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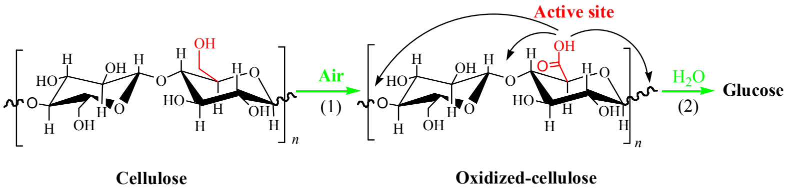

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Depolymerization of cellulose to glucose by oxidation-hydrolysis

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Oxidation-hydrolysis strategy was developed for depolymerization of cellulose. Part of hydroxymethyl groups on glucose units were oxidized to carboxyl groups in the preoxidation treatment, and the generated acid sites act as the catalytic active centers for the following depolymerization of cellulose. After α-cellulose was pretreated by air at 210 °C for 48 h, 23.3% yield of glucose was given in water at 150 °C for 8 h without additional catalyst. The ratio of cellulose/water has no obvious influence on the yield of glucose. 17.9% yield of glucose for α-cellulose can still be obtained even at the weight ratio of 0.4, where up to 75 g L^{-1} of glucose solution is given. For microcrystalline cellulose, 25.2% yield of glucose was obtained for hydrolysis at 170 °C for 8 h. It was revealed that the generated carboxyl acid groups in oxidation step are the catalytic sites for the hydrolysis of cellulose.

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Introduction

With the depletion of fossil feedstocks, the utilization of renewable resources has attracted particular attention in recent years.[1-3] As the most abundant biomass, cellulose is a homopolysaccharide composed of D-glucose units linked via β-1,4-glycosidic bonds, containing both crystalline and amorphous regions. Plenty of intra- and inter-molecular hydrogen bonds enable the molecular structure of cellulose to be fully cross-linked, which render cellulose insoluble in most solvents. More importantly, this kind of special composition and structure cause one challenging problem for cellulose depolymerization. Sugars produced from the hydrolysis of cellulose are the key platform chemicals, which can be further converted to biofuels and some other high value-added chemicals such as ethanol, ethylene glycol, glycerol, levulinic acid, and lactic acid.[4-6] If a cost-effective method for sugar production from cellulose can be developed, cellulosic biomass will become the basis of renewable fuels and chemicals.[7] Currently, a number of processes for hydrolysis of cellulose into glucose have been developed including enzymatic hydrolysis and catalytic hydrolysis with homogeneous acid or solid acid as catalyst. Enzymatic hydrolysis of cellulose can proceed in mild conditions with high selectivity, which is a promising method to obtain fermentable sugars from biomass. The high cost and low efficiency of recycling enzymes is the problems for the application of enzymatic hydrolysis.[8] The use of inexpensive mineral acids and organic acids such as H_2SO_4, HCl, acetic acid, and oxalic acid as catalysts for catalytic hydrolysis of cellulose is widely studied.[9-11] However, their use is wasteful and energy-inefficient, requiring separation, recycling,

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and treatment of the waste acids. Recyclable solid acid catalysts were used to replace mineral acids for cellulose hydrolysis progressed in recent years.[12-17] Usually, the catalytic activity of solid acid catalysts is lower and a high weight ratio of catalyst to cellulose (~1.0) is needed to attain acceptable glucose yield. The diffusion of proton/H_3O^+ to β-1,4-glycosidic bonds is one of the essential steps for hydrolysis of cellulose catalyzed by acid.[18] The crystalline structure and hydrogen bond net of cellulose, however, greatly separates the β-1,4-glycosidic bonds against their contact with the catalytic active sites, which resulted in the low efficiency of solid or mineral acid as a catalyst for hydrolysis of cellulose.

It has been reported that carboxyl groups on the cellulose chains have activation and inductive effects on the cleavage of the 1,4-glycosidic bonds inside the cellulose chains.[19] If partial hydroxymethyl groups of glucose units of cellulose chain can be converted to carboxyl groups by an oxidation step, the generated carboxyl groups can serve as catalytic active sites for scission of the neighboring β-1,4-glycosidic bonds in cellulose. As a result, the diffusion problem of proton/H_3O^+ to glycosidic bonds will be resolved, and efficient hydrolysis of cellulose to glucose can be realized.

Our research group and other researchers have reported that the hydroxymethyl groups on cellulose fibers can be selectively converted to carboxyl groups to improve the fiber properties and enlarge its application fields.[20-24] Herein, the preoxidation method was proposed to enhance the reactivity of cellulose. The hydroxymethyl groups are converted to carboxyl groups which act as catalytic active sites for both cellulose depolymerization during pretreatment and the subsequent hydrolysis of

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cellulose to glucose. This method is a self-catalysis process, in which an additional catalyst is not necessary and the problems relating to the utilization of solid or mineral acids can be avoided.

Experimental section

Materials

α-Cellulose was purchased from Sigma-Aldrich Co. Microcrystalline cellulose was from Alfa Aesar (China) Chemical Co., Ltd. The other reagents were of analytic grade and obtained from commercial sources without further purification.

Oxidation pretreatment of cellulose

(1) H_2O_2 as oxidant

α-Cellulose (5.0 g) and H_2O_2 (50 mL, 30 wt.%) were added in a round bottom flask with a condenser. The mixture was heated to 80 ^{o}C and kept constant for 5 h with stirring. Then the solid was filtrated and washed three times with deionized water. Finally, the sample was dried at 40 ^{o}C overnight.

(2) $KMnO_4$ as oxidant

$KMnO_4$ (0.7 g) and H_2SO_4 (1.0 g, 98 wt.%) were dissolved in water (100 mL). To the above solution α-cellulose (2.0 g) was added and reacted at 100 ^{o}C for 5 h under stirring. Then the solid was filtrated and washed three times with deionized water. The sample was dried at 40 ^{o}C overnight.

(3) $NaNO_2$-HNO_3 as oxidant

HNO_3 (46 mL, 69.7 wt.%), H_3PO_4 (23 mL, 85 wt.%) and α-cellulose (5.0 g) were added into a 200 mL beaker with stirring. After addition of $NaNO_2$ (1.0 g), the beaker

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was covered by a watch glass. After reaction at ambient temperature for 24 h, deionized water (50 mL) was added to quench the oxidation. The solid was filtrated and washed with deionized water. Finally, the sample was dried at 40 °C overnight.

(4) TEMPO-NaClO

Oxidation α-cellulose by TEMPO-NaClO is according to literature.[24] α-Cellulose (2.0 g) was suspended in water (150 mL) containing TEMPO (0.025 g) and sodium bromide (0.25 g). Then aqueous solution of NaClO (24 mmol, 13%) was added at room temperature. The pH was maintained at 10.5 by adding 0.5 M NaOH. When the pH was no more decreased, the reaction was finished and the pH was adjusted to 7 by adding 0.5 M HCl. The solid was obtained by filtration. Finally, the solid was washed with water and dried at 60 °C overnight.

(5) NO_2, O_2 or air as oxidant

NO_2/N_2 (V_{NO2}/V_{N2} = 1: 5), O_2 or air was used as oxidant, respectively. The oxidation was performed in a tube furnace with a quartz tube reactor (30 cm × 2 cm). After cellulose sample (4 g) was placed in a quartz tube, gas oxidant was input with a constant flow speed (50 mL min^{-1}). Then the temperature was raised to 210 °C and maintained for 6 h. After the quartz tube was cooled to ambient temperature, the gas was stopped and the oxidized cellulose was taken out.

Oxidation of cellulose by air was also performed in drying oven with force convection. The dimensions of the working chamber are 400 mm × 400 mm × 450 mm. The speed for the replacement of the atmosphere in drying oven is 7500 times/h. Cellulose (5.0 g) was laid flat on a watch glass (diameter 15 cm). After the drying

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oven reached the setting temperature, the watch glass with cellulose was placed in the drying oven for desired time. The oxidized cellulose was denoted as cellulose-*T*-*t*, where *T*/^{o}C and *t*/h are the temperature and the time for oxidation of cellulose.

Characterization method

The crystalline structures of the cellulose samples were analyzed on a Panalytical X'pert PRO instrument with Cu Kα (λ = 0.15418 nm) radiation. Fourier transform infrared (FTIR) spectra of the samples were recorded using a Nicolet IR 200 Spectrometer in KBr media. Pellets of ca. 2 mg of cellulose were prepared by mixing with 200 mg of KBr in spectroscopic grade. Solid-state cross polarization/magic angle spinning (CP/MAS) ^{13}C NMR experiments were performed on a 600 MHz NMR spectrometer (AVANCE III, Bruker Company, Switzerland) using the combined techniques of proton dipolar decoupling, magic angle spinning, and cross polarization. The average degree of polymerization of cellulose was calculated by using intrinsic viscosity of the cupriethylenediamine solution. The intrinsic viscosity of cellulose in 0.5 M cupriethylenediamine solution was measured according to ASTM standard method D1795-96. The acid density of oxidized cellulose was determined by exchange of protons with Na^+ in aqueous solution of NaCl.

Hydrolysis reaction

Hydrolysis of cellulose was performed in a 100 mL Teflon-lined stainless steel autoclave reactor. After addition of desired amount of cellulose in water, the autoclave was sealed. The atmosphere over the mixture was replaced four times with N_2. Subsequently, the reactor was heated to the desired temperature under stirring, and the

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pressure of N_2 was charged to 1.0 MPa. When the reaction was finished, the reactor was cooled down to the ambient temperature. Cellulose conversion was determined by the change of cellulose weight before and after reaction. The total reducing sugars (TRS) in the aqueous solution were analyzed using an established method with 3,5-dinitrosalicylic acid (DNS method).[13] The products in the reaction solution were identified and quantified with a Shimadzu LC-20AT HPLC analysis system. The glucose yield was analyzed with the external standard method on a Shimadzu LC-20AT HPLC analysis system equipped with an Aminex HPX-87H column and refractive index detector. 0.005 M aqueous H_2SO_4 solution was used as the mobile phase, which had a flow rate of 0.6 mL min^{-1}. ^{1}H-NMR and ^{13}C-NMR spectra of the aqueous phase recovered after hydrolysis of α-cellulose was recorded in D_2O on a Bruker DRX-400 spectrometer.

Theoretical calculations of the hydrolysis process

Geometrical optimization was carried out with the standard 6-31G(d, p) basis set by using the three-parameter hybrid functional developed by Becke in the formulation implemented in the Gaussian 09 program (B3LYP).

Results and discussion

The comparison of different pretreatment methods

Oxidation pretreatment of α-cellulose was tried first in the liquid phase employing $KMnO_4$, H_2O_2, $NaNO_2$-HNO_3, and TEMPO-NaClO as oxidants (Table 1, entries 5-8). A certain amount of acid sites were generated after oxidation while the degree of

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polymerization (DP) of oxidized α-cellulose decreased sharply. The decreased DP suggests that α-cellulose was effectively depolymerized during the oxidation process. The glucose yield from the oxidized α-cellulose by H_2O_2, $KMnO_4$, $NaNO_2$-HNO_3, and TEMPO-NaClO in liquid phase is 1.9, 3.5, 6.8, and 2.5%, respectively. It should be noted that only negligible yield of glucose (0.2%) is given for untreated cellulose without acid catalyst under comparable reaction conditions (entry 1). It suggests that the generated acid sites catalyzed the hydrolysis of α-cellulose. At the same time, lower DP is beneficial for the following hydrolysis of cellulose. Among these oxidants, $NaNO_2$-HNO_3 is the most efficient, which could in-situ generate NO_2 as an oxidant. It was reported that NO_2 is a selective reagent for oxidation of C6 primary hydroxyl groups to carboxyl groups.[25] Gas oxidant can efficiently diffuse into the inner of cellulose fibers, resulting in a uniform distribution of carboxyl groups and high reactivity. Indeed, α-cellulose that was oxidized by gas oxidants, such as NO_2, O_2 and air, all showed significant enhancement in glucose yield (Table 1, entries 9-11). Compared with those liquid oxidants, although α-cellulose samples oxidized by gas had lower acid amount and similar DP, the glucose yield reached 11.6, 6.8, and 3.8% with the oxidation treatment by NO_2, O_2, and air, respectively.

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Table 1 DP, acid amount and hydrolysis of α-cellulose treated by different methods[a]

Entry	Treatment method	DP	Acid amount (mmol g^{-1})	Glucose yield (%)
1	No	1177	~0	0.2
2[b]	No	1177	~0	0.2
3[c]	No	1177	~0	~0
4	Ball-milling	560	~0	0.4
5	H_2O_2	134	0.25	1.9
6	$KMnO_4$	130	0.24	3.5
7	$NaNO_2$-HNO_3	70	1.49	6.8
8	TEMPO-NaClO	117	0.69	2.5
9	NO_2[d]	116	0.91	11.6
10	O_2[d]	131	0.20	6.8
11	Air[d]	153	0.14	3.8

[a] Hydrolysis conditions: α-cellulose (0.3 g), H_2O (30 mL), 150 °C, 8 h, 1.0 MPa N_2. [b] Using acetic acid (5 mol%) as catalyst. [c] Using glucuronic acid (5 mol%) as catalyst. [d] The pretreatment is in a quartz tube reactor.

As a reference, pretreatment of α-cellulose by mechanical ball-milling was also studied. The DP of α-cellulose also decreased after mechanical ball-milling (Table 1, entry 4), indicating that ball-milling treatment depolymerized α-cellulose to some degree.[26] X-ray diffraction (XRD) results proved that the crystalline fraction of

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α-cellulose was reduced drastically (Fig. S1 ESI†). Hydrolysis of α-cellulose pretreated by ball-milling yielded a little amount of glucose (0.4%), which indicated that cellulose treated by ball-milling is still difficult to be hydrolyzed to glucose without adscititious catalyst. In addition, although the acidity of acetic acid or glucuronic acid is similar with the carboxyl group produced by the oxidation treatment in oxidized α-cellulose, a very low yield of glucose was obtained with these carboxyl acids as catalysts (Table 1, entries 2-3). The possible reason is the diffusion of proton/H_3O^+ (derived from adscititious organic acids) from the reaction solution to the β-1,4-glycosidic bonds is difficult. The above results indicate that cellulose treated by oxidation turned to more easily hydrolyzed.

Preoxidation of cellulose with air and the hydrolysis reaction

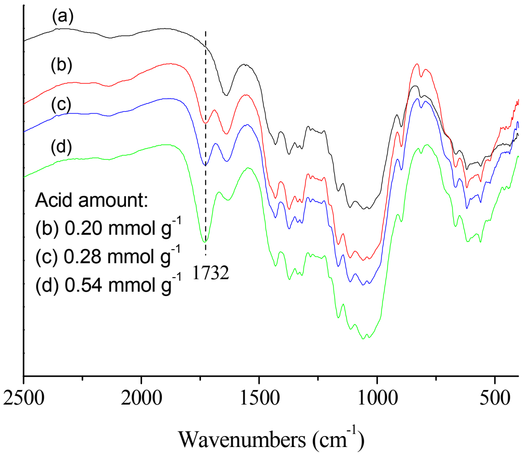

Fig. 1 FTIR spectra of α-cellulose (a), α-cellulose-210-12 (b), α-cellulose-210-24 (c), and α-cellulose-210-48 (d). The oxidation is performed using air as oxidant.

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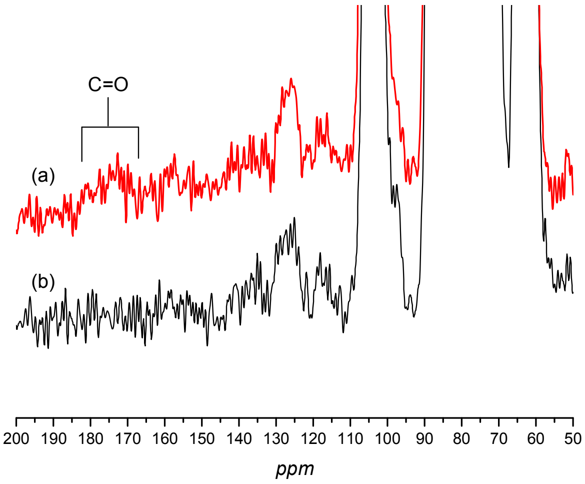

Fig. 2 Solid-state CP/MAS ^{13}C NMR spectra of α-cellulose oxidized by air at 210 ^{o}C for 48 h (a), and parent (b).

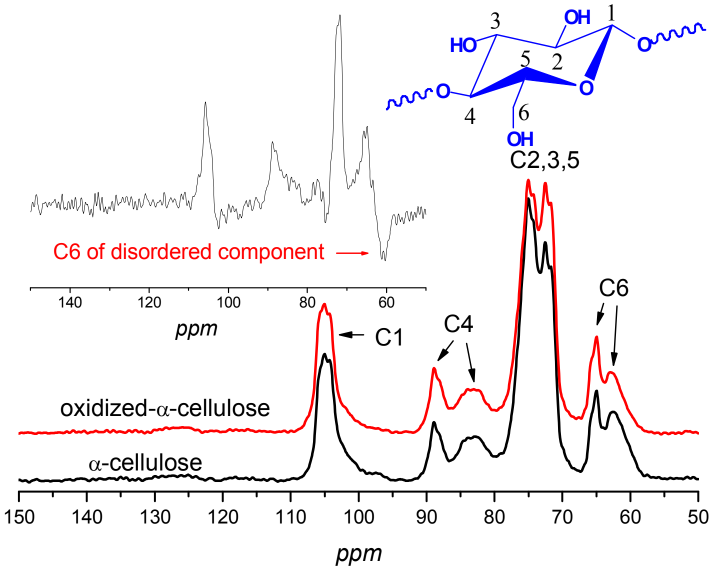

Fig. 3 Solid-state CP/MAS ^{13}C NMR spectra of α-cellulose oxidized by air at 210 ^{o}C for 48 h, and parent at low range chemical shift. The inset is the difference spectrum

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of solid-state CP/MAS ^{13}C NMR between oxidized sample and parent (the spectrum of oxidized α-cellulose minus that of parent).

In the following, air was chosen as an oxidant to realize the preoxidation of cellulose in an electric oven with forced air convection. Fig. 1 shows FTIR spectra of α-cellulose oxidized at 210 °C for different time. A new peak at 1732 cm^{-1} appeared after oxidation, which was assigned to the vibration of –(C=O)– of carboxyl group.[24] Moreover, the intensity of this peak increased with oxidation time, implying that the amount of carboxyl groups increased. The changing trend of acid amount determined by acid-base titration is in accordance with the results of FTIR. Fig. 2 shows the solid-state CP/MAS ^{13}C NMR spectra of α-cellulose. For oxidized α-cellulose, a weak peak appeared at 173 ppm that indicated the formation of –(C=O)– groups at C6 of the oxidized glucose unit of the cellulose chain.[27] The peaks in Fig. 3 were assigned to cellulose carbons according to literature.[28,29] The strong peaks of C4 and C6 are assigned to the crystalline region, while the weak peaks are attributed to the disordered component of cellulose. The decreased peak intensity of C6 belonging to the disordered component (Fig. 3, inset graph) proved that the oxidation preferentially occurred at C6 of the disordered component, because amorphous part of cellulose is more readily accessible by an oxygen molecule.[30] Consequently, it can be concluded that the –CH_2OH groups in glucose units are oxidized to –(C=O)–OH. To further prove this, the oxidation of ball-milled α-cellulose containing a more amorphous part was performed at same conditions. The acid amount of the obtained sample increased

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to 0.65 mmol g^{-1} as compared with 0.54 mmol g^{-1} for directly oxidized α-cellulose.

The crystalline structure of cellulose remained during oxidation treatment as proved by XRD patterns (Fig. S4 ESI†). SEM images indicated that the morphology of α-cellulose was also remained constant after the oxidation treatment (Fig. S5 ESI†). In addition, no significant change happened for the C/O ratio after treatment, which was detected by elemental analysis. All these results indicated that the oxidation conditions adopted in the present work are moderate. It should be noted that the weight loss was small (< 10%) after the treatment, which is attributed to the adsorbed water and the decomposition of some unstable components.[31]

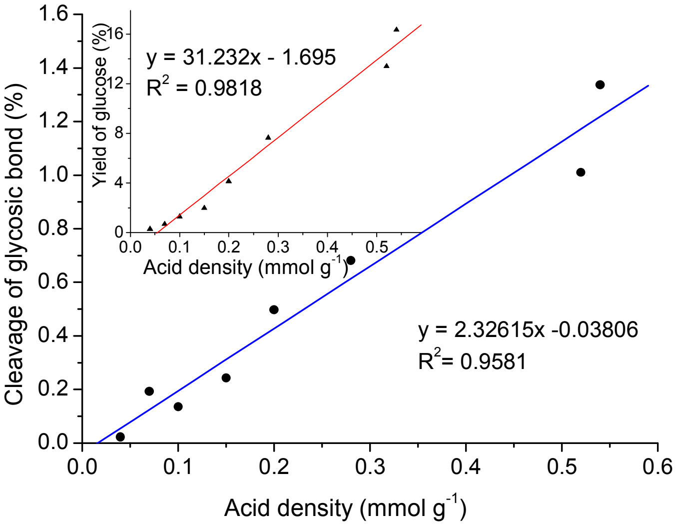

Fig. 4 The plots of the cleavage of glycosidic bonds in oxidation treatment by air *vs* acid density and the yield of glucose of oxidized α-cellulose *vs* acid density (inset). Hydrolysis reaction conditions: cellulose (0.3 g), H_2O (30 mL), 1.0 MPa N_2, 150 ^{o}C, 8 h. The cleavage of glycosidic bonds is calculated from the DP before and after oxidation.

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Oxidation temperature had a significant effect on DP and acid amount (Table S1 ESI†). The acid amount increased whereas the DP decreased with elevated temperature. The oxidation of cellulose almost did not occur at 150 °C, which proceeded to some extent at 180 °C. The decrease in DP and increase in acid amount are significant at 210 °C. To reveal the cause of decreased DP, α-cellulose was treated by N_2 under similar conditions. The DP of α-cellulose treated by N_2 is half of the parent, which is accordant with the reported results.[32] This implies that thermal decomposition is not the main reason for the obvious decreased DP in the present work. In addition, thermal treatment also showed no obvious influence on the α-cellulose reactivity because only 1.0% of glucose yield was given for hydrolysis at 150 °C for 8 h. The cleavage numbers of the glycosidic bonds in oxidation treatment versus the acid amount of the oxidized samples was plotted in Fig. 4. The linear correlation between the cleavage of glycosidic bonds and the acid amount was observed. This indicated that the acid sites catalyzed the depolymerization of cellulose during the oxidation treatment, which primarily accounted for the decrease of DP. An average of 0.106 of glycosidic bonds was broken down by each acid site. Linear correlation was also observed between the glucose yield and the acid amount (Fig. 4, inset graph), indicating that the acid sites are the catalytic active centers for the depolymerization of cellulose in the hydrolysis reaction. To further prove the reactivity of oxidized cellulose, the sample oxidized by air was stirred in water for 48 h at room temperature. This resulted in 0.2% glucose yield with 1.1% cellulose

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conversion. Under identical hydrolysis conditions, the yield of glucose from untreated cellulose was negligible. These results suggested that the reactivity of oxidized cellulose increased as compared with cellulose without preoxidation treatment. To further disclose the role of acid sites in the cleavage of glycosidic bonds, theoretical calculations of the hydrolysis process were carried out. The cleavage of the nearest glycosidic bond is through a six-membered ring structure without participation of water (Fig. S6 ESI†). The distance between the other glycosidic bond and carboxyl group is too far, so the cleavage of these bonds should involve water molecules.

The oxidation-hydrolysis method is very suitable for processing a large amount of cellulose in one pot. The yield of glucose increased with increasing cellulose amount till the weight ratio of cellulose/water reached 0.2 (Table S2 ESI†), 23.3% yield of glucose was given in water at 150 ^{o}C for 8 h. 17.9% yield of glucose can still be obtained even at the ratio of 0.4, where up to 75 g L^{-1} of glucose solution is given. High ratio of cellulose/water is very promising for industrial application, meaning a high concentration of glucose solution which is favorable for subsequent upgrading by chemical or biological processes. In most of the reported literature, the cellulose only accounts for 2-4 wt% of the water; therefore only as high as 2-4 wt% sugar solution can be obtained directly.[33,34]

^{1}H NMR (Fig. S7 ESI†) and ^{13}C NMR spectra (Fig. S8 ESI†) of the recovered aqueous solution after the hydrolysis of cellulose is very similar to those of pure glucose, which indicated that glucose is the main product. It should be noted that 5-hydroxymethyl-2-furaldehyde (HMF) and levulinic acid, presumably formed by

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glucose degradation, were also detected in the 1H NMR spectrum. HPLC analysis results revealed that the yields of these by-products were lower than 3%. The acidic products in the reaction solution can be removed by basic ion exchange resin.[35,36] The recovered by-products, such as levulinic acid, is an important platform chemical from biomass with wide applications.[37]

Table 2 Results of hydrolysis of microcrystalline cellulose (MCC) oxidized by air at 210 °C for 48 h[a]

Temperature (°C)	Conversion (%)	TRS yield (%)	Glucose yield (%)
150	25.6	24.3	16.0
160	33.0	33.0	21.9
170	38.5	36.7	25.2[b]

[a] Reaction conditions: cellulose (3 g), water (30 mL), 1.0 MPa N_2, 8 h.

[b] 0.9% yield of cellobiose, 2.8% yield of HMF and 0.8% yield of levulinic acid were detected in reaction mixture.

To check the efficiency of the preoxidation-hydrolysis method, the hydrolysis of MCC, most recalcitrant cellulose available on the market, was investigated. Table 2 shows the results of the hydrolysis of oxidized MCC. 65.5% of selectivity and 25.2% yield of glucose were obtained at 170 °C for 8 h. The yield of total reduced sugars is close to the conversion of cellulose, implying that the selectivity of our method to soluble sugars is high. The colour of the aqueous phase recovered after the hydrolysis of oxidized MCC is light yellow (Fig. S13 ESI†). The residue after MCC hydrolysis was collected for the following hydrolysis reaction. Direct hydrolysis of the residue

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gave a low yield of glucose due to the decreased acidity. When the residue was reoxidized by air, the reactivity was recovered. After three preoxidation-hydrolysis runs, the total yield of glucose reached 43.4% with 94.0% conversion of MCC (Table S3 ESI†). It was reported by Zhao et al. that 10% yield of glucose was obtained for α-cellulose hydrolysis in water using H_2SO_4 as catalyst at 175 ^{o}C for 40 min.[38] The direct microwave-assisted hydrothermal depolymerization of MCC obtained 21% yield with 36% selectivity of glucose in water at 250 ^{o}C for 1 h.[39] For MCC treated by NTAP, 25% yield of glucose was obtained in water heated by a microwave at 150 ^{o}C for 1 h with an HCl catalyst.[40,41] Cellulose pretreated by ball-milling and NTAP gave 19% yield of glucose by microwave-assisted hydrolysis at the absence of catalyst. These catalyst-free methods are newer but more competitive for the transformation of biomass to sugars. The present results are comparable or better than those reported in literature. As compared to the reported aqueous catalytic routes, our method is more simple and efficient.

Conclusion

In summary, a preoxidation-hydrolysis strategy was developed for the conversion of cellulose to glucose. The hydroxymethyl group was oxidized to a carboxyl group in the first stage of the preoxidation treatment, and the generated acid sites act as catalytic active centers for reducing the DP of cellulose and the following hydrolysis of cellulose to glucose. The preoxidation can be realized using air as oxidant. Direct hydrolysis of the preoxidized cellulose in water was realized under the effect of self-catalysis without an additional catalyst. The methods are effective for hydrolysis

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both α-cellulose and microcrystalline cellulose to glucose. In particular, the high ratio of cellulose/water is applicable for this method; as high as 75 g L^{-1} of glucose aqueous solution can be obtained directly. The present method is a low cost and green process only using water and air, which shows much predominance for industrial application in future.

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