

Preparation and Liquid Crystalline Properties of Spherical Cellulose Nanocrystals

Neng Wang,[†] Enyong Ding,[†] and Rongshi Cheng^{*,†,‡}

College of Material Science and Engineering, South China University of Technology, Guangzhou 510640, China, and Key Laboratory of Mesoscopic Materials Science, College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

Received March 11, 2007. In Final Form: November 13, 2007

A novel kind of spherical cellulose nanocrystal (SCNC) suspension was prepared by hydrolysis of microcrystalline cellulose with a mixture of sulfuric acid and hydrochloric acid under ultrasonic treatment. The mechanism of SCNC formation and the liquid crystalline properties of their suspensions were investigated. A suspension of spherical particles was usually inclined to form crystallization colloids rather than liquid crystals at high concentration. However, a SCNC suspension with high polydispersity (49%) was observed to form the liquid crystalline phase, and the liquid crystalline textures changed with increasing concentration. This observation offers an approach to the liquid crystal formation of highly polydisperse spherical nanoparticles.

Introduction

Stable suspensions of rodlike cellulose nanocrystals can be prepared by acid hydrolysis of native cellulose with sulfuric acid.^{1–5} This rodlike cellulose suspension,^{3,4,6} like many other rodlike particles,^{7–10} forms the liquid crystalline phase above a critical concentration and usually shows the chiral nematic texture. Suspensions of rodlike particles can form the liquid crystalline phase based on the excluded volume effect at high volume concentration.^{10–13} Compared with the rodlike particles, suspensions of spherical particles above the critical concentration¹⁴ incline toward the formation of crystallization colloids rather than the liquid crystalline phase due to their symmetrical shape. In addition, particles with high polydispersity were supposed to suppress the ordered structure formation in both rodlike and spherical particle systems due to the orientation of the particles being broken down by their polydispersity. On the contrary, research about polydisperse nanoparticles^{15–17} in recent years revealed the surprising observation that the polydisperse nano-

particles could form not only an ordered structure such as the liquid crystalline phase but also the coexistence of the multiphase. These findings offered access of the high polydisperse nanoparticles to diverse nanostructure materials. Research about polydisperse systems mostly focused on nonspherical nanoparticles; however, the formation of ordered structures in polydisperse spherical nanoparticle suspensions has not been reported to our knowledge.

In this letter, a novel kind of spherical cellulose nanocrystal (SCNC) suspension was prepared by using a mixture of sulfuric and hydrochloric acids to hydrolyze the microcrystalline cellulose under ultrasonic treatment. The polydispersity of the SCNC particles was up to 49%, and their suspension was observed to form the liquid crystalline phase when the solid content was above 3.9% (w/w). Our observations offered an approach to the liquid crystalline formation of spherical nanoparticles, and will advance the understanding of the mechanism of liquid crystal formation.

Experimental Section

Sulfuric acid (98% w/w), hydrochloric acid (37% w/w), and distilled water were mixed at a ratio of 3:1:6 (v/v) to obtain the mixed acid. Commercial microcrystalline cellulose (average particle size: 20 μm) was hydrolyzed by this mixed acid under ultrasonic treatment at 50 Hz (NP-B-33-400, New Power, China) for 10 h to prepare the SCNCs. After hydrolysis, the product was allowed to stand at room temperature to cool and was followed by thorough removal of the acid by repeated washing, centrifugation, and dialysis with distilled water. When the system pH reached 3–5, the supernatant became turbid and was collected to obtain the final SCNC suspension.

The final suspension was transferred into a liquid crystalline cell with a spacer (0.3 mm thick) and then was observed by using an optical polarizing microscope (ORTHOPLAN-POL, Leitz, Germany). The shape and size of the cellulose nanocrystals were investigated by transmission electron microscopy (TEM, FEI-Tecna 12, FEI) at 100 kV and by atomic force microscopy (AFM, SPI3800N, Seiko Instruments Inc.) in noncontact mode. The crystal structures of the SCNCs and microcrystalline cellulose were characterized by using an X-ray diffractometer (D/MAX-1200, Rigaku, Japan).

(17) Vroege, G. J.; Thies-Weesie, D. M. E.; Petukhov, A. V.; Lemaire, B. J.; Davidson, P. *Adv. Mater.* **2006**, *18*, 2565–2568.

* To whom correspondence should be addressed. Telephone: 086-25-83597355. Fax: 086-25-83317761. E-mail: rscheng@nju.edu.cn.

[†] South China University of Technology.

[‡] Nanjing University.

(1) Beck-Candanedo, S.; Roman, M.; Gray, D. G. *Biomacromolecules* **2005**, *6*, 1048–1054.

(2) Dong, X. M.; Revol, J.-F.; Gray, D. G. *Cellulose* **1998**, *5*, 19–32.

(3) Dong, X. M.; Kimura, T.; Revol, J.-F.; Gray, D. G. *Langmuir* **1996**, *12*, 2076–2082.

(4) Revol, J.-F.; Bradford, H.; Giasson, J.; Marchessault, R. H.; Gray, D. G. *Int. J. Biol. Macromol.* **1992**, *14*, 170–172.

(5) Marchessault, R. H.; Morehead, F. F.; Walter, N. M. *Nature* **1959**, *184*, 632–633.

(6) Revol, J.-F.; Godbout, L.; Dong, X. M.; Gray, D. G.; Chanzy, H.; Maret, G. *Liq. Cryst.* **1994**, *16*, 127–134.

(7) Revol, J.-F.; Marchessault, R. H. *Int. J. Biol. Macromol.* **1993**, *15*, 329–335.

(8) Strzelecka, T. E.; Davidson, M. W.; Rill, R. L. *Nature* **1988**, *331*, 457–460.

(9) Buining, P. A.; Philipse, A. P.; Lekkerkerker, H. N. W. *Langmuir* **1994**, *10*, 2106–2114.

(10) Folda, T.; Hoffmann, H.; Chanzy, H.; Smith, P. *Nature* **1988**, *333*, 55–56.

(11) Gabriel, J.-C. P.; Davidson, P. *Adv. Mater.* **2000**, *12*, 9–20.

(12) Gabriel, J.-C. P.; Davidson, P. *Top. Curr. Chem.* **2003**, *226*, 119–172.

(13) Li, L.-S.; Walda, J.; Manna, L.; Alivisatos, A. P. *Nano Lett.* **2002**, *2*, 557–560.

(14) Pursey, P. N.; van Megen, W. *Nature* **1986**, *320*, 340–342.

(15) van der Kooij, F. M.; Kassapidou, K.; Lekkerkerker, H. N. W. *Nature* **2000**, *406*, 868–871.

(16) van der Kooij, F. M.; van der Beek, D.; Lekkerkerker, H. N. W. *J. Phys. Chem. B* **2001**, *105*, 1696–1700.

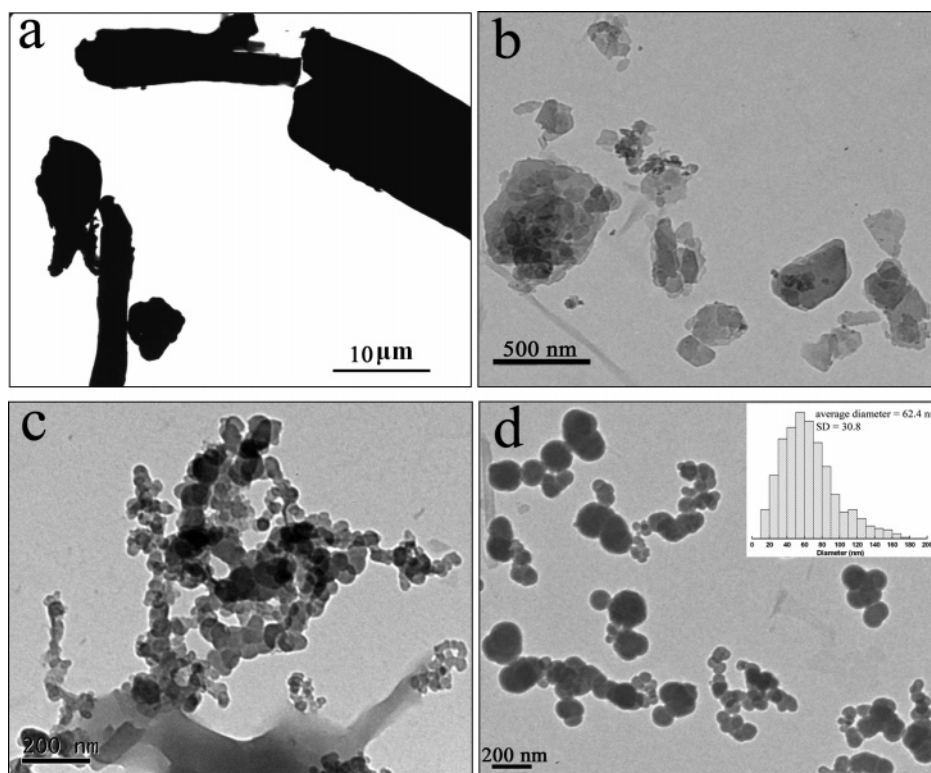


Figure 1. TEM images of microcrystalline cellulose (a) and the products hydrolyzed by mixed acid under ultrasonic treatment after (b) 2 h, (c) 4 h, and (d) 10 h. The inserted diagram corresponds to the size distribution of the SCNC particles from the TEM images.

Results and Discussion

In previous works, sulfuric acid (64 wt %) was usually used to hydrolyze the native cellulose materials for preparation of the rodlike cellulose nanocrystals. These nanocrystals usually had a higher degree of crystallinity than that of native cellulose. The explanation was that the hydrolysis reaction occurred mostly at the amorphous regions of native cellulose, and subsequently only the domain with a perfect crystalline structure remained after hydrolysis. In previous works, only the rodlike cellulose nanocrystals were reported as the hydrolysis product which is probably attributed to the hydrolysis reaction that was undertaken under the strong acidic conditions. However, our research found that if a mixture of sulfuric and hydrochloric acid with an appropriate composition was used to hydrolyze the native cellulose materials under ultrasonic treatment, a novel kind of cellulose particles, that is, the spherical cellulose nanocrystals (SCNCs), will be obtained.

In the present paper, SCNCs were prepared by hydrolysis of microcrystalline cellulose with a mixed acid composed of sulfuric acid, hydrochloric acid, and distilled water at a ratio of 3:1:6. After a given time, small amounts of the hydrolysis products were taken out and immediately diluted with distilled water for examination. The shape and size of the hydrolysis products were characterized by TEM. Their images are shown in Figure 1.

The formation process of SCNCs is clearly shown in Figure 1. The microcrystalline cellulose particles as the starting native cellulose materials were in irregular shapes, and their average size was about 20 μm . After being hydrolyzed for 2 h, the microcrystalline cellulose was damaged to sub-micrometer cellulose fragments with various shapes (Figure 1b). Subsequently, it was clearly observed that some SCNC particles began to form at the edges of the sub-micrometer fragments (Figure 1c). As the reaction time increased, the SCNC particles continuously formed, accompanied by a decrease in the mi-

crofragments. When the hydrolysis time was more than 10 h, the regular SCNC particles were basically obtained while the microfragments completely vanished (Figure 1d). In contrast with that for the hydrolysis of native cellulose in the presence of sulfuric acid for preparing rodlike cellulose nanocrystals, the reaction time was usually less than 1 h. The formation of SCNCs was ascribed to the combination of the ultrasonic treatment and mild acid concentration.

On the basis of a series of experiments, it was recognized that, in the absence of ultrasonic treatment and the mixed acid in an appropriate ratio, SCNCs could not be obtained. During preparation of the rodlike cellulose, the hydrolysis reaction occurred from the surface to the inner amorphous region. In contrast, the acid molecules quickly penetrated into the inner amorphous region of the cellulose fibrils due to the ultrasonic treatment during SCNC preparation. Therefore, the hydrolysis reaction simultaneously occurred at the surface and in the inner amorphous regions of microcrystalline cellulose. This caused the microcrystalline cellulose to first hydrolyze to the sub-micrometer fragments, instead of directly obtaining the nanocrystalline cellulose. Moreover, because the mixed acid concentration was mild, the dissolving capability of the cellulose fragments was very limited. So, the sub-micrometer fragments were further hydrolyzed by the mixed acid to form the SCNC particles gradually. From the size distribution diagram of the SCNCs, the dimension of the SCNCs was distributed in the range of 10–180 nm, mostly in the range of 20–90 nm. The average diameter was 62.4 nm, and the polydispersity¹⁸ (standard deviation of the particle size distribution by the average size) reached up to 49%.

AFM topography images of SCNCs are shown in Figure 2. SCNC particles showed some aggregations in the whole AFM images (Figure 2a and b) which are probably due to the water

(18) Fasolo, M.; Sollich, P. *Phys. Rev. Lett.* **2003**, *91*, 068301.

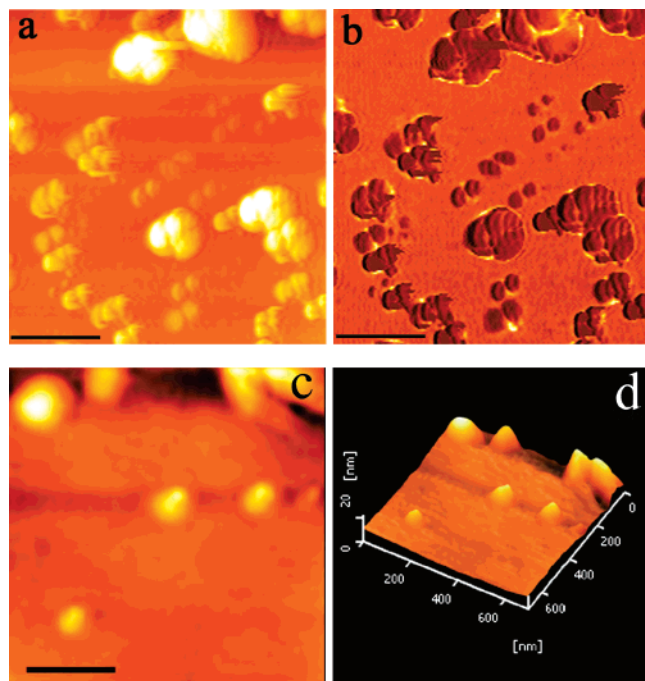


Figure 2. Noncontact mode AFM images of spherical cellulose nanocrystals immobilized on quartz surface: (a) overall AFM image and (b) corresponding phase image, and (c) magnified topography image of a selected region and (d) corresponding three-dimensional image rotated 30°. All of the scale bars represent 200 nm.

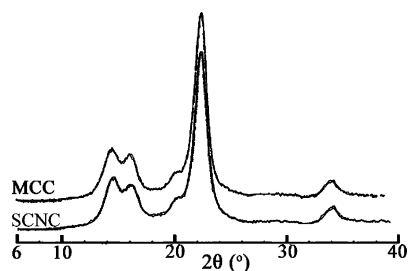


Figure 3. X-ray diffraction diagram of microcrystalline cellulose (MCC) and spherical cellulose nanocrystals (SCNC).

evaporation. However, some isolated individual particles were clearly observed, especially in the AFM phase image (Figure 2b). From the magnified image of the SCNCs and the corresponding three-dimensional image, it was clearly recognized that the SCNC particles indeed were the regular spherical particles. The particle size of the SCNCs mostly distributed in the range of 20–90 nm, which is similar to the results from the TEM images.

The X-ray diffraction patterns of SCNCs and commercial microcrystalline cellulose are shown in Figure 3. Surprisingly, their diffraction patterns were almost identical. The original crystalline structure of the cellulose fibril was essentially maintained in the SCNC particles. In contrast to the rodlike cellulose nanocrystals with higher crystallinity after hydrolysis, the crystallinity of the SCNCs was slightly lower than that of microcrystalline cellulose. This observation meant that during SCNC formation the hydrolysis reaction not only occurred at the amorphous region of cellulose fibrils but also occurred at their crystalline region, or else the SCNCs should have a higher crystallinity than that of cellulose fibrils.

Suspensions of SCNCs with different concentrations were prepared by exact dilution with deionized water from a stock suspension. The stock was prepared by evaporating the final suspension of SCNCs at room temperature by desiccation in an

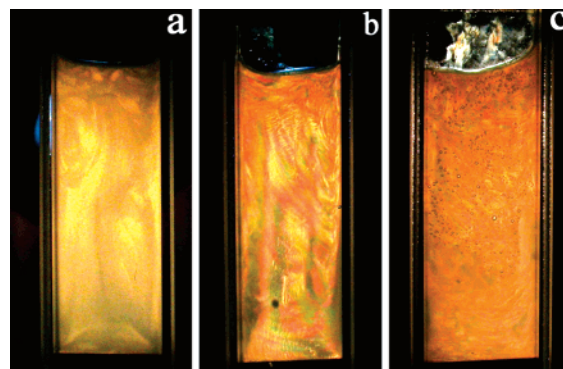


Figure 4. Birefringent patterns of spherical cellulose nanocrystal suspensions (a) at 2.0%, just after injection, (b) at 4.5%, and (c) at 7.1% at rest 3 days after injection. All suspensions were photographed between the crossed Nichols, and the sample cell is 10 mm wide and 1.0 mm thick.

oven. The solid content of the stock suspension was determined by drying it to a constant weight at 80 °C.

The birefringent patterns of SCNC suspensions at various concentrations are shown in Figure 4. From the birefringent patterns, it was observed that the phase behaviors of spherical particle suspensions also possessed some particularities as those of rod-like particles. At lower solid content (<wt 3.0%), the SCNC suspension was isotropic and showed the flow birefringence pattern just after injection and then the pattern vanished after standing at rest (Figure 4a). As the concentration exceeded 4.5%, the suspension showed the remarkable chromatic birefringence at rest (Figure 4b and c).

Photos of the liquid crystalline textures of SCNC suspensions obtained by using a polarizing optical microscope are shown in Figure 5. When the solid content was above wt 3.9%, the suspension began to show the liquid crystalline phase (Figure 5a). At 3.9% concentration, the SCNC suspension showed some birefringent domains. When the polarizer and the analyzer were rotated, some of the birefringent domains turned from bright to dark or dark to bright. As shown in Figure 5b, the suspension at wt 4.5% showed the chromatic color and was observed to have a banded texture. At high solid content (wt 7.1%), a crosshatch pattern was observed (Figure 5c). This pattern closely resembled the “frozen in shear structure” in the “birefringent glassy phase”,^{9,19} and it was remarkably different from the fingerprint pattern of the rodlike cellulose suspension.^{4,20} The crosshatch pattern was stable for at least 2 months, that is, it was not a transient state. In addition, the high content SCNC suspension (7.1%) still could flow even after standing for more than 1 month; that is, the suspension did not form a gel or crystallization colloid and was a true “glassy phase”.

According to Onsager’s theory,²¹ the liquid crystalline phase formation of the rodlike particles is attributed to the repulsive force of interparticles and their corresponding liquid crystal textures strongly depend on the anisotropy of the particles. The liquid crystalline phases of the rodlike suspensions are thermodynamically stable, arising from gaining translation entropy that overrides the loss of orientation entropy associated with the particle alignment.²² In light of this theory, it is difficult for a suspension of spherical particles to form the liquid crystalline phase due to their symmetrical shape and thermodynamically

(19) Araki, J.; Wada, M.; Kuga, S.; Okano, T. *Langmuir* **2000**, *16*, 2413–2415.

(20) Revol, J.-F.; Godbout, L.; Dong, X. M.; Gray, D. G.; Chanzy, H.; Maret, G. *Liq. Cryst.* **1994**, *16*, 127–134.

(21) Onsager, L. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 627–659.

(22) Jana, N. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1536–1540.

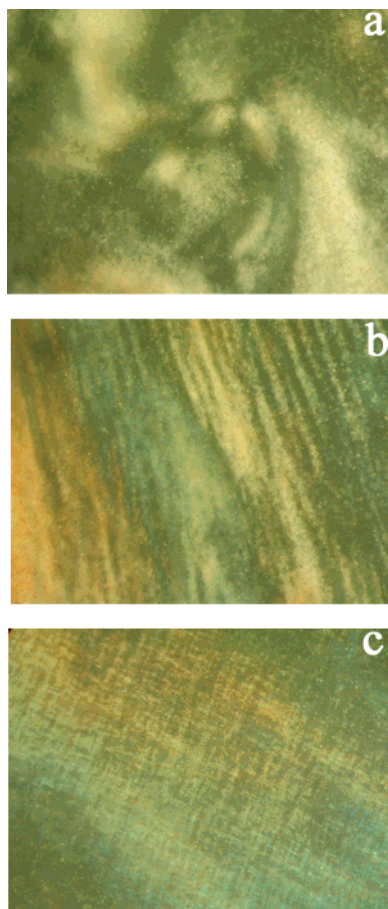


Figure 5. Polarization of the micrographs of spherical cellulose nanocrystals. Cellulose solid content was at (a) 3.9%, (b) 4.5%, and (c) 7.1%. The liquid crystalline cell is 0.2 mm thick.

instability. However, in this experiment, we observed liquid crystalline phase formation in the highly polydisperse (49%) SCNC suspension. This is the first instance, to our knowledge, of the formation of the liquid crystalline phase in a suspension of spherical nanoparticles.

Since the polydispersity of the SCNCs studied in this experiment was up to 49%, which was remarkably higher than the terminal polydispersity,^{23–25} crystallization did not occur in the suspensions of SCNCs. Therefore, this behavior is because the SCNC suspension had a chance to arrange the particles to

form the ordered structure. On the other hand, during the hydrolysis process, the sulfate groups were inevitably introduced into the surfaces^{2,26} of the SCNCs. The amount of sulfate groups in the SCNC suspensions was determined as 22 mmol/kg by conductometric titration.²⁷ The presence of sulfate groups will inevitably change the effective particle shape²⁸ of the SCNCs. According to these experimental results at present, we deduced that the combination of the high polydispersity and the presence of sulfate groups should play an important role in liquid crystalline formation in SCNC suspensions. However, the observation is that polydisperse charged spherical nanoparticles at low ionic strengths form an ordered phase whose nature is currently unknown.

Conclusion

A novel kind of spherical cellulose nanocrystal (SCNC) suspension was prepared by hydrolysis of microcrystalline cellulose with mixed acid under ultrasonic treatment. The formation of SCNCs was attributed to the combined action of the mixed acid and the ultrasonic treatment. The polydispersity of the SCNC suspension was high up to 49% according to the distribution obtained by TEM. When the solid content was above wt 3.9%, the formation of a liquid crystalline phase was observed in the SCNC suspension. **To our knowledge**, this is the first report of such behavior in a spherical nanoparticle suspension. This observation offered an access to the liquid crystal formation of highly polydisperse nanoparticles and will be in favor of further understanding of the mechanism of liquid crystalline formation. With the various concentrations, the suspension showed the different colors and the liquid crystalline structure. These characters might give rise to potential applications as functional materials.

Acknowledgment. We gratefully acknowledge the help of Dr Z. Y. Chen for making the AFM pictures and Dr J. Ma for performing the polarizing optical microscope experiments.

Supporting Information Available: Complete preparation method of spherical cellulose nanocrystals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

LA702923W

(23) Bolhuis, P. G.; Kofke, D. A. *Phys. Rev. E* **1996**, *54*, 634–643.
 (24) Chaudhuri, P.; Karmakar, S.; Dasgupta, C.; Krishnamurthy, H. R.; Sood, A. K. *Phys. Rev. Lett.* **2005**, *95*, 248301.

(25) Kofke, D. A.; Bolhuis, P. G. *Phys. Rev. E* **1999**, *59*, 618–622.
 (26) Dong, X. M.; Gray, D. G. *Langmuir* **1997**, *13*, 2404–2409.
 (27) Araki, J.; Wada, M.; Kuga, S.; Okano, T. *Colloids Surf., A* **1998**, *142*, 75–82.
 (28) Orts, W. J.; Godbout, L.; Marchessault, R. H.; Revol, J.-F. *Macromolecules* **1998**, *31*, 5717–5725.