Supporting Information

Regenerated Cellulose I from LiCl•DMAc Solution

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1. Materials

Molecular sieve (4 Å), dehydrated lithium chloride (LiCl, >99.0 %), dimethyl-acetamide (DMAc, 99.0 %) and ethylenediamine (>99.0 %) were purchased from Aladdin (Shanghai, China). DMAc was pre-dried by molecular sieve for overnight before use. Cadmium oxide (CdO, AR) was obtained from the Third Tianjin Chemical Reagent Factory (Tianjin, China). Deionized water was prepared by an ultra-pure water system (model ROP-15L, >15MΩ) made by Heal Force Bio-Meditech Holdings Limited (Shanghai, China). Cadoxen was prepared according to the reported method.¹ MCC (cotton linter) was purchased from Henan Henrui Food Additive Ltd Corp. (Zhengzhou, China).



Figure S1. Values of $\ln \eta_{\rm rel}/c$ and $\eta_{\rm sp}/c$ for dissolved (A) MCC and (B) regenerated cellulose I in cadoxen.

The viscosity average molecular weight of cellulose was measured in cadoxen at 25 °C using a U-shape viscometer, and was calculated by the following equation:¹

$$[\eta] = 3.85 \times 10^{-2} M_{\eta}^{0.76}(\frac{mL}{g})$$

Where η is the intrinsic viscosity, M_{η} is viscosity average molecular weight. Based on equation 1, the viscosity average molecular weight of MCC and regenerated cellulose I are 2.3(0.1)×10⁴ g/mol and 1.9(0.1)×10⁴ g/mol, respectively. The decrease of molecule weight was most possibly caused by the cellulose degradation during high temperature dissolution at 110°C for 50 – 60 min.

(1)

2. Experimental and Flow Chart



Figure S2. Experimental Flow Chart.

MCC Solution Preparation: MCC were vacuum dried at 60 °C until reach a constant weight before use. For pre-activation, 40 g of MCC powder was soaked in 400 ml DI water at 25 °C for 24 hr with stirring, vacuum filtered, and then dried at 60 °C until constant weight. Then, the water treated MCC was activated by DMAc under same conditions. The LiCl•DMAc system was prepared by dissolving 8 g of LiCl into 92 g of DMAc at 60 °C under magnetic stirring until a transparent solution was obtained. For the dissolution of MCC, 90 g LiCl•DMAc was pre-heated to 110 °C, then 10 g pre-activated MCC was slowly added into LiCl•DMAc under vigorous magnetic stirring. The MCC suspension was kept at 110 °C for less than 1 h, then Finally, the battle containing the suspension was put inside a pre-heated oil bath (30 °C) and kept stirring for overnight to obtain a homogeneous MCC solution.

Sol-gel Transition: The prepared MCC solution was sealed in a glass vial, then placed inside oil bath maintained at 60 °C for various times.

Solvent Exchange by Water: Excess amount of DI water was mixed with MCC solution to exchange the solvent from DMAc to water.

The detailed procedures are shown in Figure S2.

Characterizations: The structural parameters of MCC based materials were measured by X-ray diffraction (XRD, Bruker D8 Advance, German) at a 2ϑ scanning speed of 4 °/min. The obtained XRD curves were analyzed by Jade software. The crystalline index (*CI*) of cellulose was calculated by the following equation:²

$$CI(\%) = \frac{I_{002} - I_{AM}}{I_{002}} \times 100\%$$

(2)

where I_{002} is the maximum intensity of the diffraction peak of (002) lattice planes, and IAM is the intensity of amorphous fraction of cellulose (20=18°). The rheology of MCC solution was measured by a rheometer (Anton Paar A-8054 Graz, Austria) using a pair of parallel plates (diameter 25 mm). For temperature ramp scanning, temperature was increased from 25 to 60 °C at a heating rate of 0.5 °C/min. The morphologies of samples were recorded by scanning electron microscope (SEM, JEOL JSM-7001F, Japan) at an acceleration voltage of 5~10 kV after gold sputter coating. Raman spectra were measured by Raman spectroscopy (Model: XploRA, HORIBA Scientific, USA) operating with an excitation laser of 532 nm. The spectra were recorded over the range of 100~400 cm⁻¹ using an exposing time of 10 sec. and 5 times of scanning. The Fourier transform infrared spectra (FTIR) were measured by IR spectroscopy (Bruker Vertex 80v) under vacuum circumstance using KBr pellets.

3. SEM, Raman and FTIR of MCC and the Regenerated Cellulose

From reports ^{3, 4}	Peak positions (cm ⁻¹)	This paper	Peak positions (cm ⁻¹)
Cellulose I	379 (s)	MCC	370 (s)
	435, 457, 518 (m)		428, 449, 508 (m)
	329, 566 (w)	Regenerated Cellulose I	370 (s)
			428, 452, 508 (m)
Cellulose II	352 (s)	Regenerated Cellulose II	345 (s)
	418, 456, 491 (m)		410, 443, 483 (m)
	311, 576 (w)		304 <i>,</i> 569 (w)



Figure S3. SEM of MCC and Regenerated Cellulose.

All regenerated cellulose showed morphologies obviously different from the source MCC. I-R showed an inter-connected fibrillary structure, whereas II-R and A-R showed dense structure.



Figure S4. FTIR spectra of regenerated cellulose I (I-R) and cellulose II (II-R).

From reports ⁵	Peak positions (cm ⁻¹)	This paper	Peak positions (cm ⁻¹)
Cellulose I	1431 (m)	Regenerated Cellulose I (I-R)	1432 (m)
	1114 (m)		1112 (m)
	668 (m)		670 (m)
	1165 (m)		1167 (m)
	1376 (m)		1375 (m)
	894 (w)		894 (w)
Cellulose II	1431 (w)	Regenerated Cellulose II (II-R)	1432 (w)
	1114 (w)		1112 (w)
	668 (w)		670 (w)
	1162 (w)		1163 (w)
	1263 (w)		1261 (w)
	1376 (w)		1375 (w)
	894 (m)		894 (m)

Table S2. IR peaks of regenerated celluloses.

4. Preliminary Identification of the Key Processing Steps



Figure S5. (A) Flow chart of different types of regenerated cellulose undergoing different dissolution conditions; and (B) temperature dependent (G') storage modulus and (G") loss modulus of MCC solutions.

Pre-activated MCCs were dissolved in LiCl•DMAc under different temperature profiles. Both solutions exhibited sol-gel transitions during heating. The MCC dissolved in LiCl•DMAc at a relatively low temperature at 30 °C only regenerated cellulose II even after gelation at 60 °C for 30 days. Whereas, the MCC dissolved at high temperature of 110 °C for about 1 h before at 30 °C regenerated cellulose I after gelation at 60 °C, and the proportion of cellulose I in the regenerated cellulose increased at a longer gelation duration.

5. Thermal Stability of MCC Solution



Fig. S6. (A) G' and G" of c-sol_MCC_A2 as a function of time at various temperatures. (B) Gelation times and G' at the gelation point of MCC solution as a function of temperature.

Time dependent gelation behaviors of MCC solution were measured by isothermal scanning and are shown in Figure S5A. Solution became gelled after certain periods of time. The gelation times at various temperatures are plotted in Figure S5B. It was observed that the gelation time decreased while temperature increased. The sol-gel transition occurred in just few minutes when temperature was higher than 40 °C, for example, the gelation time was 8 min at 45 °C. At above 50 °C, the solution became gelled even during heating process. It was also found that the storage modulus, when storage modulus and loss modulus crossed over and the solution became gelled, became lower at a higher gelation temperature. These results suggest that the stability of MCC solution is improved at a lower temperature.



Fig. S7. Gelation temperature as a function of cellulose concentration.

The gelation temperature of the MCC solutions depended on many factors, including MCC concentration and dissolution procedures. At a lower MCC concentration, the gelation temperature increased. When MCC concentration was higher than certain point (15~20 wt%?), the MCC couldn't be completely dissolved.

6. WAXD and Raman Spectra of the Regenerated Cellulose Along with Gelation Times



Figure S8. XRD curves of regenerated cellulose after various gelation durations at 60 °C.

1.



Figure S9. Raman spectra of regenerated cellulose at various gelation durations. (Δv is Raman shift frequency)

7. Summary of Regenerated Cellulose from Various Solvents from Previous Reports

Solvent	Sol-Gel Transition	Regeneration Process	Cellulose Type	Reports
NMMO aqueous solution	Ν	Solvent Exchange	II	6-12
NaOH/urea/thiourea aqueous solution	Υ		II or Amorphous	13, 14
	N		II	15-19
ionic liquids	N		II	20, 21
	Y		II or Amorphous	22-25
LiCI/DMAc	N		II	26-29

Table S3. Summary of the Regenerated Cellulose Types from Various Solvents.

8. Photos of the Regenerated Cellulose Aerogel and Fiber



Figure S10. Photos of Regenerated Cellulose Aerogel and Fiber.

The aerogel was prepared by soaking pre-gelled MCC/LiCl•DMAc solution in DI water for 2 days, and then the regenerated cellulose hydrogel was freeze-dried to obtain the regenerated cellulose aerogel. For regenerated cellulose fibers, the pre-gelled MCC/LiCl•DMAc solution stored in a 50-ml stainless steel syringe was extruded through a half-inch long blunt tip needle (Inner diameter: 300μ m) at an extrusion rate of 0.3 ml/min using a high torque syringe pump. The cellulose dope was maintained at 60 °C by wrapping the syringe with flexible heating belts. Room temperature DI water was used as coagulation component. Both wet-spinning and dry-jet wet-spinning (2 mm air gap) could be carried out, and their maximum as-spun draw ratios were 8 and 24, respectively. The collected regenerated cellulose fibers were soaked in DI water for 2 days to totally remove the residual solvents, and then were vacuum dried at 60 °C for 1 day.

The cellulose I aerogel was the regenerated cellulose I-R, which had a void fraction of more than 80%. The mechanical testing of the aerogel at a 20 mm gauge length showed a strength of ~150 MPa and Young's Modulus of 6~8 GPa. It is noted that the mechanical property calculation was based on the entire cross-section area of the aerogel, which includes both cellulose and void.

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