Supporting information for

Capturing CO_2 for Cellulose Dissolution

Haibo Xie,* Xue Yu, Yunlong Yang and Zongbao Kent Zhao

Dalian Institute of Chemical Physics, Chinese Academy of Sciences; Dalian National Laboratory for Clean Energy 457, Zhongshan Rd., Dalian, P. R. China（116023）E-mail: hbxie@dicp.ac.cn

Materials and Methods

Microcrystalline cellulose (MCC, Fluka, Avicel PH-101, particle size: ~50 μm). α-cellulose (Aladdin, particle size: ~50 μm). Cellulose powder from spruce (Fluka, particle size: 0.02-0.15 mm). Sulfate poplar wood pulp was supplied by Shandong Tralin Paper Co., Ltd. 1,1,3,3-tetramethyl guanidine was purchased from J&K Chemical Co., Ltd. and used for the experiments after drying by KOH. DMSO was supplied by Beijing Chemical Works and used after drying with 4 A molecular sieves. Methanol anhydrous (Damao Chemical Reagents Ltd, Tianjin, China) and ethanol anhydrous (Damao Chemical Reagents Ltd, Tianjin, China),1-propanol (Kermel Chemical Reagents Ltd), n-butanol (Bodi Chemcial Reagents, Tianjin, China) and ethylene glycol (Bodi Chemcial Reagents, Tianjin, China) were analytical grade and dried by 4 A molecular sieves before use. CO_2 was supplied from Beijing Bei Temperature Gas Factory with a purity of >99.999%.

The microscopy images were captured by a Nikon ECLIPSE 80i microscope. NMR spectra were recorded on a Bruker Avance 500 spectrometerat 500 MHz (^{1}H NMR), 126 MHz (^{13}C NMR). *In situ* IR spectra 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. Thermogravimetric analysis (TGA) was performed on a Shimadzu Thermal Analyzer DT-20B at air atmosphere. Wide X-Ray diffraction (WXRD) analysis of cellulose and regenerated cellulose samples were recorded on a X′pert Pro Super, PAN Analytical. Scans were collected from 2θ = 5° to 60°. The diffract meter was equipped with a Cu Kα radiation source (λ=0.15432 nm), operating at 40 kV and 40 mA. The following empirical equation was adopted to estimate the amount of cellulose I crystallinity in the cellulosic samples (Eqn. 1).

$$CrI=[I_{total}-I_{am}]/ I_{total} \times 100 \qquad \text{(Eqn. 1)}$$

Where I_{total} is the intensity of the main peak intensity (~22°) and I_{am} is the intensity at the minimum between the main peak and the secondary peak (~16°) in its XRD pattern.

Polarity measurements were performed according to previous publications[1] with minor modification on a UV-Vis Spectrophotometer NanoDrop ND-1000. Approximately 200 μL of the mixed corresponding molecular solvents were placed in 2 mL dry vials. The solvatochromatic dye, Nile red dye, was added into the mixed molecular solvents at an appropriate concentration to obtain a wavelength of maximum absorbance, λ_{max} between 0.5 and 1.5. The λ_{max} of Nile red dye in mixed molecular solvents were measured, and then, the vials were put in a 100 mL of stainless steel high pressure reactor. Subsequently, 2.0 MPa of CO_2 was introduced into the reactor in order to form the reversible ionic compounds in DMSO, and was sustained for 20 min. After releasing the CO_2, the formed mixed ionic solvents were submitted for measurement of λ_{max} again. The experiments were performed triple for each solvent, and the reported λ_{max} values (Fig. 5) are the average of the three values obtained.

Typical procedure for CO_2 capture experiments

The procedure was use according to previous publication.[2] The CO_2 capture efficiency was evaluated using a Sartorius BSA124S-CW Electro-balance. The microbalance has 120 g capacity and 1.0 μg sensitivity. CO_2 gas (99.99%) was dried by passing a drying column (length×diameter: 300 mm×80 mm) packed with anhydrous silica gel and was introduced into the 50 ml there-necked flask containing mixed solution of TMG (0.036 mol) and EG (0.018 mol) or mixed solution of TMG (0.036 mol) , EG (0.018 mol) and DMSO (0.16 mol) with mechanical stirrer at the designed conditions (e.g. temperature, CO_2 pressure, etc.). The increasing weight of the absorbing system was recorded by the Electro-balance.

Typical procedure for dissolution experiments

Cellulose (1.0 g) was added into a mixture of DMSO (12.7 g, 0.16 mol), TMG (4.2 g, 0.036 mol), Ethylene glycol (1.2 g, 0.018 mol) in a 100 mL of stainless steel high pressure reactor equipped with a magnetic stirrer. A pressure of 0.5 MPa CO_2 was introduced into the system after sealing the reactor, and the reversible ionic compounds-DMSO mixed solution $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$/DMSO ($X_{RICs}$=0.1) was formed. Subsequently, the reactor was heated in an oil bath at 60 °C for 1 h, and then the heater was removed. When the temperature of the system was down to room temperature, the extra CO_2 was released, thus a transparent 5 wt% of cellulose solution was obtained.

The procedure for the *in situ* IR analysis of the formation and stable existing state of $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$ in DMSO during the dissolution process

A mixture of DMSO (6.4 g), TMG (0.018 mol, 2.07 g), EG (0.09 mol, 0.57 g), was added into a 50 mL of stainless steel high pressure reactor equipped with a magnetic stirrer and an IR detector. A spectrum was collected per 30 s. Serials of spectra of TMG and EG in DMSO were collected before the addition of CO_2 at room temperature (Fig. 2, Bottom, range A; Top: spectrum a), and then, with the addition of 0.8 MPa of CO_2, serials of spectra of the *in situ* formed $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$ were collected at room temperature (Fig. 2, Bottom, range B; Top: spectrum b) till the strength of characteristic bands of $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$ was stable. MCC (0.5 g, 5 wt%) was added into the reactor after releasing the CO_2 pressure, and then, the reactor was refilled with 0.8 MPa of CO_2 (Fig. 2, Bottom, range C; Top: spectrum c). Subsequently, the mixture was stirred at room temperature, and serials of spectra were collected with evidence of the stable existing state of $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$ (Fig. 2, Bottom, range D; Top: spectrum d). Continually, serials of spectra were collected with evidence of the stable existing state of $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$ till the end of the full dissolution of MCC in this system when the temperature was increased from room temperature to 60 °C (Fig. 2, Bottom, range E; Top: spectrum e).

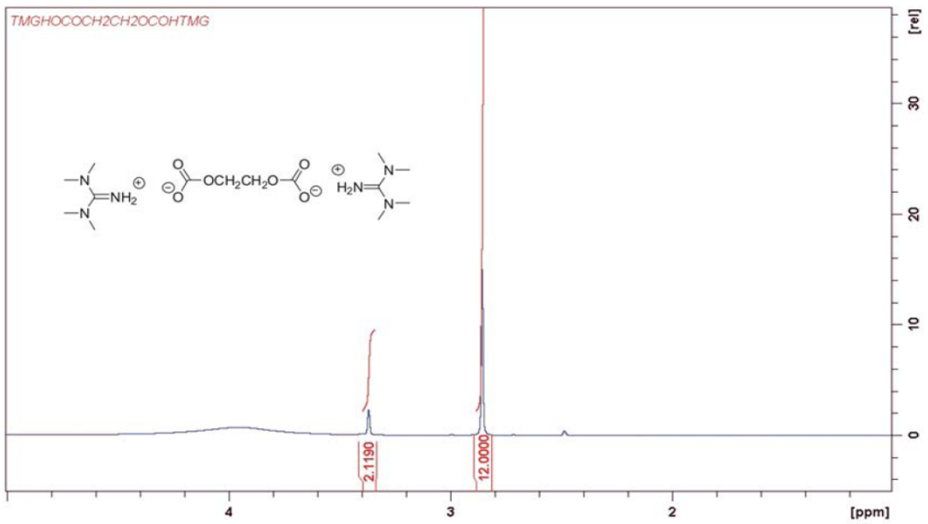

Figure. S1 The ^1H NMR spectra of formed $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$ in d_6-DMSO

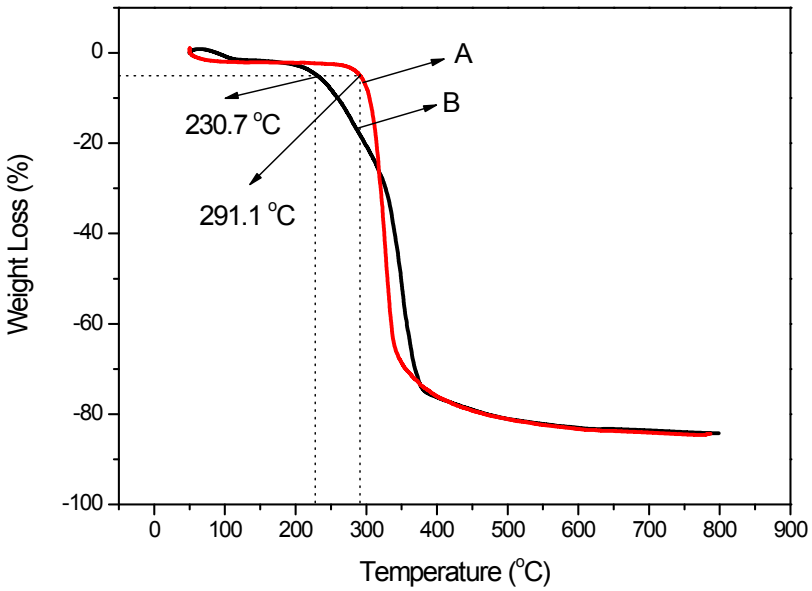

Figure S2. TGA analysis of A: raw MCC and B: regenerated cellulose from 5 wt% of $2[TMGH]^{+}[O_2COCH_2CH_2OCO_2]^{2-}$/DMSO ($X_{RICs}$=0.1) cellulose solution by methanol.

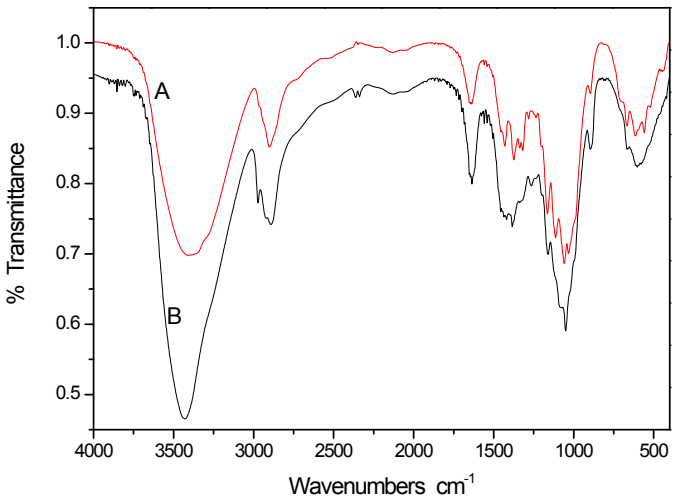

Figure S3. FTIR analysis of A: raw MCC and B: regenerated cellulose from 5 wt% of $2[TMGH]^{+}[O_2COCH_2CH_2OCO_2]^{2-}$/DMSO ($X_{RICs}$=0.1) cellulose solution by methanol.

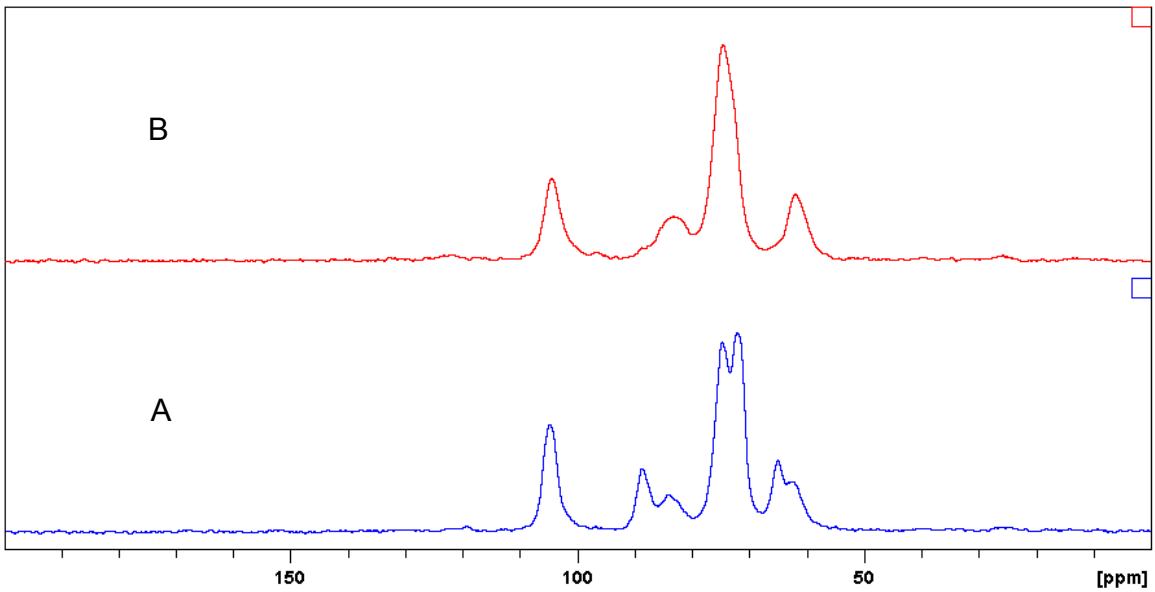

Figure S4. A: ^{13}C CP/MAS NMR spectra of MCC, B: ^{13}C CP/MAS NMR spectra of regenerated cellulose from 5 wt% of $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$/DMSO ($X_{RICs}$=0.1) cellulose solution by methanol. The comparative spectra of MCC and regenerated cellulose confirm that backbone of cellulose are preserved during the dissolution/regeneration process; full transformation of cellulose I to cellulose II; there is no TMG and DMSO residuals in the regenerated sample.

References:

[1][a]Carmichael, A. J.; Seddon, K. R. *J. Phys. Org. Chem.* **2000**, *13*, 591-595. [b]Jessop, P. G.; Jessop, D. A.; Fu, D.; Lam, P. *Green Chem.* **2012**, *14*, 1245-1259.[c]Phan, L.; Andreatta, J. R.; Horvey, L. K.; Edie, C. F.; Luco, A.-L.; Mirchandani, A.; Darensbourg, D. J.; Jessop, P. G. *J. Org. Chem.* **2008**, *73*, 127-132.
[2] Xie, H.; Zhang, S.; Li, S. *Green Chem.* **2006**, *8*, 630-633.