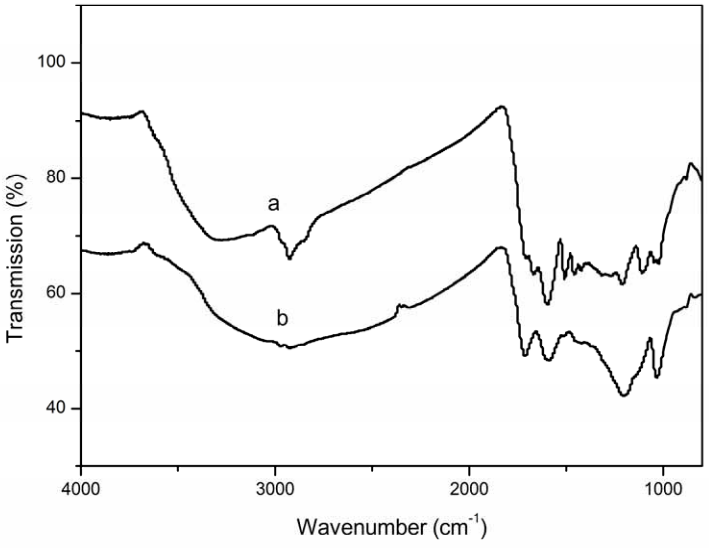


Figure S2. FT-IR spectra of bamboo char material (a) and bamboo char sulfonic acid BC-SO_3H-1 (b)

Figure 2 is the FTIR spectra for the carbonized (a) and sulfonated (b, BC-SO_3H-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}.[3] The sulfonated material (BC-SO_3H-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_3H groups into bamboo charred material.[4]

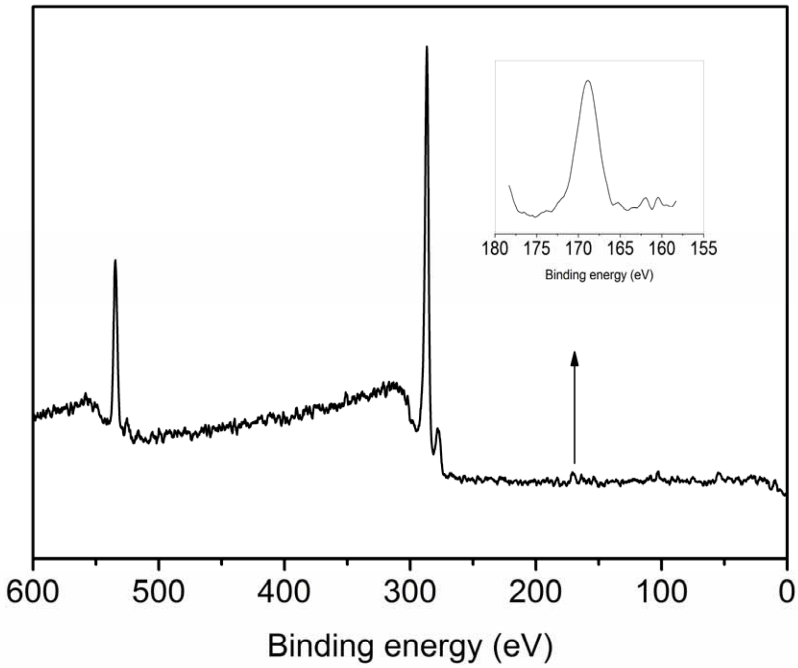
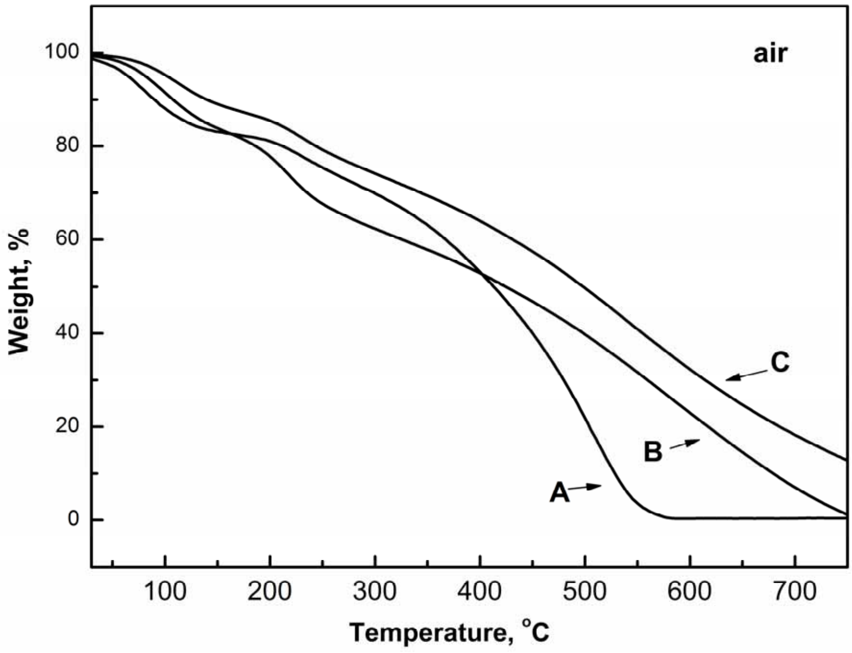


Figure S3. XPS spectra of the BC-SO_3H-1

The XPS spectrum for the BC-SO_3H-1 exhibited a single S_{2p} peak at 168 eV, which is assigned to SO_3H groups.[5] This indicated that all S atoms in the BC-SO_3H-1 are contained in SO_3H groups.



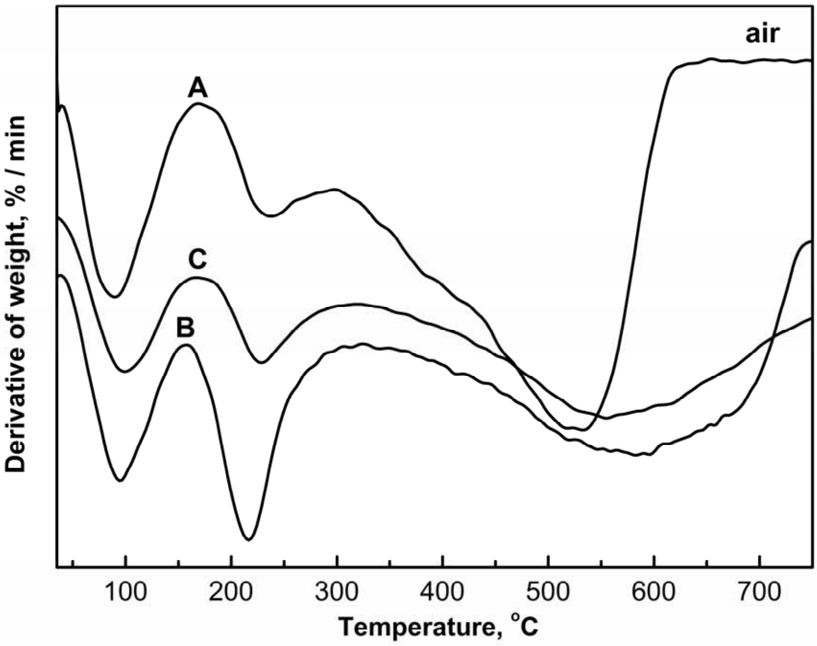


Figure S4. TG and DTG curves of the BC-SO_3H-1 (A), BC-SO_3H-2 (B), BC-SO_3H-3 (C) under air atmosphere

In all TGA curves, the weight losses below 150°C apparently resulted from evaporation of adsorbed water. Under air, the decomposition behavior of -SO_3H groups in various BC-SO_3H samples was nearly the same,[6] most weight loss taking place at 210-240 °C by 10 °C/ min heating.

References

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