Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Improved dissolution of cellulose in quaternary ammonium hydroxide by adjusting temperature

Wei Wei[1], Xiao Wei[1], Guangjun Gou[1], Man Jiang[1], Xiaoling Xu[1], Yong Wang[1], David Hui[2], and Zuowan Zhou[*,1]

1. Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu, Sichuan, 610031, China

2. Department of Mechanical Engineering, University of New Orleans, New Orleans, LA 70148, United States

[A] Preparation of TBAH aq. solution

The 40 wt% TBAH aq. solution (L02809) is supplied from Alfa Aesar Corporation. It is reported that cation of alkali metal, such as Li^+, Na^+ and K^+, can inhibit the dissolution of cellulose.[1] Hence the concentrations of alkali metals are analysed through Atomic Absorption Spectra (AAS) with a Varian SpectrAA 220FS. Lithium is below the detection limit (1.25 mg/L) of this instrument. The concentrations of Sodium and Potassium are 22.0 and 2.53 mg/L respectively, which indicates a low content of alkali metal ions in the received TBAH solution. The effect of alkali metal can be ignorable. A concentrated TBAH solution is obtained through distillation under a reduced pressure of -0.1 MPa at 45 ºC. The concentration of obtained TBAH solution is proportional to the concentration of OH- in solution, which can be confirmed by acidimetry. A desired concentration of TBAH solution is achieved by the attenuation with deionized water.

[B] TEM images of microcrystalline cellulose

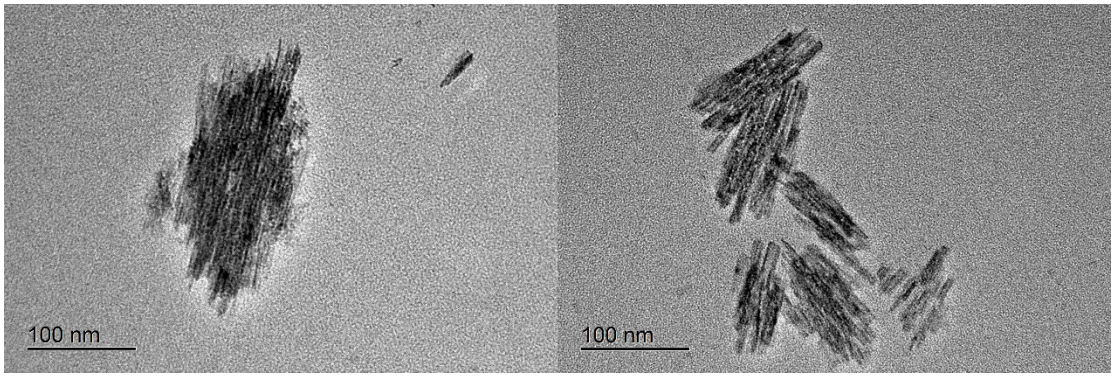

Fig. S1 TEM images of microcrystalline cellulose used in this experiment.

[C] FT-IR result

The Fourier transform infrared (FT-IR) spectra of cellulose before and after dissolution furtherly confirmed the evidence of dissolution of cellulose (Fig. S2). The disappeared absorptions at 3340-3375 and 3270 cm^{-1} were due to the O(3)H···O(5) intramolecular hydrogen bond and O(6)H···O(3) intermolecular hydrogen bond of cellulose respectively,[2] indicating a destruction of original cellulose hydrogen-bonded networks. A peak at 2923 cm^{-1} had formed, corresponding to the $C(6)H_2$ stretching vibration. The peaks at 1430 and 1033 cm^{-1} were attributed to the symmetric bending of $C(6)H_2$ and stretching vibration of C(6)-O in MC respectively, which shifted to 1420 and 1022 cm^{-1} in regenerated cellulose.[3] Those changes involving C(6), O(3), O(5) and O(6) in D-glucose unit of cellulose indicated the transformation of hydrogen bond network associating with O_6.[4-6]

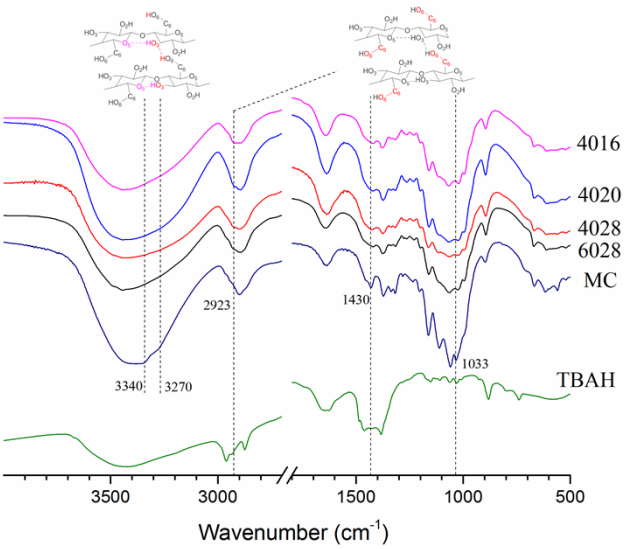

Fig. S2 FT-IR spectra of (TBAH) freeze dried TBAH, (MC) microcrystalline cellulose, cellulose after dissolution in (6028) 60 wt% TBAH aq. solution at 28 ºC, (4028) 40 wt% TBAH aq. solution at 28 ºC, (4020) 40 wt% TBAH aq. solution at 20 ºC and (4016) 40 wt% TBAH aq. solution at 16 ºC, are recorded on a Nicolet 6700 (Thermo Scientific Inc.) with a resolution of 2 cm^{-1} in the range from 4000 to 400 cm^{-1} at room temperature.

[D] DSC curves of 40 wt% and 60 wt% TBAH aq. solution

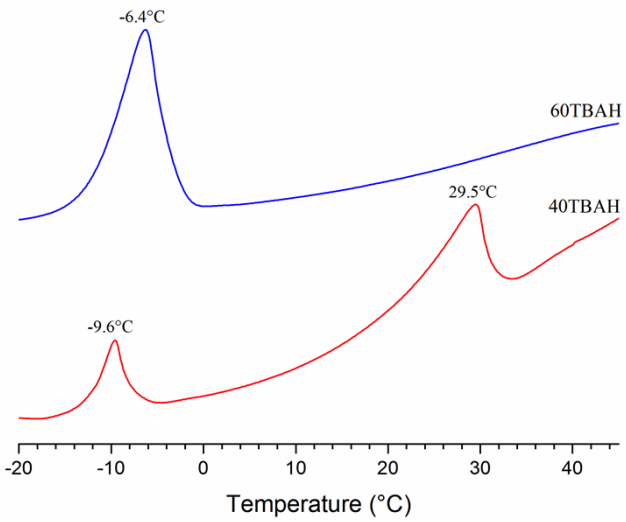

Fig. S3 DSC curves of 40 wt% and 60 wt% TBAH aq. solution. It is recorded on a STA449C (NETZSCH Inc.) with stainless steel crucibles. Samples are pre-cooled to -30 °C and kept for 30 min and then heated to +75 °C with heating rate of 1 °C/min.

[E] TEM images and ED patterns of 40 wt% TBAH aq. solution

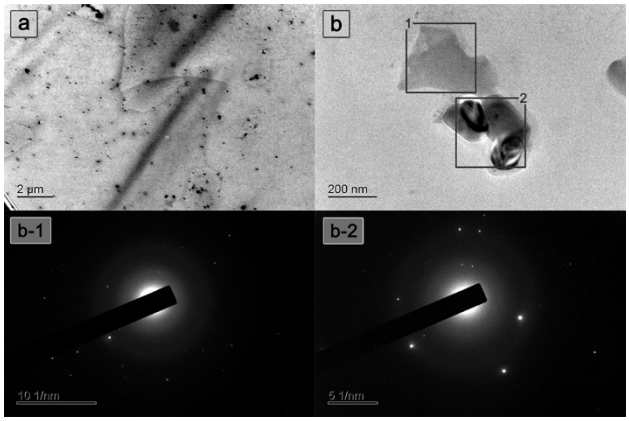

Fig. S4 TEM images of 40 wt% TBAH aq. solution **(a)&(b)** and their ED patterns of crystals **(b-1)&(b-2)**, corresponding to the square-1 and square-2 in picture **(b)** respectively. A thin layer of 40 wt% TBAH aq. solution is suspended on a holey carbon film and dries in air at 19 ºC for about 10 min.

[F] Molecular model of elemental fibril of cellulose I_β

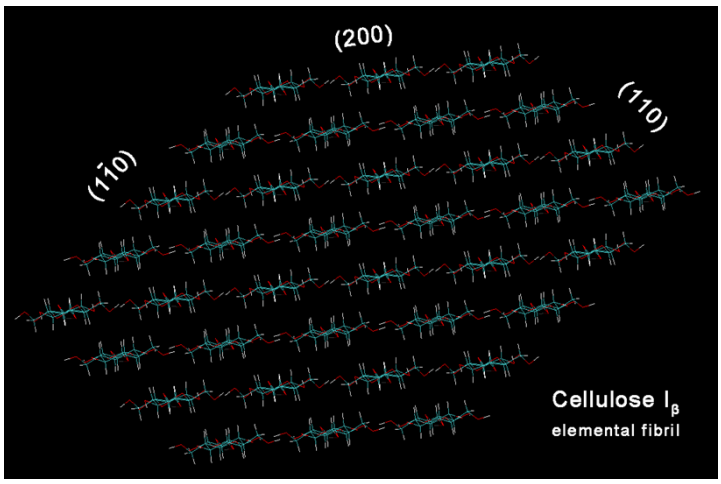

Fig. S5 A molecular model of elemental fibril of cellulose I_β proposed by Himmel.[7] It is built by cellulose-builder.[8]

References

1. T. Ema, T. Komiyama, S. Sunami and T. Sakai, *RSC Advances*, 2014, **4**, 2523-2525.
2. T. Kondo, *Cellulose*, 1997, **4**, 281-292.
3. J. Han, C. Zhou, A. D. French, G. Han and Q. Wu, *Carbohydrate Polymers*, 2013, **94**, 773-781.
4. C. Zhong, C. Wang, F. Huang, H. Jia and P. Wei, *Carbohydr. Polym.*, 2013, **94**, 38-45.

5. H. S. Barud, R. M. N. Assunção, M. A. U. Martines, J. Dexpert-Ghys, R. F. C. Marques, Y. Messaddeq and S. J. L. Ribeiro, *J. Sol-Gel Sci. Technol.*, 2007, **46**, 363-367.
6. L. Zhang, D. Ruan and S. Gao, *J. Polym. Sci., Part B: Polym. Phys.*, 2002, **40**, 1521-1529.
7. S. Ding and M. E. Himmel, *J. Agric. Food Chem.*, 2006, **54**, 597-596.596.
8. T. C. Gomes and M. S. Skaf, *Journal of computational chemistry*, 2012, **33**, 1338-1346.