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ARTICLE TYPE

Capturing CO$_2$ for Cellulose Dissolution

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

5 The design of a system using 1,1,3,3-tetramethyl guanidine in conjunction of ethylene glycol in DMSO after CO$_2$ capture created a new solvent capable of dissolving up to 10 wt% of cellulose under mild conditions, which opened a new window for the homogeneous utilization of cellulose for production of sustainable materials, chemicals and energy in the future.

The utilization of both CO$_2$ and biomass as resources are urgent 10 and challenging research topics, because CO$_2$ is regarded as a main gas responsible for climate change, and its effective capture, storage (CCS) and utilization can reduce the accumulation of CO$_2$ in the atmosphere;[1, 2] the utilization of biomass as raw feedstock to produce sustainable materials, energy and chemicals 15 contributes to reduce our current dependence on fossil resources and establish a sustainable economy.[3, 4] Development of reversible CO$_2$ capture systems with strong ability to dissolve cellulose after CO$_2$ capture is highly desirable for efficient integration of CCS and cellulose utilization processes.
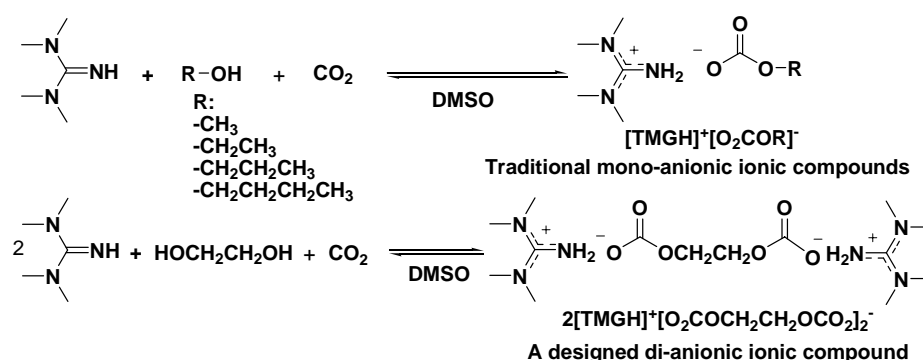

Scheme 1 TMG-based reversible mono-anionic and di-anionic ionic compounds screened in this study

Cellulose, a linear and semi-flexible polymer, is the most abundant renewable resource. Since cellulose cannot be melted and dissolved easily in conventional solvents, dissolution has 25 become a major obstacle preventing its subsequent processing in various forms (e.g. fibres, films), derivatisation as well as catalytic conversion. Therefore, the search of effective solvents for the dissolution of cellulose has been a popular research topic since its isolation in the nineteenth century.[5] To date, a rather 30 limited number of solvents are available via non-derivatising or derivatising pathways, such as cuprammouium hydroxide solution, monohydrate of N-methyl-N-morpholine oxide (lyocell process), CS$_2$-NaOH aqueous solution (viscose process), LiCl-based solvents, ionic liquids,[6] NaOH-urea-water.[7] The viscose 35 process and lyocell process (production over 3,000,000 tons per year) have dominated the production of regenerated cellulose fibers in fiber industry so far.[8, 9] The recently developed ionic liquids and NaOH-urea-water systems have significantly promoted the utilization of biomass in terms of catalytic 40 conversion and sustainable material development under homogeneous conditions.[10-12] However, these processes in general have drawbacks including environmental pollution, high cost and recycling problems, etc. Therefore, the design of environmentally friendly, effective and cheap solvents with good 45 recyclability and reusability for cellulose dissolution processing and conversion is of still prime importance.[5, 13]

The reversible CO$_2$ capture based on an exothermic transformation using a strong organic base in conjunction with a proton donor proposed by Jessop et al. is one of the most 50 fascinating strategies for the CCS process.[1, 2, 14] With the reversible compositional change under mild conditions from molecular liquids to ionic compounds, in association with other switched properties, such as polarity and viscosity, the proposed system introduced a variety of possible opportunities in catalysis 55 and separation processes.[15-19] Although the formed reversible ionic compounds (RICs) have been used as extracting solvents for fractionation of lignocellulose,[20, 21] they are not successful for full dissolution and processing of cellulose yet. Our results showed that the formed viscous or solid RICs after CO$_2$ capture 60 when 1,1,3,3-tetramethyl guanidine (TMG) was used as a base, in conjunction with commonly used alcohols, such as methanol,

ethanol, n-propanol and n-butanol (Scheme 1), could only slightly swell microcrystalline cellulose (MCC). The addition of dimethyl sulfoxide (DMSO, one of the commonly used co-solvents; X_{RICs} =0.2, X_{RICs}: the mole fraction of formed RICs after CO_2 capture in the mixture) can significantly decrease the viscosity of the RICs and enhance their solubility to MCC, but only semi-transparent or opaque cellulose solution achieved under identical conditions. The moderate solubility of these formed reversible RICs was evidenced from the pictures of opaque and viscous cellulose solutions (Fig. 1, top: B, C, D, E) and the results of wide angle X-ray diffraction (WXRD) analysis of the regenerated cellulose by methanol (Fig. 1, bottom panel).
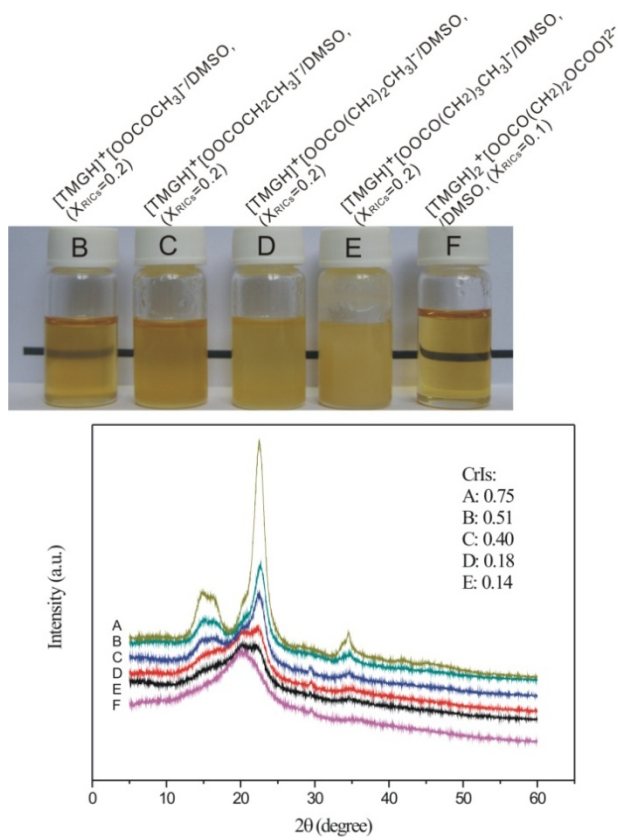

Fig.1 Top: Pictures illustrating the dissolution state of 5 wt% of MCC in the screened solvents. Bottom: Comparative WXRD analysis of MCC (A) and the regenerated cellulose (B, C, D, E, F) by methanol from screened mixed solvents. Experimental conditions: RICs/DMSO mixed solution (20.0 g), MCC (1.0 g), T= 60 °C, P_{CO_2}=2.0 MPa, t = 2 h.

The degree of de-crystallization of cellulose was closely related to the length of the aliphatic chain; accordingly, the crystallinity index (CrIs) of cellulose was decreased from 0.75 to 0.51, 0.40, 0.18, and 0.14 in the cases of *n*-butanol, *n*-propanol, ethanol, and methanol, respectively (Fig. 1, bottom spectra E, D, C, B).

The better de-crystallization outcome of $[TMGH]^+[O_2COCH_3]^-$ in DMSO to MCC prompted the subsequent optimization of the dissolution system. Interestingly, a replacement of methanol with ethylene glycol [22], which has a high boiling point and a similar structure to methanol, to construct the mixed solvents as di-1,1,3,3-tetramethyl guanidine ammonium ethylene di-carbonate (Scheme 1)

$(2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$/DMSO ($X_{RICs}$=0.1)) resulted in a fully transparent cellulose solution (Fig. 1, Top F) under these conditions. WXRD analysis of the regenerated cellulose demonstrated that the diffractive peaks of cellulose I in raw MCC disappeared completely, which further corroborated the full dissolution of MCC (Fig. 1, bottom panel: F). Decreasing temperature from 60 °C to 40 °C or the pressure of CO_2 from 2.0 MPa to 0.1 MPa resulted in an opaque and viscous solution of swollen cellulose, which demonstrated that suitable temperature and CO_2 pressure are important factors influencing the solubility of MCC in the system. Further experiments demonstrated that the mixed solvents of $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$/DMSO ($X_{RICs}$=0.1) was capable of dissolving up to 10 wt% of MCC at 60 °C in 1 h with 0.5 MPa of CO_2 pressure. The solution remained stable for a couple of months. Other commercially available cellulose samples, including α-cellulose, cellulose powder from spruce and sulfate poplar wood pulp were also examined with appreciable solubility of 10 wt%, 8 wt% and 5 wt% observed respectively under identical conditions.
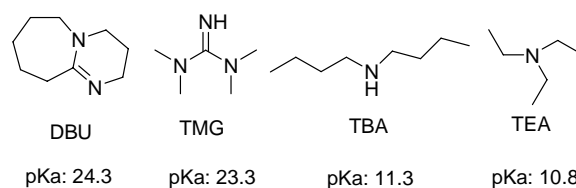
Scheme 2 Organic bases used in this study with various pKa of conjugated acids

To better understand the underlying mechanism for the dissolution of cellulose in this new solvent system, other organic bases with various pKa of conjugated acids[22] (Scheme 2) were also used to construct the solvent system with methanol and EG in DMSO for this purpose under identical conditions. Beside the TMG-EG-DMSO based system, only DBU-EG-DMSO based system showed moderate solubility to MCC (5 wt%, 0.5 MPa of CO_2, 60 °C, 1 h), while the systems based on TBA and TEA are not capable of dissolving MCC, implying that, the structure and the basicity of organic bases were important factors, determining their performance in their solubility to cellulose in DMSO after CO_2 absorption. Only strong organic bases, such as DBU and TMG in conjunction with alcohols were able to rapidly capture CO_2 for the formation of amidinium/guanidinium alkylcarbonate salt [23] as shown in Scheme 1, leading good performance in the dissolution of cellulose.

The formation of $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$ between TMG and EG in DMSO in the presence of CO_2 was identified by ^1H NMR (ESI, Fig. S1) and ^{13}C NMR. In the ^{13}C NMR spectrum, a new signal at δ=159.2 ppm after CO_2 addition revealed the formation of carbonate carbon structure between EG and CO_2 (Fig. 2).[23, 24] Simultaneously, the protonation of TMG resulted in a shift change of the central carbon in TMG from 166.7 to 161.7 ppm, but did not affect the chemical shifts of other carbons both in TMG and ethylene glycol obviously.

The formation and existing state of it during the dissolution process were also monitored by *in situ* IR (Fig. 3). A strong C=NH stretching vibration absorption band of TMG was detected at 1595 cm^{-1} before the introduction of CO_2 and cellulose.

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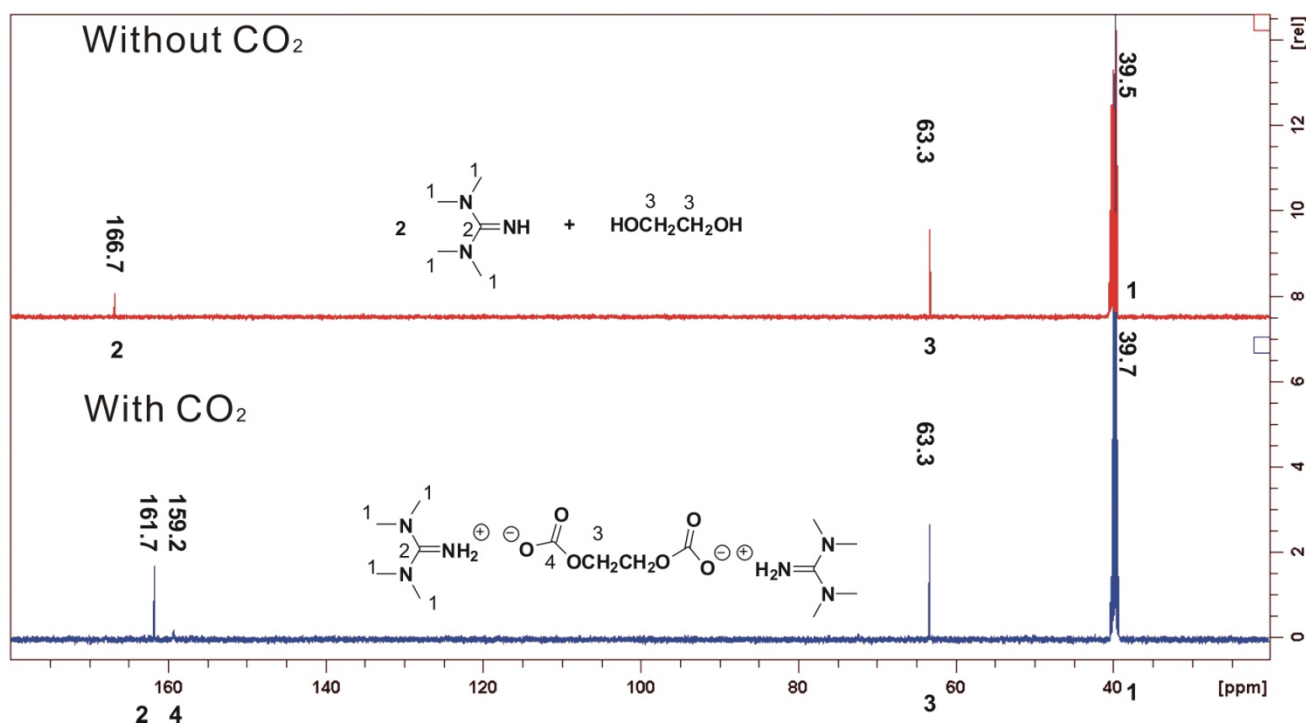
Fig.2 The comparative ^{13}C NMR spectra of TMG/ethylene glycol (2:1, molar ratio) in d_6-DMSO without and with CO_2 addition. A new signal assigned to the carbonate carbon appeared at $\delta=159.2$ ppm after CO_2 addition, which indicated the formation of $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$

Newly formed asymmetric and symmetric carbonyl stretching bands at 1663 and 1410 cm^{-1}, asymmetric and symmetric C-O-C, stretching vibrations at 1265 and 1030 cm^{-1}, and protonated $C=NH_2^+$ stretching vibration at 1573 cm^{-1} were observed after 0.8 MPa of CO_2 was introduced into the DMSO-TMG-EG mixture.[25, 26] The protonation of TMG resulted in a shift of the characteristic C=N stretching vibration band from 1595 to 1601 cm^{-1}. These results further indicated the in situ formation of $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$ in DMSO. The subsequent addition and dissolution of MCC in the formed solvent did not lead to shifts of the characteristic bands related to carbonate ions in $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$, which implied that $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$ acted as a stable non-derivitizing solvent for cellulose in this system.

The switchable polarity of the mixed molecular solvents and ionic solvents was assessed by the solvatochromic behavior of Nile red dye. The Nile Red wavelength of maximum absorbance, λ_{max}, directly correlates with solvent polarity and has previously been used as a polarity probe with ionic liquids.[27] The results demonstrated that the ionic solvents were more polar than that of the corresponding molecular solvents, as indicated by larger λ_{max} values of the ionic solvents (Fig. 4). Higher polarity could be achieved with shorter chain aliphatic alcohols applied. The polarity of these systems was correlated to their solubility to cellulose in a certain extent. In general, a solvent with higher polarity had better solubility to cellulose.
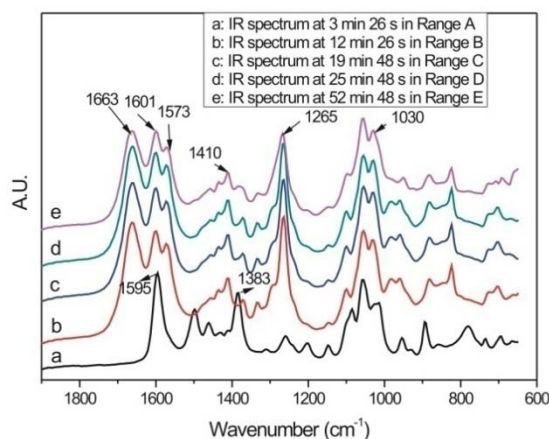
Fig.3 Two–dimensional stacked spectra of in situ Infrared spectroscopy (IR) analysis of the formation of $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$ in DMSO, and its existing state during the dissolution of MCC in $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$/DMSO ($X_{RICs}$=0.1) solution at 60 °C in the presence of 0.8 MPa CO_2. The spectrum of DMSO was subtracted as background. Range A: spectra of mixture of DMSO, TMG and EG at room temperature; Range B: spectra of the formation of $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$ when 0.8 MPa CO_2 was introduced; Range C: the process of adding 5 wt% of MCC; Range D: spectra of the dissolution process at room temperature; Range E: spectra of the dissolution process at 60°C.

However, the polarity of $[TMGH]^+[O_2COCH_3]^-$/DMSO

$(X_{RICs}=0.2)$ and $[TMGH]^+[O_2COCH_2CH_3]^-/DMSO$ $(X_{RICs}=0.2)$ was higher than that of $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$/DMSO $(X_{RICs}=0.1)$, but cellulose solubility in such systems was poor. The observation indicated that the polarity was probably not the only factor affecting their solubility to cellulose.
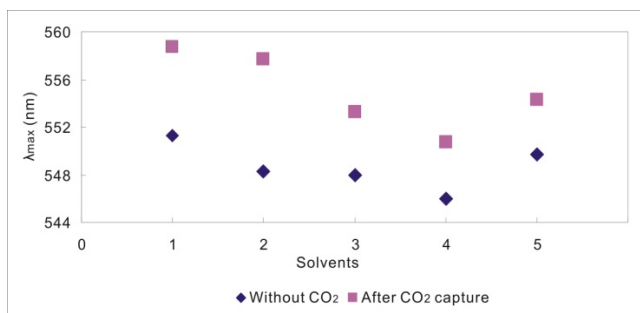
Fig. 4 Switchable λ_{max} of Nile red dye in the mixed molecular solvents and corresponding mixed ionic solvents:
1: $[TMGH]^+[O_2COCH_3]^-/DMSO$ $(X_{RICs}=0.2)$;
2: $[TMGH]^+[O_2COCH_2CH_3]^-/DMSO$ $(X_{RICs}=0.2)$;
3: $[TMGH]^+[O_2COCH_2CH_2CH_3]^-/DMSO$ $(X_{RICs}=0.2)$;
4: $[TMGH]^+[O_2COCH_2CH_2CH_2CH_3]^-/DMSO$ $(X_{RICs}=0.2)$;
5: $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$ $(X_{RICs}=0.1)$.
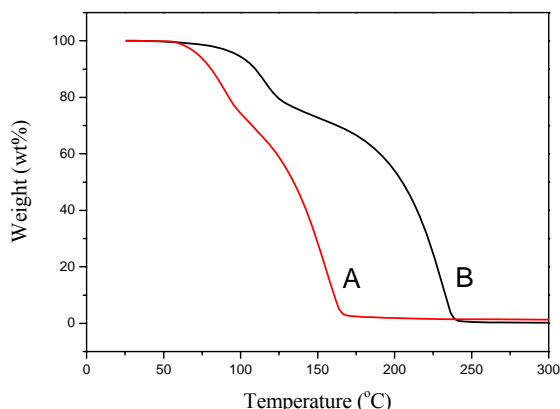
Fig. 5 The TGA graphs (A): $[TMGH]^+[O_2COCH_3]^-$; (B): $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$

The reaction between TMG and alcohols in the presence of CO_2 was enthalpically favored while the reverse was entropically favored. Comparative TGA analysis demonstrated that $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$ had better thermal stability than $[TMGH]^+[O_2COCH_3]^-$ (Fig. 5). These observations were consisted with the research for ionic liquids that the di-cationic or di-anionic ionic liquids had better thermal stability than mono-ionic liquids.[27] The better thermal stability was anticipated to determine the effective concentration of the ionic compounds at 60 °C, which might explain their differences in solubility of cellulose in DMSO. Similarly, increasing CO_2 pressure could facilitate the CO_2 capture and formation of carbonate anion at 60 °C, thus enhancing the solubility of cellulose in $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$/DMSO $(X_{RICs}=0.1)$. The synergetic effect of the solvents' polarity, thermal stability of the formed ionic compounds and swollen ability of DMSO determined the solubility of cellulose in this system under mild

conditions. With the assistant of DMSO, the formed carbonate ions acted as hydrogen bond acceptors in the mixed solution, which then interacted with the hydroxyl groups and ether bonds of the cellulose and by disrupting and breaking the intramolecular hydrogen-bonding network, thus leading to the dissolution of cellulose, which was similar with the role of ionic liquids for cellulose dissolution.[28-32]

The concept of CO_2 capture for facile dissolution and regeneration of cellulose based on the reversible properties was easily appreciated by the means of microscopic imaging (Fig. 6). Raw cellulose powders were observed in DMSO-TMG-EG mixture (Fig. 6A). A transparent and homogeneous solution was achieved after 0.5 MPa CO_2 was introduced at 60 °C for 1 h (Fig. 6B) and no cellulose residual in the transparent solution was observed, further supporting the fact of full dissolution of MCC in the mixed solution. Further purging N_2 into the obtained cellulose solution to remove CO_2 for 20 min at 70 °C resulted in gelation of cellulose (Fig. 6C), implying the regeneration of cellulose.[14]

The formed ionic compounds could be reversed thermally at moderate temperature to their molecular precursors (Fig. 5), which offered much more advantages in terms of economic recycling and purification of the solvents.[33] Firstly, the solvents could be distillated out fully from the as-prepared cellulose solution for reuse with the regenerated cellulose as residuals. Secondly, pouring the cellulose solution slowly into anti-solvents (e.g. methanol and ethanol) under intensive stirring led to the precipitation of cellulose as gelled powder, and the mixed solvents can be extracted from the gelled powder by the anti-solvents. The mixed solvents of DMSO, TMG and EG can be recycled with a >99% yield and reused without decreased solubility after filtration of the regenerated cellulose and removal of the anti-solvents. Further comparative TGA (ESI, Fig. S2) and FTIR (ESI, Fig. S3) analysis of raw MCC and regenerated cellulose demonstrated that no ionic compounds and DMSO residuals was left in the regenerated cellulose. The absence of TMG and DMSO residues in the regenerated cellulose and transformation of cellulose I to cellulose II were also evidenced by ^{13}C CP/MAS NMR (ESI, Fig. S4). The regenerated cellulose exhibited a lower onset temperature for decomposition, possibly due to the transformation of a cellulose crystalline structure, which was consistent with the previous results.[6]

A major obstacle to the broader application of cellulose lies in its facile dissolution.[8] Herein, we demonstrated that a novel invented system based on TMG in conjunction of EG in DMSO after CO_2 capture could dissolve up to 10 wt% of cellulose under mild conditions. We proposed that the interactions of the *in situ* formed carbonate anions with hydroxyl groups in cellulose acted as driving forces for cellulose dissolution in $2[TMGH]^+[O_2COCH_2CH_2OCO_2]^{2-}$/DMSO $(X_{RICs}=0.1)$ under mild conditions. In conclusion, the study demonstrated a facile integrated strategy for CCS and cellulose dissolution processing and conversion by using cheap, commercially available compounds under mild conditions with good recyclability and reusability, which offered insights in the design of solvents for biopolymers and opportunities on both of CO_2 and biomass utilization.

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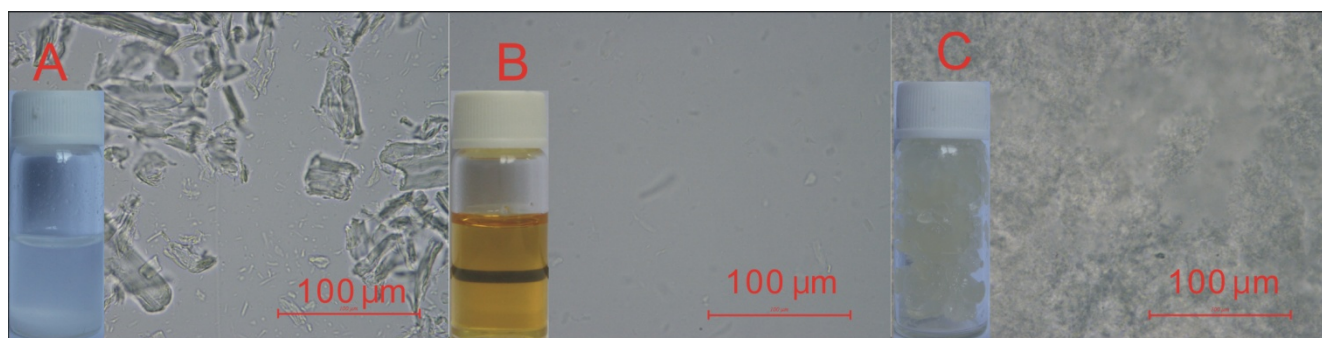
Fig. 7 MCC suspension in scintillation bottles and its microscopic images. A: Suspension of 5 wt% MCC powder in DMSO-TMG-EG (X_{RICs}=0.1); B: 5 wt% MCC 2[TMGH]$^+$[O$_2$COCH$_2$CH$_2$OCO$_2$]$^{2-}$/DMSO (X_{RICs}=0.1) solution; C: Cellulose gel regenerated from 5 wt% of MCC 2[TMGH]$^+$[O$_2$COCH$_2$CH$_2$OCO$_2$]$^{2-}$/DMSO (X_{RICs}=0.1) solution by N$_2$ at 70 ^{o}C for 20 min.

Notes and references

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Graphical Abstract

Capturing CO_2 for Cellulose Dissolution

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The design of organic liquids in DMSO after CO_2 capture created a new solvent capable of dissolving up to 10 wt% of cellulose under mild conditions.