Preparation of Cellulose Nanofibers/Nanoparticles via Electrospray

Xiaofeng Sui,[1] Jinying Yuan,*[1,2] Weizhong Yuan,[1] and Mi Zhou[1]
[1]*Key Laboratory of Organic Optoelectronics & Molecular Engineering of Ministry of Education,*
Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China
[2]*Key Laboratory of Cellulose and Lignocellulosics Chemistry, Chinese Academy of Sciences,*
Guangzhou 510650, P. R. China

(Received July 23, 2007; CL-070778; E-mail: yuanjy@mail.tsinghua.edu.cn)

Cellulose nanomaterials (100–500 nm in diameter) including fibers and particles have been produced from nonvolatile room-temperature ionic liquid (RTIL) solvent by electrospray. Solvents are extracted from the biopolymer materials after the formation using cosolvent–water. The fundamental role of concentration has been investigated. Structural, morphological, and crystalline phase features were studied by SEM, TGA, and XRD.

Cellulose is the most abundant and renewable biopolymer provided by nature; it is a kind of cheap and nontoxic raw material for various applications.[1] More recently, there is increased use of cellulose nanomaterials in developing new and inexpensive biodegradable materials owing to low weight, low cost, and lack of abrasiveness during processing.[2] Cellulose nanomaterials are used for the encapsulation of functional species in the cosmetics, nutrition, pesticide, and food industries. Acid hydrolysis of original cellulose has been traditionally used to produce cellulose nanomaterials. However, this method has some disadvantages especially the pollution. With increasing governmental regulations in industries, the need to implement "green" processes for preventing the pollution is becoming increasingly important.

The electrospray is one of the important tools of nanotechnology.[3] This technique, applied to polymer solutions above a critical value, bears nanofibers, and the process is called electrospinning.[4] By changing the concentration of polymer solution, both nanofibers and nanoparticles can be easily produced.

Little research has been done on the use of cellulose as a raw material within electrospray.[5] The processing of cellulose is restricted by its limited solubility in common solvents and its inability to melt because of its numerous intermolecular and intramolecular hydrogen bonding.

Now room-temperature ionic liquids (RTILs) have proven to be promising solvent system for cellulose.[6] RTILs are considered as desirable green solvents for a wide range of separation and as reaction media for processes.[7]

In this work, we have produced well-defined nanomaterials from cellulose solution in 1-allyl-3-methylimidazolium chloride (AMIMCl), a kind of RTILs. Since AMIMCl is a low-melting salt having very low vapor pressure, it is impossible to evaporate it. As AMIMCl was miscible with water in any ratio, the regenerated cellulose nanomaterials were easily obtained by coagulation in water. So the solvent is removed from cellulose by applying coagulation with water before further investigation.

The method needs four steps: Synthesis of AMIMCl; Preparation of a cellulose/AMIMCl/DMF solution; Collection of cellulose nanomaterials; Recycling of AMIMCl.

The AMIMCl was synthesized according to the literatures.[8] Typically, 1-methylimidazole and allyl chloride in a molar ratio 1:1.25 were added to a round-bottomed flask fitted with a reflux condenser for 8 h at 55 °C with stirring. The unreacted reagents were removed by vacuum distillation, and the obtained product is slightly amber.

The wood pulp (α-cellulose 94.9%) was used as the original cellulose material. The viscosity-average degree of polymerization (DP) measured using an Ubbelohde viscometer in cupriethylenediamine hydroxide solution was 650. Briefly, a 4% (w/w) cellulose solution was prepared by heating 24 g of AMIMCl, addition of 1 g of cellulose, and vortex mixing to afford a clear yellow solution. The temperature was kept below 80 °C to avoid degradation. The solution was too viscous for electrospray at the room temperature. So DMF was added as a diluent into the cellulose solution.

Homogeneous cellulose solution was subjected to electrospray at room temperature. A 10-mL portion of the solution was transferred to a syringe, and a high voltage 30 kV was applied to the needle of the syringe, to overcome the surface tension of the solution by electrostatic forces. Charged materials were sprayed from the tip and discharged on an aluminum sheet placed beneath a water bath collector. The distance from the needle to the coagulation bath surface was 15 cm.

After the regeneration of cellulose nanomaterials, the residual AMIMCl in the coagulation bath was recovered by simply reducing the pressure and subsequently distilling to remove water and DMF.

To remove the AMIMCl from regenerated cellulose nanomaterials, the samples were first soaked in distilled water overnight and then washed with distilled water until no Cl^- ions were detectable by the $AgNO_3$ test. The result is confirmed by the FT-IR results. It can be seen that the spectra of original cellulose and regenerated cellulose nanomaterials are quite similar, and no new peaks appear in the cellulose nanomaterials, indicating that AMIMCl completely disappears after the coagulation.

Figure 1 shows various SEM images of the resulting cellulose nanomaterials. As shown in Figures 1a–1d, the diameter of the nanofibers was around 500–100 nm. The concentrations were 3.5–2%. There was likely a slight increase in fiber diameter with increasing cellulose concentration. Some fibers sticking together during the process of removing AMIMCl were not quickly separated. With the cellulose concentration decreased to 1%, the concentration of the polymer was below the "nonfiber forming concentration" and the nanofibers totally disappeared. Figures 1e and 1f show the morphologies of the cellulose nanoparticles. In particular, the complete disappearance took place at a concentration between 2 and 1%. The particles do not have smooth surfaces and spherical structure because the samples shrank considerably when they were allowed to air dry.

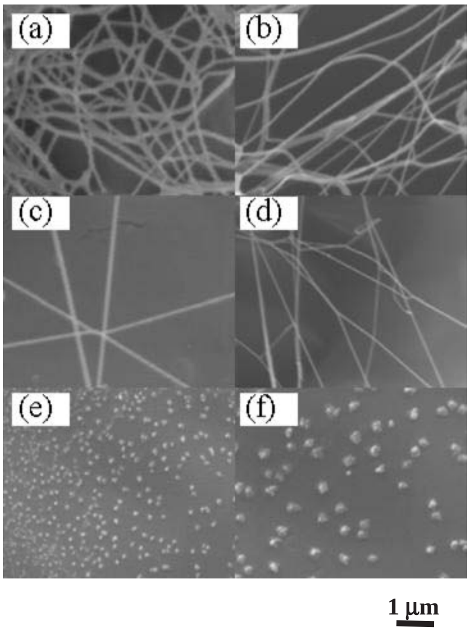

Figure 1. SEM images of cellulose nanomaterials prepared with various cellulose concentrations (w/w/w, cellulose/RTIL/DMF): (a) 3.5/84/12.5%; (b) 3/72/25%; (c) 2.5/56/41.5%; (d) 2/48/50%; (e) 1/24/75%; (f) 1/24/75%.

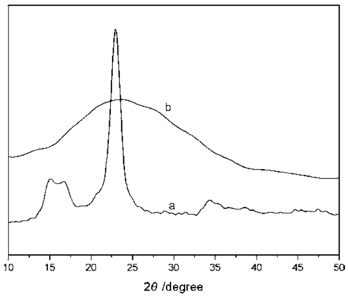

Figure 2. XRD patterns of (a) original cellulose and (b) regenerate cellulose nanomaterials (sample showed in Figure 1a).

There was also a change in crystalline structure of the cellulose before and after electrospray. The original cellulose presents the crystal form of cellulose I. The electrosprayed nanomaterials display a different one, mostly an amorphous phase, as seen in Figure 2. This indicates that the timescale associated with electrospray is shorter than that for cellulose crystallization.[5b]

Figure 3 shows thermal behavior of cellulose nanomaterials. Rapid decomposition in a narrow temperature range from 350 to 360 °C is observed for original cellulose. The regenerated cellulose nanomaterials via electrospray exhibit a lower onset temperature for decomposition but give a higher char yield on pyrolysis, indicated by the high residual masses after the decomposition step.

In conclusion, we have obtained cellulose nanomaterials including fibers and particles via electrospray in RTIL-AMIMCl without its derivatization. The solution was very viscous even at cellulose concentration of only 4%; DMF was added as a diluent to form different concentrations. The fundamental role of concentration for the morphologies has been investigated. SEM images show the formation of nanomaterials. XRD studies reveal that the cellulose nanomaterials obtained are mostly amorphous. The application of electrospray on cellulose/RTIL solution is a relatively simple and environment-friendly way to make various cellulose nanomaterials which will be useful in biomedical applications.

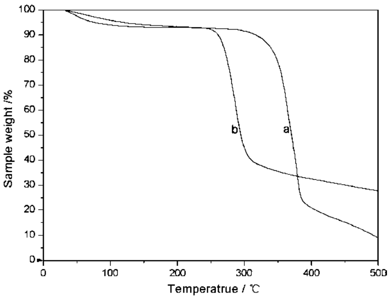

Figure 3. TGA curves of (a) original cellulose and (b) regenerate cellulose nanomaterials (sample showed in Figure 1a).

This work was supported by National Natural Science Foundation of China (Nos. 20574042, 50373023, and 50433020).

References

1 D. Klemm, B. Heublein, H. P. Fink, A. Bohn, *Angew. Chem., Int. Ed.* **2005**, *44*, 3358.

2 a) X. Cao, H. Dong, C. M. Li, *Biomacromolecules* **2007**, *8*, 899. b) M. M. D. S. Lima, R. Borsali, *Macromol. Rapid Commun.* **2004**, *25*, 771. c) M. A. S. A. Samir, F. Alloin, A. Dufresne, *Biomacromolecules* **2005**, *6*, 612. d) A. Sturcova, G. R. Davies, S. J. Eichhorn, *Biomacromolecules* **2005**, *6*, 1055.

3 a) D. Fantini, M. Zanetti, L. Costa, *Macromol. Rapid Commun.* **2006**, *27*, 2038. b) A. Jaworek, *J. Mater. Sci.* **2007**, *42*, 266. c) O. V. Salata, *Curr. Nanosci.* **2005**, *1*, 25.

4 a) N. Ashammakhi, A. Ndreu, A. Piras, L. Nikkola, T. Sindelar, H. Ylikauppila, A. Harlin, E. Chiellini, V. Hasirci, H. Redl, *J. Nanosci. Nanotechnol.* **2006**, *6*, 2693. b) W. E. Teo, S. Ramakrishna, *Nanotechnology* **2006**, *17*, R89. c) D. Li, Y. N. Xia, *Adv. Mater.* **2004**, *16*, 1151. d) M. G. McKee, J. M. Layman, M. P. Cashion, T. E. Long, *Science* **2006**, *311*, 353. e) R. Hao, J. Yuan, Q. Peng, *Chem. Lett.* **2006**, *35*, 1248. f) B. Duan, X. Yuan, Y. Zhu, Y. Zhang, X. Li, Y. Zhang, K. Yao, *Eur. Polym. J.* **2006**, *42*, 2013.

5 a) G. Viswanathan, S. Murugesan, V. Pushparaj, O. Nalamasu, P. M. Ajayan, R. J. Linhardt, *Biomacromolecules* **2006**, *7*, 415. b) C.-W. Kim, M. W. Frey, M. Marquez, Y. L. Joo, *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 1673. c) P. Kulpinski, *J. Appl. Polym. Sci.* **2005**, *98*, 1855. d) C.-W. Kim, D.-S. Kim, S.-Y. Kang, M. Marquez, Y. L. Joo, *Polymer* **2006**, *47*, 5097.

6 a) R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers, *J. Am. Chem. Soc.* **2002**, *124*, 4974. b) S. Zhu, Y. Wu, Q. Chen, Z. Yu, C. Wang, S. Jin, Y. Ding, G. Wu, *Green Chem.* **2006**, *8*, 325.

7 T. Welton, *Chem. Rev.* **1999**, *99*, 2071.

8 H. Zhang, J. Wu, J. Zhang, J. He, *Macromolecules* **2005**, *38*, 8272.