Supplementary Material for "Chitin and chitosan dissolving in ionic liquids as reversible sorbents of CO_2"

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1. Experimental Section

1.1. Materials and instrument

N-methyl-imidazole (Sinopharm Chemical Reagent Co., Ltd.) was dried using NaOH for at least one week, and then distilled and conserved with 4A molecular sieves prior to use. 1-Chlorobutane (Sinopharm Chemical Reagent Co., Ltd.) was distilled and conserved with 4A molecular sieves prior to use. CH_3CN was refluxed for 4 h with CaH_2 and distilled prior to use, ethyl acetate

(Sinopharm Chemical Reagent Co., Ltd.) were used directly. The chitin (Sinopharm Chemical Reagent Co., Ltd.), (Biochemistry Reagent, N%=6.0-7.0%) was purified by normal treatment with 2N HCl and NaOH at constant stirring for 2 h, respectively. The obtained chitin by filtrating was washed with pure water until the solution is neutrality, and then the chitin was dried at 100 □ in vacuum oven for 10 hours to get rid of the water absorbed. The chitosan (Sinopharm Chemical Reagent Co., Ltd.) with a degree of deacetylation of 88% was used directly after being dried at 100 □ in vacuum oven for 10 hours to get rid of the water absorbed.

The X-ray diffraction data were collected on a SiemensP44-circle diffractometer at 293K under monochromatized Cu Ka radiation.

1.2. Synthesis and purification of Ionic Liquid

1-Methyl-3-butyl-imidazolium chloride (BmimCl)[1]: N-Methyl-imidazole (1.0 mol), 1-Chlorobutane (1.2 mol) and CH_3CN (150ml) were charged into a dried 500 ml three-necked bottle, the mixture was refluxed for 24 h under N_2. CH_3CN (about 100 ml) was removed by distillation, and the obtained concentrated BmimCl/CH_3CN solution was slowly added into cold ethyl acetate (about 300 ml), then the mixture was filtered to give white crystal of BmimCl. This purification process was repeated twice to get pure ionic liquid in the yield of 90%. And then, in order to remove the traces of water and solvent, the BmimCl was dried at 100 □ in a vacuum with stirring over for 48 hours prior to use. Mp□65 □□δH (300 MHz, $CDCl_3$) 0.95-1.00 (3 H, t), 1.34-1.46 (2 H, m), 1.87-1.97 (2H, m), 4.15 (3 H, s), 7.51 (1 H, s), 7.61 (1H, s), 10.83 (1H, s).

1.3. Dissolution of Chitin in Ionic Liquids

10 g of ionic liquid was charged into a 50 ml dried three-necked flask under inert atmosphere of N_2. The temperature of the dissolving process was controlled by oil bath at 110 □. The chitin

was added in portions of only 1 wt% of ionic liquid each time with stirring, and new solid was allowed to be added after the disappearance of crystalline particles. During the course of dissolving, a little amount of solution was taken out from the flask and painted on a glass plate. The dissolution was monitored by observing the liquids on the glass plate by eyes (**Figure S1**). None of crystalline particles were found in a 10 wt% of chitin/ILs solution, indicated a clear solution was obtained.

In order to prove the dissolution behavior of chitin in ionic liquid, the obtained solution was determined by WAXD, which is one of the useful scientific means to prove the dissolution of crystal polymers in solution[2]. For comparison, a chitin DMAc/LiCl solution was prepared by dissolving 0.5 g of chitin in 26 ml DMAc containing 1.3g of lithium chloride[3]. The resulting solution was taken to examine by WAXD after filtration using a G2 filter funnel. It was found from **Figure S2** and **Figure S3** that a 10 wt% of chitin ionic liquid solution showed an amorphous diffraction pattern about $2\theta=20^{o}$, and no obvious diffraction peaks $2\theta=9.3^{o}$, 19.5^{o}, 20.5^{o} corresponding to the characteristic diffraction peaks of chitin was found. From **Figure S4** we can find that the WAXD of chitin DMAc/LiCl solution also only showed an amorphous pattern near $2\theta=20^{o}$. Based on the comparison of the WAXD of chitin in ionic liquid and in DMAc/LiCl, we conclude that the chitin has been dissolved in ionic liquid. But the obtained solution has no satisfactory membrane forming capability.

1.4. Dissolution of Chitosan and chitin in a blend of 1-methy-3-hydrogen imidazolium chloride and 1-methy-3-butyl imidazolium chloride Ionic Liquids

1-methy-3-hydrogen imidazolium chloride □1-Methylimidazole (61.5 g, 0.75 mol) was placed in a three necked flask, which was provided with a stirrer and cooled to 0°C. Then hydrochloride acid (0.75 mol, 37% solution in water) was added slowly over a period of 30 min. Water was removed in

vacuum to give 1-methy-3-hydrogen imidazolium chloride as a colorless liquid, which solidified on cooling.

9.0 g of 1-methy-3-butyl imidazolium chloride and 1.0 g of 1-methy-3-hydrogen imidazolium chloride ionic liquids were charged into a 50 ml dried three-necked flask under inert atmosphere of N_2. The temperature of the dissolving process was controlled by oil bath at 90 □. The chitosan was added in portions of only 1 wt% of ionic liquid each time with stirring, and new solid was allowed to be added after the disappearance of crystalline particles. A clear and viscous of 3 wt% chitosan ionic liquids solution was obtained in four hours. A flexible and transparent film can be cast from this solution. Chitin also displayed the similar solubility behavior and film forming ability in this blend of ionic liquids.

2. Reversible CO_2 Fixation and Release Measurements

The CO_2 fixation and release of chitin and chitosan ionic liquid solution was evaluated using a Mettler Toledo AB104-S Electro-balance. The microbalance has 100 g capacity and 1.0 μg sensitivity. The experimental apparatus was shown in **Scheme S1**. CO_2 gas (99.99%) was dried by passing a drying column (length×diameter: 300 mm×80 mm) packed with P_2O_5 □ and was introduced into the 50 ml there-necked flask containing chitosan ionic liquids 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.

a

b

Figure S1 : 10 wt% (a) and 1 w t% (b) of chitin ionic liquid solution

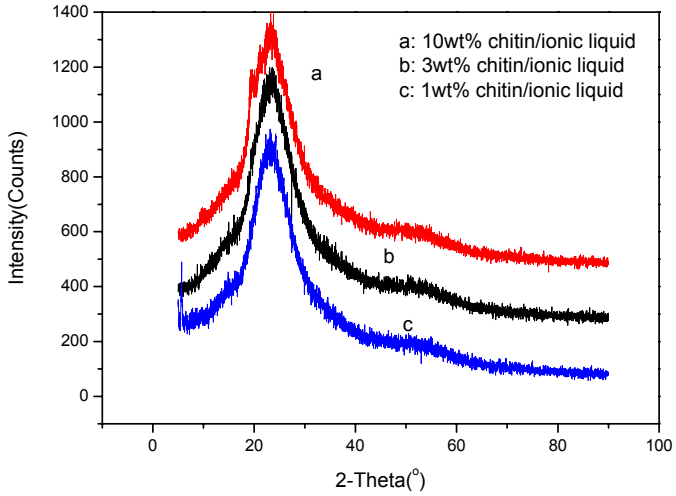


Figure S2 WAXD of 1wt% chitin/ionic liquid, 3 wt% chitin/ionic liquid, 10 wt% chitin/ionic liquid

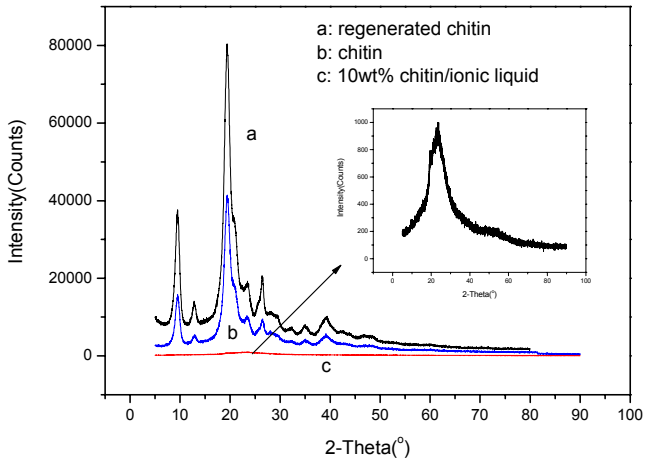


Figure S3 WAXD of chitin, regenerated chitin from methanol and 10 wt% chitin solution of ionic liquid.

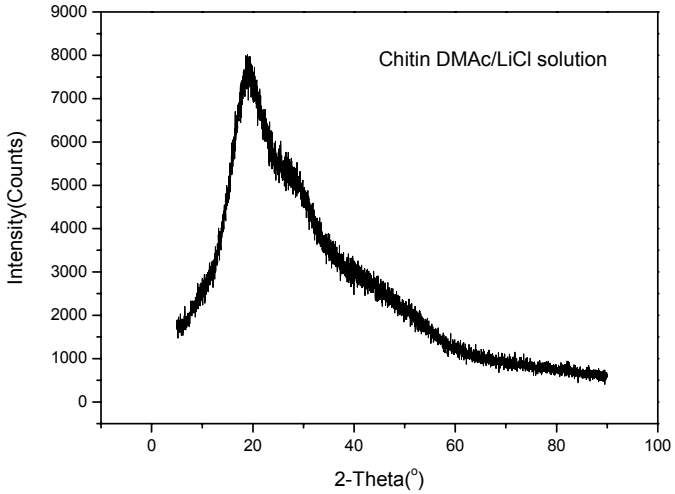


Figure S4 WAXD of Chitin DMAc/LiCl solution

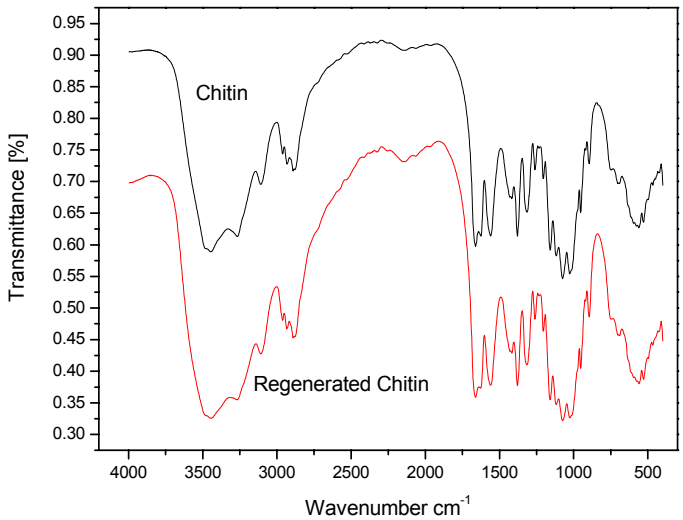


Figure S5 IR of chitin and regenerated chitin

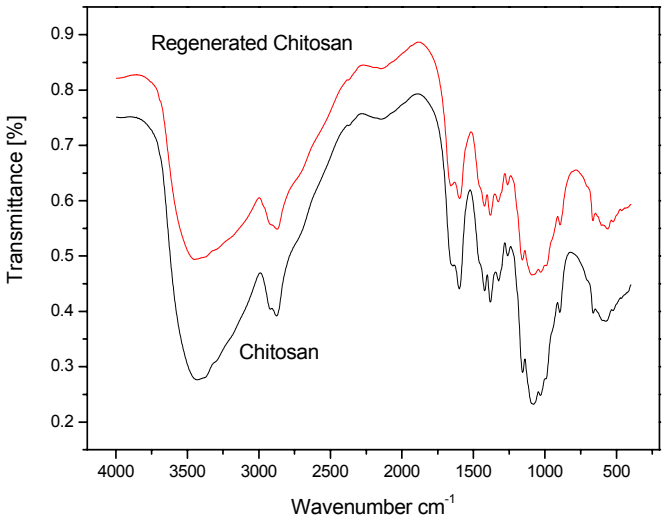


Figure S6 IR of chitosan and regenerated chitosan

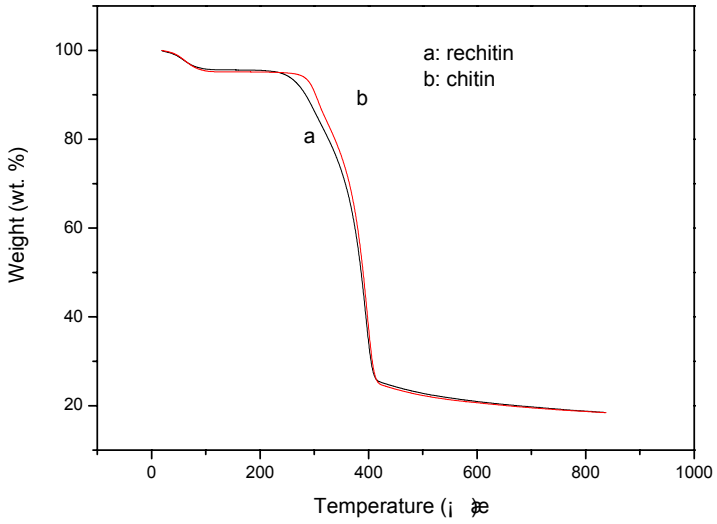


Figure S7 TGA of chitin and regenerated chitin

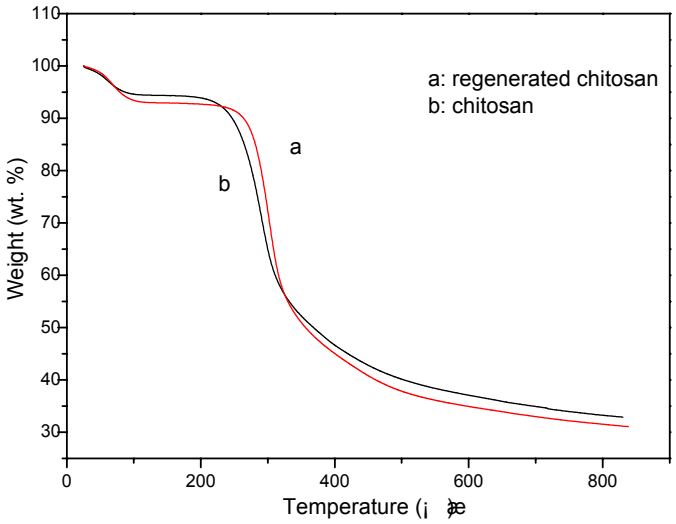
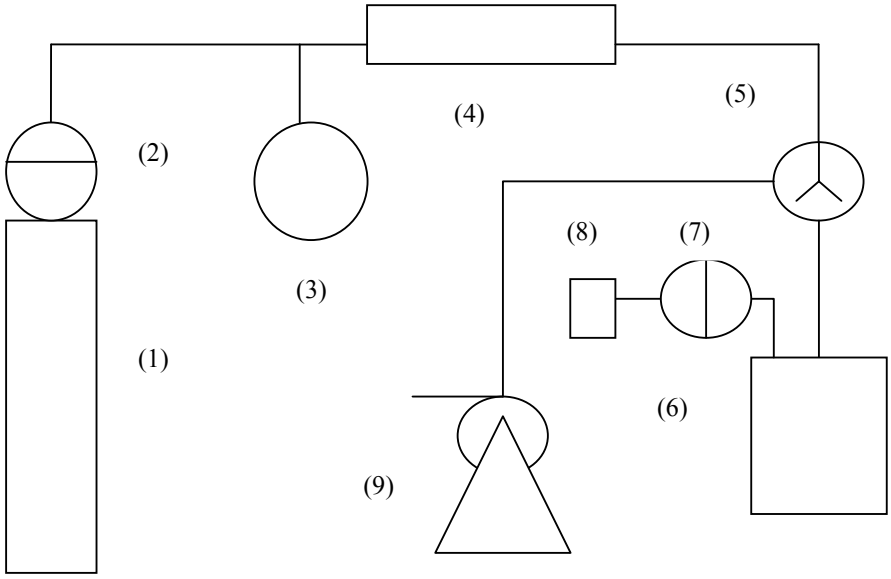


Figure S8 TGA of chitosan and regenerated chitosan



Scheme S1. Schematic diagram of experimental apparatus

(1) gas cylinder; (2) decreasing pressure valve; (3) balloon; (4) dryer; (5) three way valve; (6) CO_2 capture and release system; (7) two way valve; (8) gas outlet (sealed with paraffin oil); (9) vacuum pump.

References:

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and T. Zigras, *J. Chem. Soc., Dalton Trans.,* 1997, 3465.

[2] D. M. Phillips, L. F. Drummy, D. G. Conrady, D. M. Fox, R. R. Naik, et al, *J. Am. Chem. Soc.* 2004, 126, 14350.

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