

## Electronic supplementary information for

### Depolymerization of cellulose to glucose by oxidation-hydrolysis

Lipeng Zhou, Xiaomei Yang\*, Jiaolong Xu, Meiting Shi, Feng Wang, Chen Chen, Jie Xu

**Table S1**

The DP and acid amount of  $\alpha$ -cellulose after oxidation treatment by air<sup>a</sup>

Sample	Acid amount (mmol/g)	DP	Conversion (%)	TRS yield (%)	Glucose yield (%)
$\alpha$ -cellulose-150-24	0.04	945	12.9	4.8	0.3
$\alpha$ -cellulose-180-24	0.07	375	18.6	8.3	0.7
$\alpha$ -cellulose-210-3	0.10	470	15.8	6.3	1.3
$\alpha$ -cellulose-210-6	0.15	318	19.9	9.1	2.0
$\alpha$ -cellulose-210-12	0.20	180	29.3	12.4	4.1
$\alpha$ -cellulose-210-24	0.28	137	36.9	20.6	7.6
$\alpha$ -cellulose-210-36	0.52	96	43.0	26.2	13.4
$\alpha$ -cellulose-210-48	0.54	74	47.7	30.7	16.3

<sup>a</sup> Hydrolysis reaction conditions: cellulose (0.3 g), H<sub>2</sub>O (30 mL), 1.0 MPa N<sub>2</sub>, 150 °C, 8 h.

**Table S2**Influence of the weight ratio of cellulose/water on the hydrolysis of  $\alpha$ -cellulose<sup>a</sup>

Cellulose/water (w/w)	Conversion (%)	TRS yield (%)	Glucose yield (%)
0.01	47.7	30.7	16.3
0.05	42.4	36.8	21.2
0.10	40.6	33.0	22.2
0.20	40.7	34.9	23.3
0.30	39.1	38.2	17.7
0.40	40.7	30.9	17.9

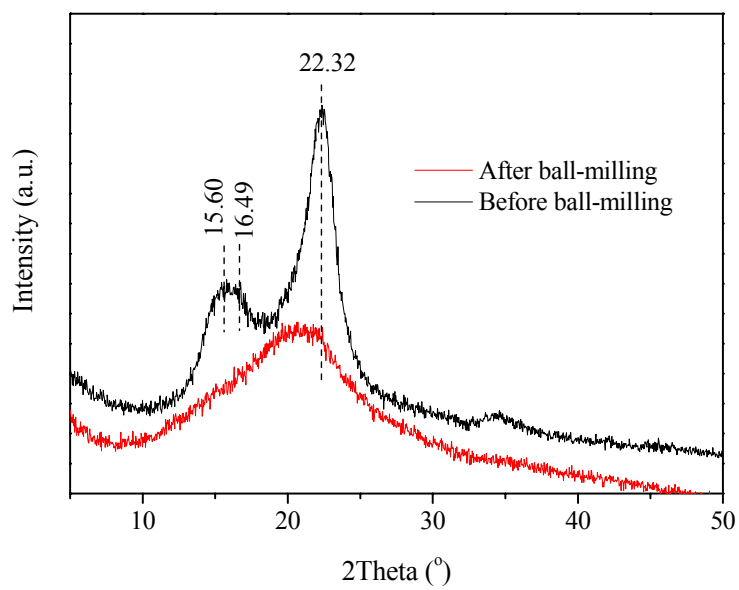
<sup>a</sup> Reaction conditions: H<sub>2</sub>O (30 mL), 150 °C, 8 h, 1.0 MPa N<sub>2</sub>,  $\alpha$ -cellulose oxidized by air at 210 °C for 48 h was used as the substrate.

**Table S3**The results of three preoxidation-hydrolysis runs for MCC<sup>a</sup>

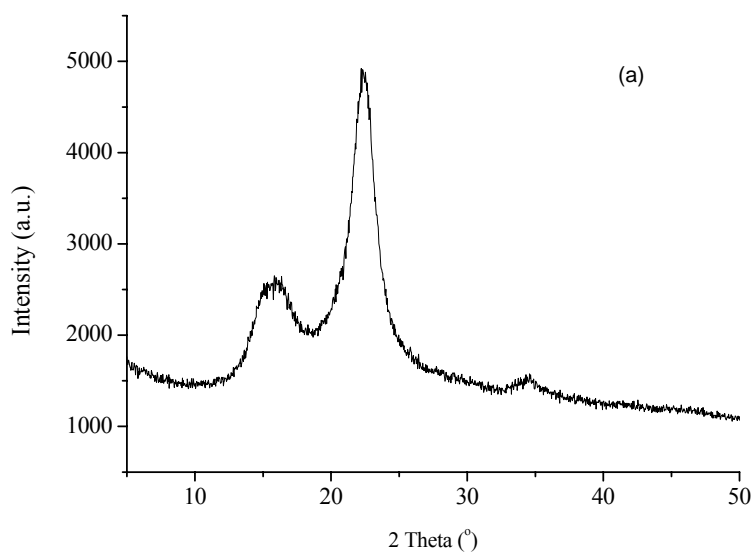
Reaction runs	Mass of cellulose for hydrolysis (g)	Conversion (%)	TRS yield (%)	Glucose yield (%)
1 <sup>st</sup>	3.0023	38.5	36.7	25.2
2 <sup>nd</sup>	1.2653	48.8	45.0	38.2
3 <sup>rd</sup>	0.2915	38.2	30.8	24.4
Total <sup>b</sup>	-	94.0	58.6	43.4

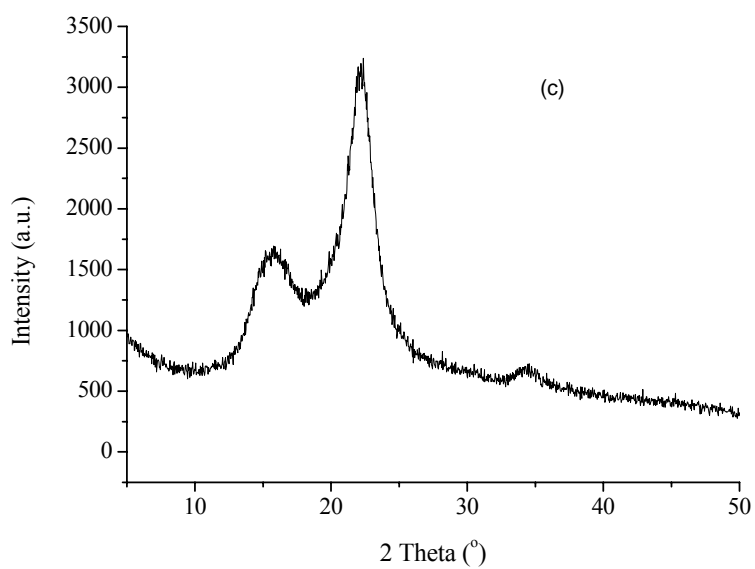
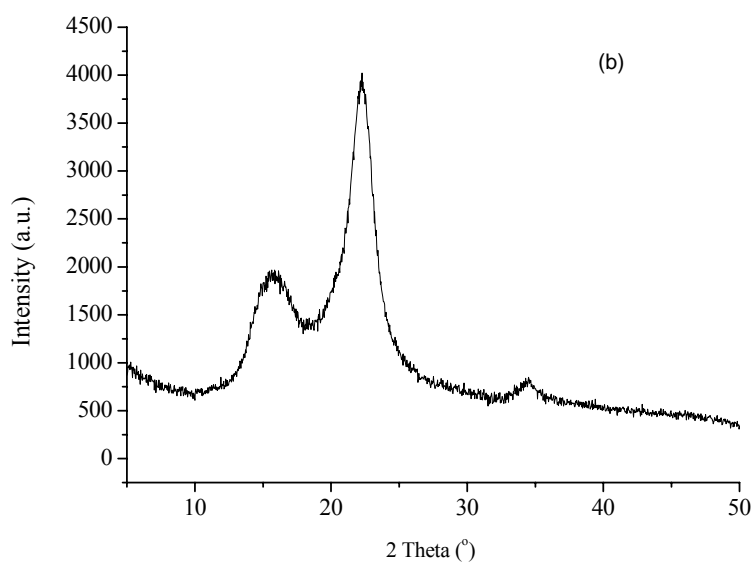
<sup>a</sup>After hydrolysis reaction, the residue was washed twice with water and ethanol separately. After drying at 110 °C for 8 h, the obtained solid was oxidized by air at 210 °C for 48 h. Hydrolysis reaction conditions: cellulose/water = 0.1 g/mL, 1.0 MPa N<sub>2</sub>, 170 °C, 8 h.

<sup>b</sup>Total conversion = the weight of the solid residue after the 3<sup>rd</sup> run/ the initial cellulose weight.

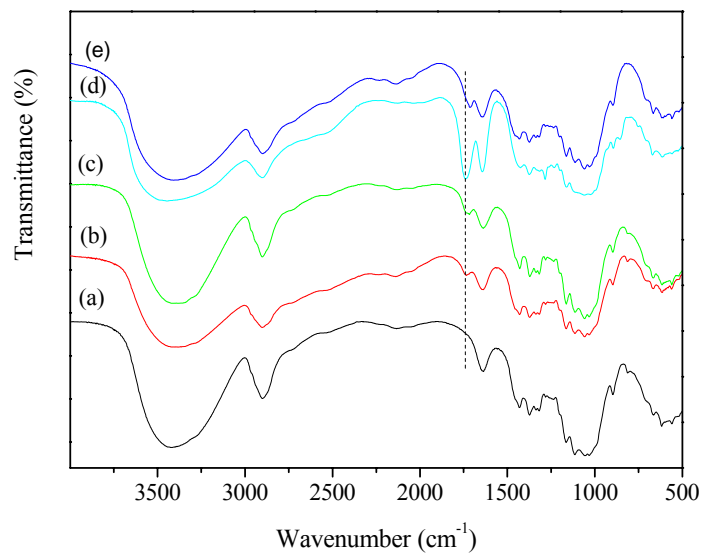


**Fig. S1** XRD patterns of  $\alpha$ -cellulose before and after ball-milling.

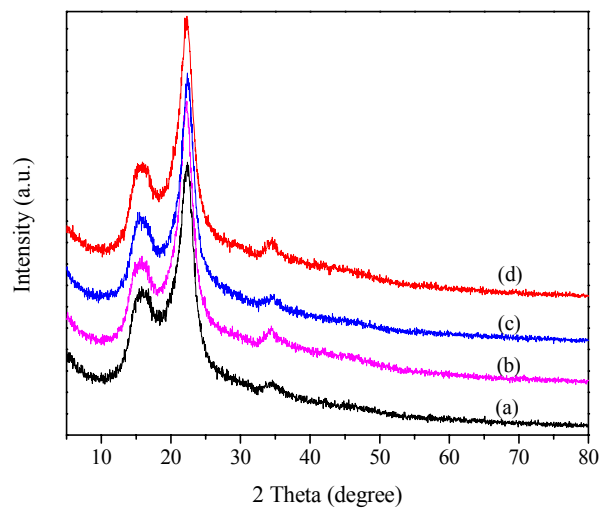




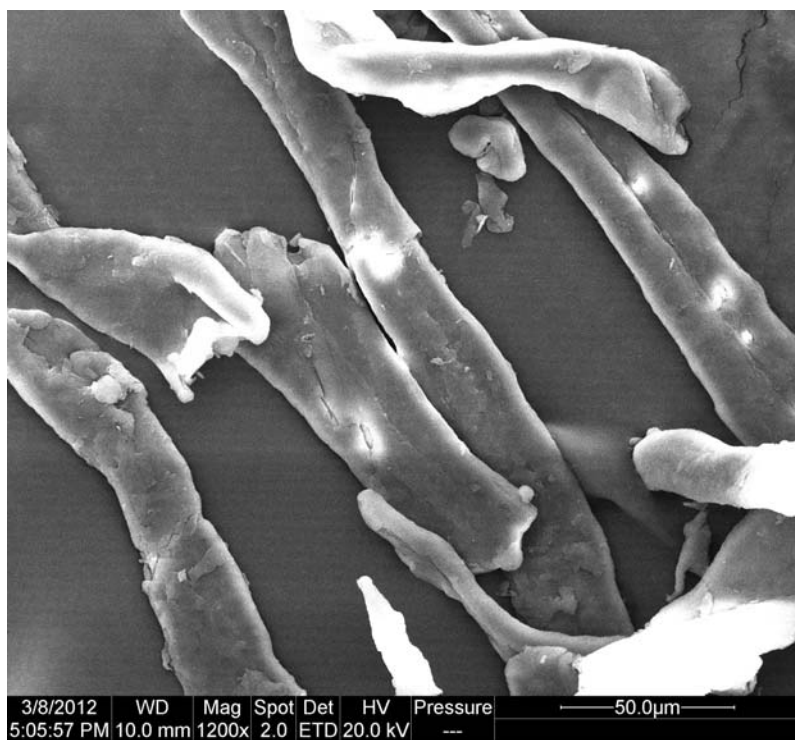
**Fig. S2** XRD patterns of  $\alpha$ -cellulose after oxidation in a tube furnace with a quartz tube reactor by  $NO_2$  (a),  $O_2$  (b) and air (c).



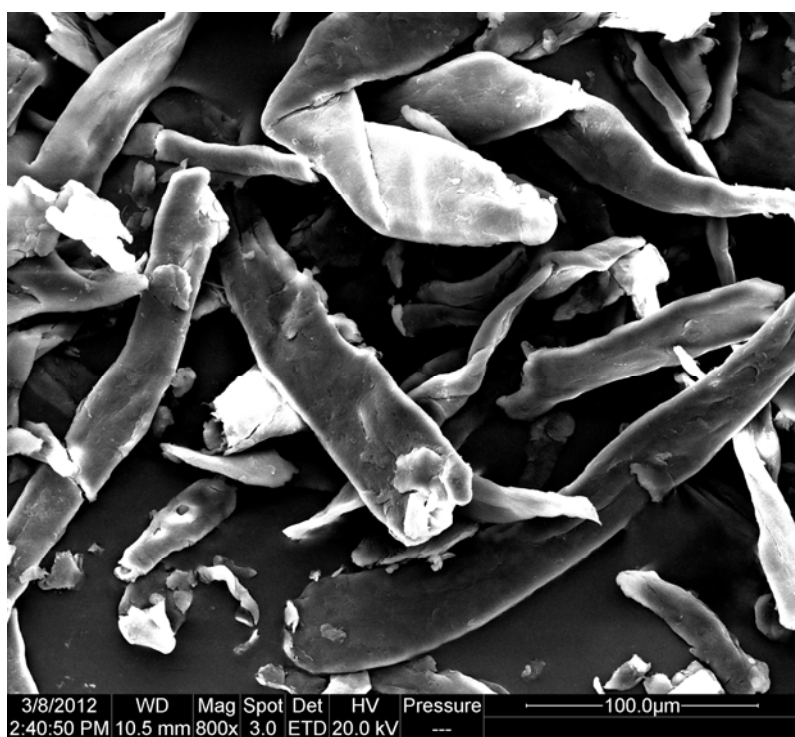
**Fig. S3** FTIR spectra of  $\alpha$ -cellulose without pretreatment (a),  $\alpha$ -cellulose-H<sub>2</sub>O<sub>2</sub> (b),  $\alpha$ -cellulose-KMnO<sub>4</sub> (c),  $\alpha$ -cellulose-HNO<sub>3</sub>-NaNO<sub>2</sub> (d), and  $\alpha$ -cellulose-TEMPO-NaClO (e).



**Fig. S4** XRD patterns of  $\alpha$ -cellulose (a) and  $\alpha$ -cellulose oxidized by air:  $\alpha$ -cellulose-210-12 (b) and  $\alpha$ -cellulose-210-24 (c) and  $\alpha$ -cellulose-210-48 (d)



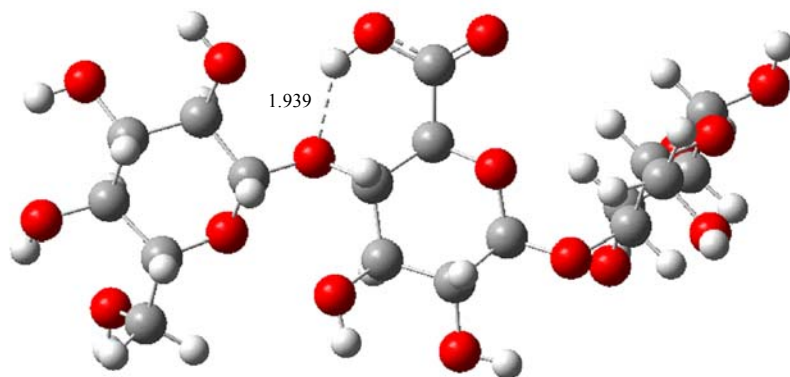
(a)



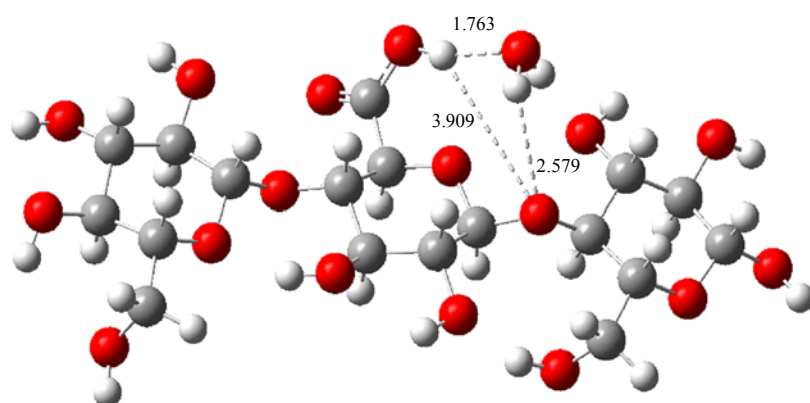
(b)

**Fig. S5** SEM images of  $\alpha$ -cellulose before (a) and after oxidation in air (b).

(a)

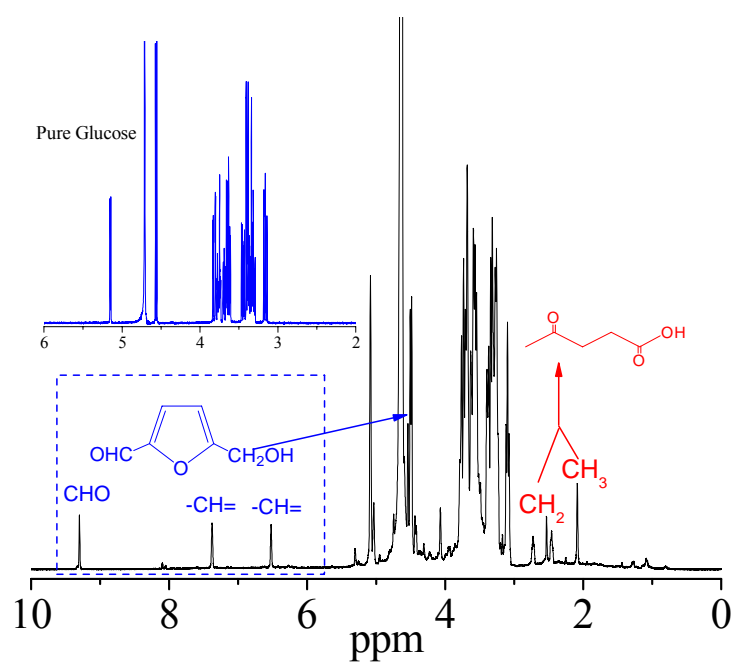


(b)

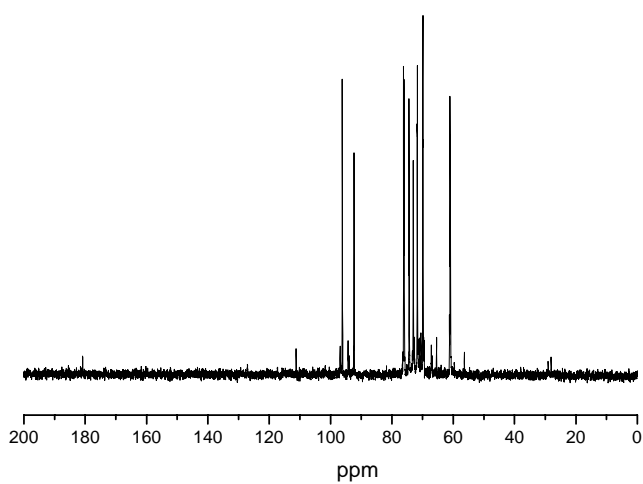


**Fig. S6** Theoretical calculations of the structure for hydrolysis of glycosidic bond located on both sides of  $\text{-COOH}$ .

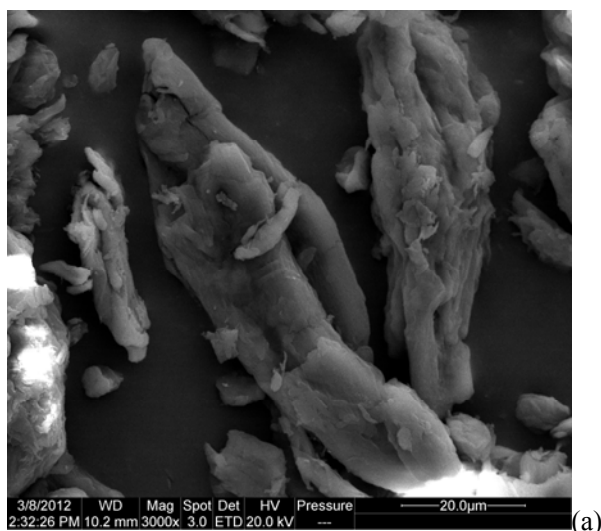




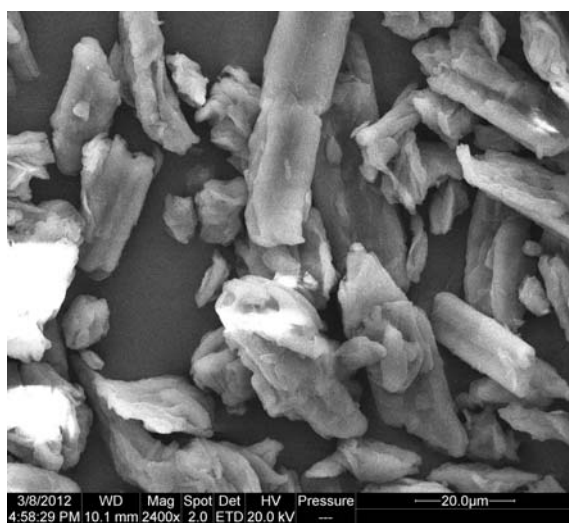
**Fig. S7**  $^1\text{H}$  NMR spectra of the aqueous phase recovered after the catalytic hydrolysis of  $\alpha$ -cellulose.



**Fig. S8**  $^{13}\text{C}$  NMR spectra of the aqueous phase recovered after the catalytic hydrolysis of  $\alpha$ -cellulose.

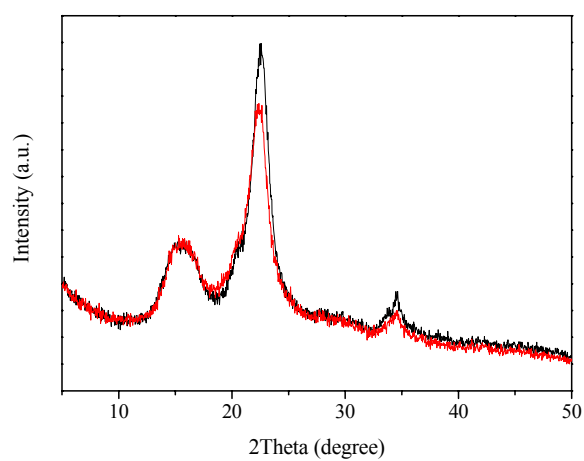


(a)

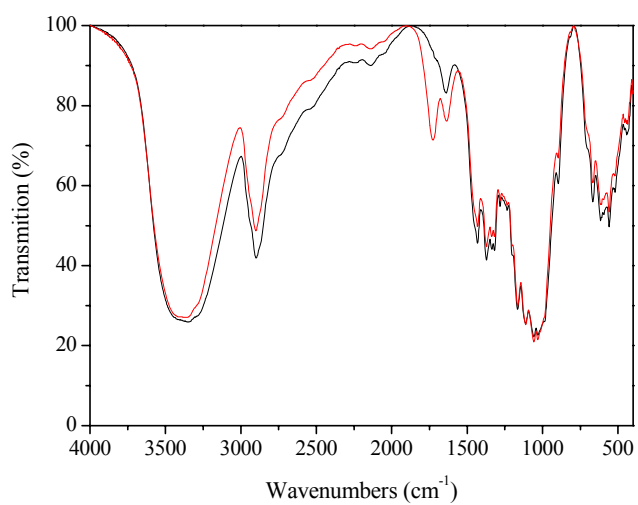


(b)

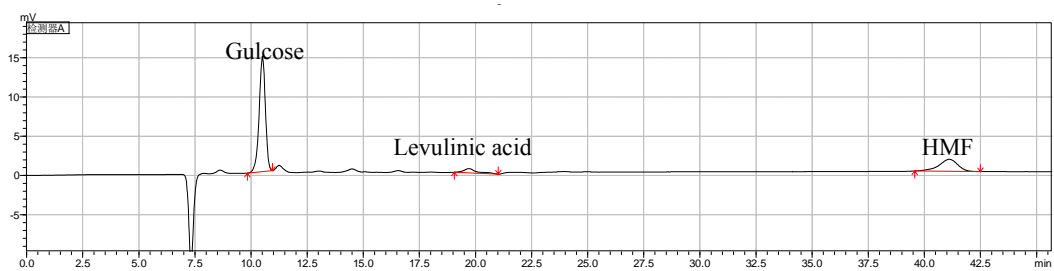
**Fig. S9** SEM images of MCC before (a) and after oxidation by air (b).



**Fig. S10** XRD patterns of MCC parent (black) and after oxidation by air (red).



**Fig. S11** FTIR spectra of parent MCC (black) and MCC after oxidation by air (red).



**Fig. S12** HPLC results of MCC hydrolysis.



**Fig. S13** The picture of the aqueous phase recovered after hydrolysis of oxidized MCC.