Supporting information

Activating cellulose *via* its reversible reaction with CO_2 in the presence of 1,8-Diazabicyclo[5.4.0]undec-7-ene for efficient synthesis of cellulose acetate

Yunlong Yang,[a,c] Longchu Song,[a,c] Chang Peng,[a,b] Enhui Liu[c] and Haibo Xie, [a,b]*

[a]Division of Biotechnology, Dalian Institute of Chemical Physicals, Chinese Academy of Sciences, Dalian, 116023; Email: hbxie@dicp.ac.cn.
[b]Bioenergy Research Division, Dalian National Laboratory for Clean Energy, Dalian, 116023
[c] Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan, China, 411105

1. Experimental Details

1.1. Materials

Cotton cellulose pulp with a degree of polymerization (DP) of 700 was obtained from Shandong Henglian Paper Group, and was dried at 60 °C for 24 h in vacuum oven before use. CO_2 with a purity of >99.999% was supplied from Beijing Bei Temperature Gas Factory. DMSO was purchased from Beijing Chemcial Reagent Co., Ltd and was dried by 4 A molecular sieves. Acetic anhydride (Ac_2O) was purchased from Sinopharm Chemcial Reagent Co., Ltd. and was purified by distillation. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Aladdin Commerce Reagent Co. Ltd., was dried by KOH, and then was purified by distillation. All chemical reagents were analytical reagents.

1.2 Measurements

The IR spectra of the samples were recorded with a Fourier transform IR spectrometer (FTIR PE-2000, the United States). The test specimens were prepared by the KBr-disk method.

In situ IR spectrum were collected on a React IRTM 15, Mettler, TOLEDO, equipped with a diamond detector (Valid wavenumber range: 2800-2250 cm^{-1},1950-650 cm^{-1}). A spectrum was collected per 30 s. All the IR spectra were presented after subtracting the IR spectrum of DMSO as background.

^1H NMR spectrum were recorded on a Bruker AV 500 spectrometer with 16 scans in DMSO-d_6 or $CDCl_3$. The DS of cellulose ester was calculated by Eq. (1):

$$DS = \frac{7 * (I_{\text{-CH3}})}{3 * I_{H,AGU}}$$

Where I_{CH3} is the peak integral of methyl protons and I_{AGU} is the peak integral of anhydroglucose unit.

The ^{13}C NMR spectra of cellulose ester in DMSO-d_6 were recorded at 25℃ on a Bruker AV-500 instrument.

Wide-angle X-ray powder diffraction (WAXD) was performed by X'pert Pro-1 X-ray diffractometer using Ni-filtered Cu KR radiation (40 kV, 30 mA) with 5°/min scanning rate at room temperature. Diffraction intensity was measured in a range of 2θ=5-60°.

Differential scanning calorimetry (DSC) analysis of the cotton cellulose pulp and cellulose esters were conducted on a DSC 204 HP. In order to provide the same thermal history before the measurement, each sample was heated from 5 to 200 °C at a scanning rate of 10 °C/min and kept at 200 °C for 5 min and quenched to room temperature. All the reported T_g's were observed in the second scan.

Thermogravimetric analysis (TGA) was carried on a Synchronous type thermal analyzer STA 449 F3 with a heating rate of 10 °C/min from 50 to 600 °C under nitrogen atmosphere.

1.3 CO_2-Derivative Dissolution of Cellulose in DMSO

A mixture of pulp cellulose (0.4 g 2.5 mmol) , 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.2 g, 7.4 mmol) and DMSO (6.1 g, 78.1 mmol) was added into a high pressure reactor, and then 2 bar of CO_2 was introduced into the system to stabilize for 5 min till the pressure of CO_2 stabilized. Then the solution was heated at 50 ^oC for 3 h with vigorous magnetic stirring. When the temperature decreased to room temperature, the CO_2 was released slowly, and a 5 wt% of cellulose solution was obtained, which was ready for subsequent reactions. The dissolved cellulose can be regenerated by adding methanol into the solution rapidly, and then washed by methanol (100 mL × 3) to remove the solvents and dried in a vacuum oven at 60 ^oC for 24 h for WXRD analysis.

1.4 Acetylation procedure

A typical acetylation procedure was used as following: Acetic anhydride (1.3 g, 12.5 mmol) was dropped with a pipet into 8.0 g of 5 wt% of cellulose solution in a flask equipped with a mechanical stirrer under N_2 atmosphere at room temperature, and then the reaction temperature was increased to 80 ^oC for 5 h with vigorous mechanical stirring. After the reaction, the cellulose acetate was precipitated by adding 50 mL of methanol, and separated by filtration. Cellulose acetate (0.59 g, 91% yield, DS=2.27) was obtained after subsequent wash with water (100 mL × 3), and dried in a vacuum oven at 60 ^oC for 24 h.

1.5 Preparation of DMSO-saturated cellulose gel and the cellulose gel as raw materials for the preparation of cellulose acetate in the presence of DBU or in the absence of DBU

To identify the catalytic role of DBU during the acetylation process, firstly, a mixture of DBU (1.9 g), DMSO (10.0 g) and cellulose pulp (0.67 g) was added into a high pressure reactor, and then 2 bar of CO_2 was introduced into the system to stabilize for 5 min till the pressure of CO_2 stabilized. Then the solution was heated at 50 ^oC for 3 h with vigorous magnetic stirring. Viscous cellulose solution was obtained after the CO_2 was released when the temperature was decreased to room temperature. Secondly, 100 mL of methanol was added into the solution and cellulose gel was formed. Then the cellulose gel was cutted into gel powder with diameter of 0.5-2 mm, and was extracted further with DMSO (20 mL × 4) in order to form a DMSO saturated and DBU free cellulose gel (5.0 g). Thirdly, the DMSO saturated cellulose gel powder was divided averagely into two portions for subsequent preparation of cellulose acetate in the presence of DBU or in the absence of DBU. The procedure is shown below:

(1) One portion of DMSO saturated cellulose gel powder (2.5 g) was mixed with DBU (0.95 g) and the mixture was added into a 50 mL of two necked glass flask equipped with a mechanical stirrer. Acetic anhydride (1.05 g) was added into the mixture under N_2 atmosphere at room temperature, and then the mixture was heated at 80 ^oC for 1 h with

vigorous mechanical stirring. After the reaction, a homogeneous solution was achieved, and the cellulose acetate was precipitated by adding 100 mL of methanol, and separated by filtration. Cellulose acetate was obtained after subsequent wash with water (100 mL X 3), and and freezing dried. ^{1}H NMR analysis of the as-prepared sample showed that the DS was 2.19.

(2) Another portion of DMSO saturated cellulose gel powder (2.5 g) was added into a 50 mL of two necked glass flask equipped with a mechanical stirrer. Acetic anhydride (1.05 g,) was added into the mixture under N_2 atmosphere at room temperature, and then the mixture was heated at 80 ^{o}C for 1 h with vigorous mechanical stirring. After the reaction, the mixture was still heterogeneous, and the sample was precipitated by adding 100 mL of methanol, and separated by filtration. The sample was obtained after subsequent wash with water (100 mL × 3), and freezing dried. FT-IR analysis of the as-prepared sample showed that the acetylation did not occur.

2. Tables and Figures

Table S1 Distribution of acetyl moiety among the three OH groups of AGU in CAs

Code	Total DS	Distribution of substituent		
		C6	C2	C3
CA-4	1.78	0.83	0.54	0.41
CA-5	2.27	0.92	0.88	0.47
CA-6	2.87	1.0	1.0	0.87

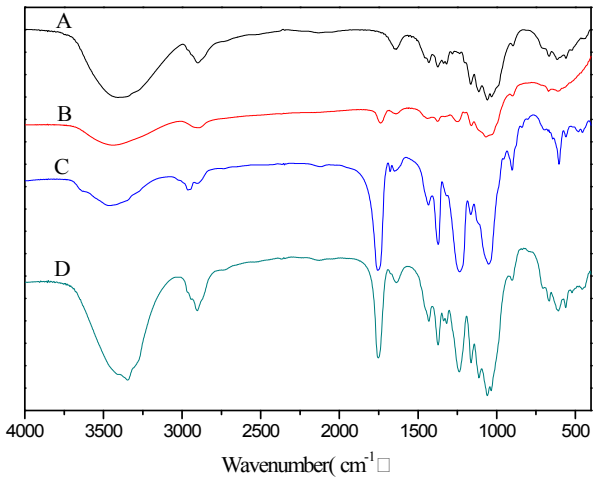

Figure S1 Comparative FT-IR spectra of cellulose pulp and cellulose acetate prepared under different conditions (Conditions: 80 ^{o}C, 1 h, Molar ratio of Acetate anhydride to AGU in cellulose=5:1), A: Raw cellulose pulp; B: DMSO-saturated cellulose gel as raw material in the absence of DBU; C: DMSO-saturated cellulose gel as raw material in the presence of DBU as catalyst (DS=2.19) ; D: Cellulose pulp as raw materials without dissolution activation in the presence of DBU (insoluble in DMSO, $CHCl_3$).

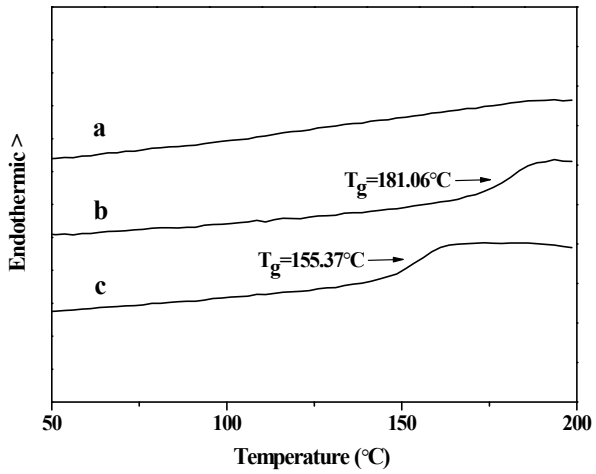

Figure S2. DSC spectra of cotton pulp (spectrum a) ; CA-9 (spectrum b，DS=2.26) ; CA-8 (spectrum c，DS=2.87).

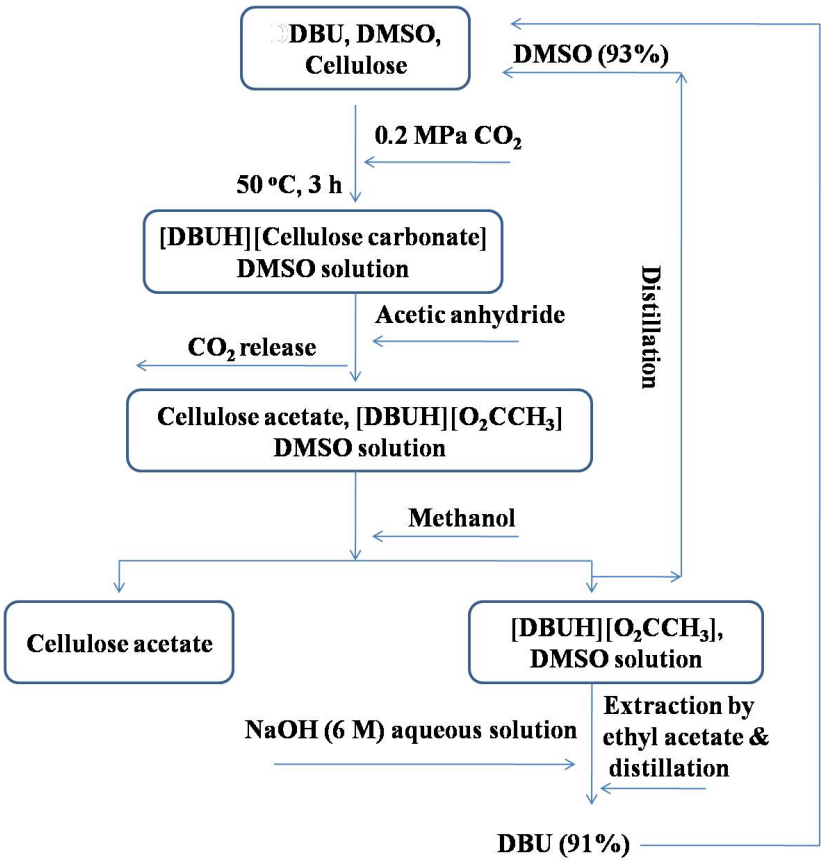

Figure S3 Flowchart to recycle DBU and DMSO

.

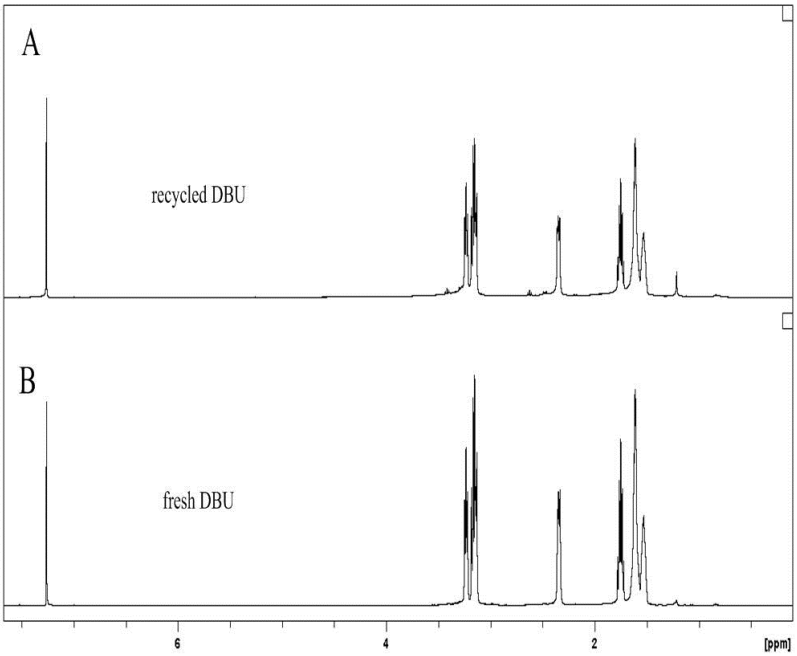

Figure S4. Comparative ^{1}H NMR spectra of fresh DBU and recycled DBU.

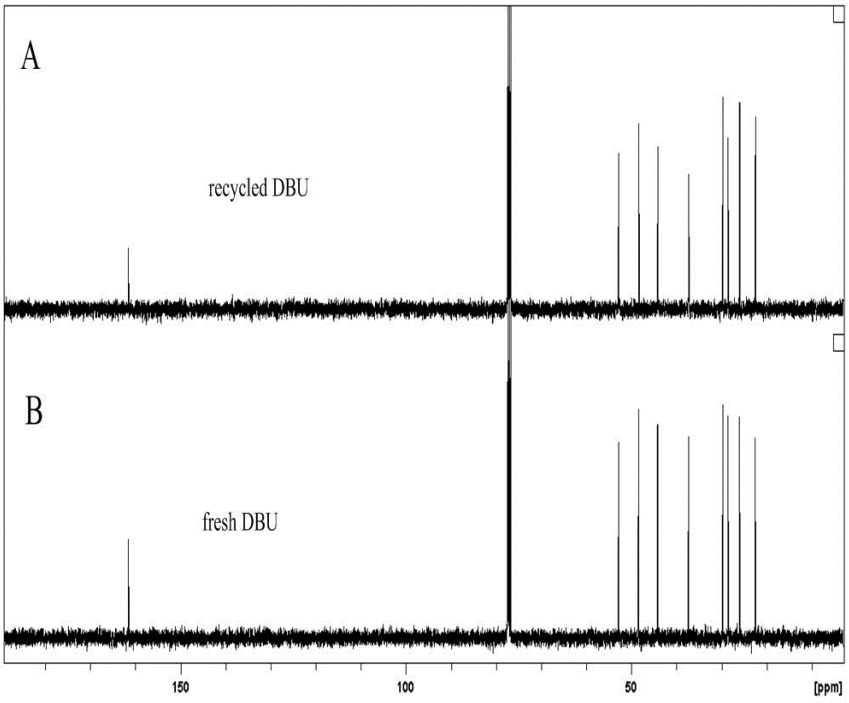

Figure S5. Comparative ^{13}C NMR spectra of fresh DBU and recycled DBU.

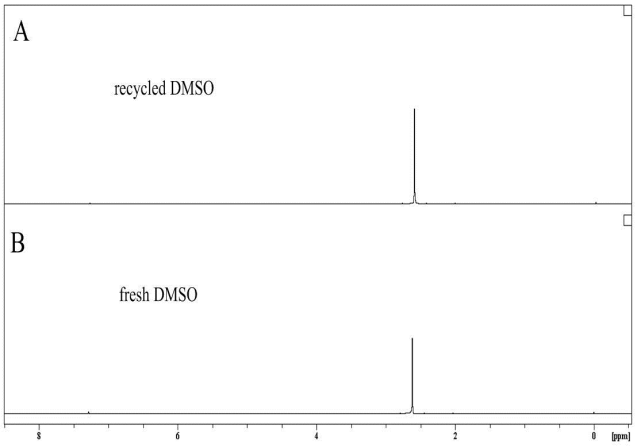

Figure S6. Comparative ^{1}H NMR spectra of fresh DMSO and recycled DMSO.

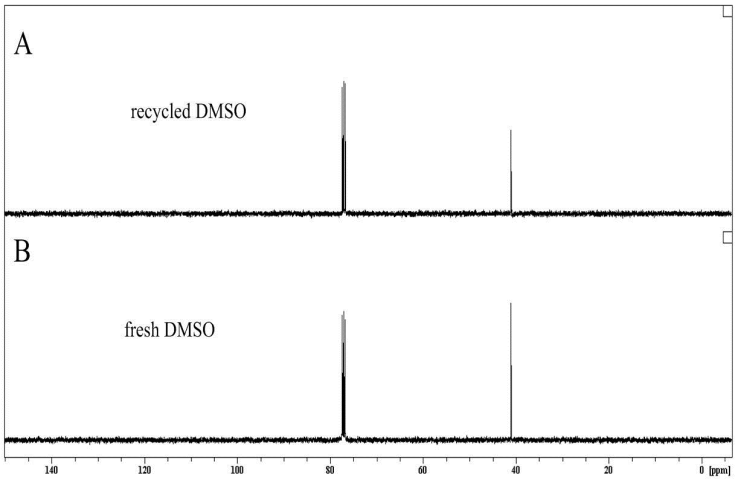

Figure S7. Comparative^{13}C NMR spectra of fresh DMSO and recycled DMSO.