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ORIGINAL PAPER

Construction of cellulose/ZnO composite microspheres in NaOH/zinc nitrate aqueous solution via one-step method

Sen Wang · Yiwen Yang · Ang Lu · Lina Zhang

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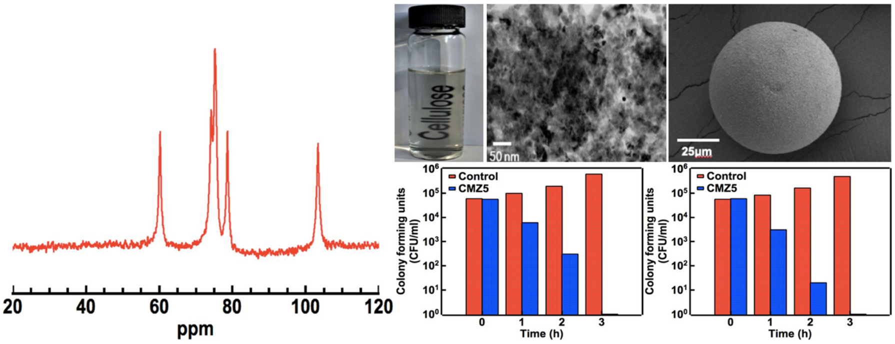
Abstract In the present paper, NaOH/zinc nitrate aqueous solution was successfully developed as a novel solvent to dissolve cellulose from cotton linter pulp via cooling. The ^{13}C NMR result proved that the dissolution was a physical process without derivatization. Dynamic light scattering, viscometry and rheology measurements were used to investigate the solution properties of cellulose in different concentration regimes. The rheological test results proved that cellulose dissolved in NaOH/zinc nitrate solution was relatively stable at room temperature, which benefits commercial scale production of cellulose materials. Interestingly, single cellulose chains tended to aggregate in the solution, which facilitated their self-assembly into regenerated cellulose microspheres (CM). During the regeneration, the precursor zinc salts in the solution precipitated as ZnO nanoparticles, which were further embedded in the porous structure of CM. Thus, composite microspheres (CMZ) consisted of cellulose and ZnO with an average size of about 12 nm were facilely fabricated via one-step method, and mean diameter of the CMZ microspheres was 60 μm. The results of FT-IR, scanning electron microscope, X-ray diffraction, and thermo gravimetric analysis demonstrated that ZnO having hexagonal wurtzite structure were evenly embedded in the cellulose microspheres, leading to the formation of cellulose/ZnO composite. Antimicrobial tests indicated that cellulose/ZnO microspheres displayed good antibacterial properties. This work provided new pathway to utilize a water-based and eco-friendly solvent of cellulose to construct environmentally friendly and sustainable organic/inorganic hybrid materials.

S. Wang · Y. Yang · A. Lu (✉) · L. Zhang (✉)
College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China
e-mail: anglu@whu.edu.cn

L. Zhang
e-mail: zhangln@whu.edu.cn

Graphical abstract



Keywords Cellulose solvent · ZnO · Microspheres · Antibacterial properties

Introduction

In recent years, the plastic waste has been classified as hazardous in many countries in terms of the fact that plastics can not only physically harm the wildlife but also be chemically detrimental in some contexts (Rochman et al. 2013). More severely, the plastic waste has spread from continents to ocean, which is crippling and depleting more than 1300 species (Bergmann et al. 2017). Yet, only 14% of all plastic waste is collected for recycling after use, and vast quantities escape into the environment (MacArthur 2017). Human beings must urgently act on the crisis of plastic waste before this environment issue gets out of hand and becomes a fatal threaten to earth. Thus, in 2017, more than 200 countries signed a resolution to address the marine litter and micro-plastics at the United Nation Environment Assembly, in hope of restraining the deterioration of current situation and boosting the economy transition from C\H to C\H\O. Moreover, the trend of science and technology is tending towards environmentally friendly materials, renewable resources and energy, as well as sustainable techniques and processes (Wang et al. 2016). Sustainable polymers derived from renewable biomass resources have been attracted much attentions. It is noted that cellulose is the most copious natural raw material on earth, and is considered as a kind of promising biomass. However, the numerous hydrogen bonds made the dissolution of cellulose a bottleneck for its wide utilization. In the past decades, various solvents have been developed to dissolute cellulose such as the LiCl/DMAc (McCormick et al. 1985; Morgenstern and Kammer 1996; Matsumoto et al. 2001) *N*-methylmorpholine-*N*-oxide (NMMO) (Fink et al. 2001; Rosenau et al. 2001, 2002) ionic liquids (Swatloski et al. 2002; Abe et al. 2015; Chang et al. 2015) and NaOH aqueous solution (Isogai and Atalla 1998). In our laboratory, alkali/urea (or thiourea) aqueous solution have been used as novel solvent to disolve cellulose solution with high molecular weight and good stability (Cai and Zhang 2005; Wang et al. 2017b) and a lot of new cellulose materials have been fabricated, showing applications in various fields.

It is well-known that ZnO is a very important and promising semiconductor material, which is widely used as optical devices, UV blocking, photocatalysis, sensors etc. (Daneshvar et al. 2004; Özgür et al. 2005). In recent years, there is increasing interest for the combination of ZnO and cellulosic materials for various applications. For example, ZnO–cellulose composite fibers could be fabricated by a simple mixture using high energy mixer/mill under high pressure for UV sensing (Gimenez et al. 2013). Unfortunately, the simple mechanical mixing could not induce nano-scale interaction of ZnO and cellulose matrix, which led to low ZnO loading and relatively poor mechanical properties. The composite fibers were also prepared by modification of cellulose fibers with saccharide modified ZnO for the antibody immobilization. It had two steps, in which the ZnO were firstly synthesized in the presence of other saccharides as capping agents for stabilization of the growth of inorganic nanoparticles (Khatri et al. 2014). Hydrothermal synthesis of ZnO was the most common method, by which the cellulose fibers, cotton fabrics or filter papers were immersed into the precursor solution for the ZnO to grow on the matrix (Gonçalves et al. 2009; Kumar et al. 2011; John et al. 2011; Costa et al. 2013; Katepetch et al. 2013). The reaction usually needs a high temperature or ultrasonic and several hours to allow the full conversion of zinc salts to ZnO. To the best of our knowledge, the current methods all need a two-step process, including the synthesis of ZnO and the incorporation into cellulose matrix. As mentioned above, our lab has developed a series of water-based cellulose solvents for the dissolution and regeneration, and the aqueous solvent systems have been proved effective with different variety of the alkali (LiOH/NaOH/KOH) and organic additive (urea/thiourea). Since the precursor zinc salts are also soluble in water, we take the endeavor to fulfill the construction of cellulose–ZnO composites in one step, by attempting to develop the new solvent containing inorganic salts as additives. This is also our outlook to expand the cellulose aqueous solvent systems with other inorganic additives, which will be very promising for the development of more cellulose/inorganic (metal oxide) hybrid materials, especially in the fields of electronics and energy.

In this paper, NaOH/zinc nitrate aqueous solution with cooling was developed to dissolve cellulose with high degree of polymerization (DP) of 680 to obtain a good dissolution of cellulose with stability. Moreover, cellulose/ZnO composite microspheres were facilely fabricated in situ from the solution by one step, taking advantage of the zinc salts in the cellulose solvent itself. This is a new pathway to construct inorganic/organic hybrid materials, which would also be helpful for the development of water-based and cheap cellulose solvents. It was different from the organic additives of urea or thiourea in aqueous alkaline solutions with cooling. The inorganic additives (zinc salts) for the dissolution of cellulose in NaOH solution should be emphasized, which is a favor to, both for the dissolution of the biomass and the fabrication of inorganic/organic composite materials. Therefore, this work is important for the conversion of natural biomass into new materials and fits the strategy of sustainable development, suggesting a virtuous circle of the natural world.

Experimental section

Materials

Cellulose (cotton linter pulp) with a certain degree of polymerization (DP = 680) was supplied by Hubei Chemical Fiber Co. Ltd. (Xiangfan, China). The cellulose sample was vacuum-dried at 60 °C for 48 h to remove any moisture before use. Deuterium oxide was supplied by Sigma-Aldrich (99.9 at.% D, USA). Commercially available NaOH, zinc nitrate hexahydrate, isooctane, sorbitan monooleate (Span 80), ethylene glycol and other reagents were of analytical grade (Shanghai Chemical Reagent Co., China), and used without further purification.

Dissolution of cellulose in NaOH/zinc nitrate

The cellulose solvent was prepared by mixing NaOH, zinc nitrate hexahydrate and water [8:n:(92-n)] by weight percentage) with vigorous stirring. A certain amount of cellulose sample was fully dispersed in the solvent and then the mixture was stored in a refrigerator at − 22 °C until frozen. Afterwards, it was thawed and stirred at room temperature to obtain the transparent cellulose solution.

Fabrication of cellulose/ZnO composite microspheres

The regenerated cellulose/ZnO composite microspheres were fabricated by a sol–gel transition method. In details, 4 wt% cellulose solution was prepared by the process mentioned above and degassed by centrifugation at 10,000 rpm for 5 min at 0 °C. To prepare suspension 300 g isooctane and 10 g Span 80 were well mixed in a reactor in ice-water bath and stirred at 800 rpm for 10 min. Subsequently, 80 g fresh cellulose solution was dropped into the suspension within 5 min. The suspension was kept stirring at 1200 rpm in ice-water bath. The bath was removed after 2 h and then 200 g ethylene glycol was rapidly poured into the suspension for the regeneration of cellulose/ZnO microspheres (CMZ). The stirring was stopped after another 0.5 h, and the microspheres were washed with deionized water and ethanol for several times. The microspheres were subjected to solvent-exchange with tert-Butanol, then frozen by immersing into liquid nitrogen, and finally freezedried for further characterization. The cellulose microspheres without ZnO (CM) were obtained by washing the CMZ with dilute sulfate acid and deionized water to remove the ZnO. It was noted that two kinds of cellulose solution were prepared in the beginning of this part and used for the fabrication of composite microspheres, namely, cellulose was dissolved in 6 wt% zinc nitrate hexahydrate/8 wt% NaOH and 5 wt% zinc nitrate hexahydrate/8 wt% NaOH solution, respectively, and the obtained microspheres were coded as CMZ6 and CMZ5, respectively.

Characterization

Solubility test was performed by the following process. A certain amount of cellulose sample was fully dispersed in the solvent and then the mixture was stored in a refrigerator until frozen. Afterwards, it was stirred and thawed at room temperature. The cellulose mass of the resultant solution (m_s) and precipitate (m_p) were obtained by centrifugation

$$S = \frac{m_s}{m_s + m_p} \times 100\% \tag{1}$$

at 10,000 rpm at 0 °C for 15 min. The solubility (S) was then calculated according to the following equation:

^{13}C nuclear magnetic resonance spectroscopy (^{13}C NMR) spectra were recorded on a Bruker AVANCE III 500 NMR spectrometer with BBO probe at 278 K. The concentration of cellulose solution was 3 wt%. Deuterium oxide was used instead of H_2O in the solution to lock the signal.

Dynamic light scattering (DLS) were characterized by a modified commercial light scattering spectrometer (ALV/SP-125, ALV, Germany) at 25 °C equipped with an ALV-5000/E multi-τ digital time correlator and a He–Ne laser ($\lambda = 632.8$ nm) was used at scattering angle θ of 30°. The sample solutions were prepared by diluting the original solution with the concentration of 1.0×10^{-3} g/mL and made optically clean by filtration through 0.22 μm Millipore filters. The CONTIN program (Jouault et al. 2012) was used for the analysis of dynamic light-scattering data

$$R_h = \frac{k_B T}{6\pi\eta_0 D}. \tag{2}$$

The hydrodynamic radius (R_h) was calculated by using the Stokes–Einstein relation as: where k_B was the Boltzmann constant, T the temperature in units of K, η_0 the viscosity of the solvent, and D the translational diffusion coefficient.

TA discovery hybrid rheometer (HR-2) was used for the rheology test. Temperature sweep was conducted under oscillation mode at 5 °C/min to obtain the storage modulus (G′) and loss modulus (G″) by using a double-concentric cylinder geometry at a constant frequency of 1 rad/s. The value of the strain amplitude was set as 10%, which was checked to ensure that all measurements were within a linear viscoelastic regime. Fresh cellulose solution with a certain concentration was prepared and degassed before pouring into the geometry without preshearing or oscillating.

X-ray diffraction (XRD) measurements were performed on an XRD diffractometer (D8-Advance, Bruker, Germany). The patterns of CuKα radiation ($\lambda = 0.15418$ nm) at 40 kV and 30 mA were recorded in the 2θ region from 3° to 80° at a scanning speed of 2°/min. FT-IR spectra were recorded on a Bruker TENSOR 27 spectrometer. The normal transmission mode was employed for IR measurement and spectra were recorded by overlaying 32 scans at a 4 cm^{-1} resolution. Thermogravimetric analyses were performed on TA Q500 under air atmosphere from 30 to 800 °C with a heating rate of 10 °C min^{-1}. Nitrogen physisorption measurements were carried out on Autosorb-iQ instrument, and Brunauer–Emmett–Teller specific surface area, Barrett–Joyner–Halendar (BJH) analysis were done automatically. The morphology of composite microspheres was observed by scanning electron microscopy (ZEISS SIGMA FE-SEM). Transmission electron microscopy (TEM) images were observed on a JEOL JEM-2010 (HT) electron microscope, using an accelerating voltage of 200 kV.

Antibacterial test

To determine the antibacterial properties of the cellulose/ZnO composite microspheres, time-kill tests were conducted of CMZ5 against Gram-positive bacterium *Staphylococcus* (*S. aureus*) and Gram-negative bacterium *Escherichia coli* (*E. coli*), respectively. 100 mg CMZ5 were dispersed in 50 mL bacterial suspension. The evaluation was performed with a final inoculum of approximately 5×10^4 CFU/mL. The resulting curves were obtained from counting the surviving cells in samples by a standard plate count method after 0, 1, 2, and 3 h of incubation at 37 °C. The disc diffusion method was performed using Luria–Bertani (LB) medium solid agar in Petri dishes. 0.2 g samples were incubated with the bacterial-cultured agar plates at 37 °C for 24 h before observation. Pure cellulose microspheres (CM) without ZnO were used as control.

Results and discussion

Dissolution and solution properties of cellulose in NaOH/zinc nitrate system

The addition of zinc nitrate to NaOH aqueous solution could significantly improve the solubility of cellulose with a high degree of polymerization (DP) of 680, as shown in Fig. 1. The result proved the cellulose solubility increased with the higher amount of zinc nitrate, indicating the effectiveness of zinc nitrate as an inorganic additive for improving the cellulose dissolution. As the zinc salts were added in the NaOH solution, Zn^{2+} transformed into $Zn(OH)_4^{2-}$, and formed stronger hydrogen bonds with cellulose than NaOH, as a result of the relatively slow motion. To fulfill the maximum of the solubility, more zinc nitrate addition was preferred. However, the excessive content of $Zn(OH)_4^{2-}$ in NaOH solution was unstable, leading to the precipitation of ZnO in the solution.

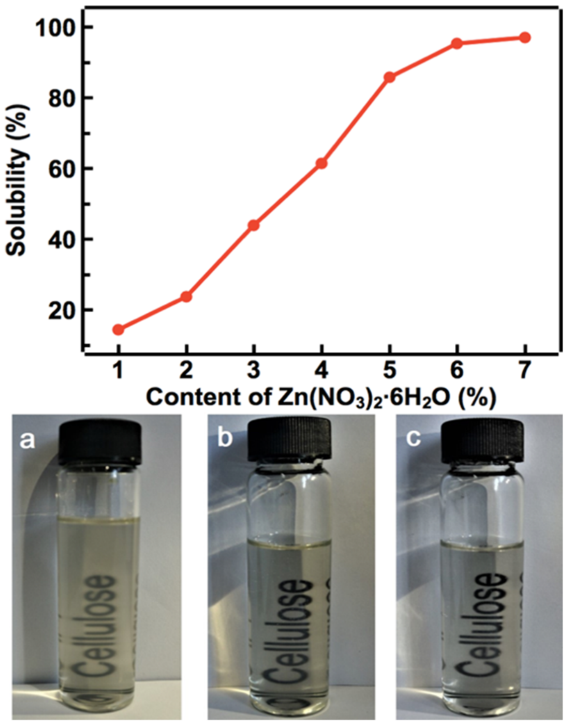


Fig. 1 The solubility of cellulose in NaOH aqueous solution with different content of zinc nitrate hexahydrate, as well as photographs of cellulose solution in **a** 8 wt% NaOH/5 wt% zinc nitrate hexahydrate, **b** 8 wt% NaOH/6 wt% zinc nitrate hexahydrate, **c** 8 wt% NaOH/7 wt% zinc nitrate hexahydrate

Therefore, the content of zinc nitrate hexahydrate was chosen to be 6 wt% in 8 wt% NaOH for this investigation, which could well dissolve cellulose without ZnO precipitation.

In our previous studies, NMR has been proved to be an effective method to investigate the dissolution of cellulose in various solvent systems (Wang et al. 2017a, c; Isogai 1997; Zhang et al. 2014). Figure 2 shows the ^{13}C NMR spectra of cellulose solution dissolved in NaOH/zinc nitrate aqueous solution. The chemical shifts were clearly identified as C_1 (103.5 ppm), C_4 (78.9 ppm), $C_{3,5}$ (75.3 ppm), C_2 (74.2 ppm) and C_6 (60.3 ppm) of cellulose with apparent sharpness, similar to the previous reported results (Isogai 1997; Cai et al. 2008). No additional signal of the cellulose derivatives was observed, indicating the dissolution of cellulose in NaOH/zinc nitrate was a physical process, and no derivatization occurred.

The hydrodynamic distribution of the dilute cellulose solution in NaOH/zinc nitrate is shown in Fig. 3. Two separate peaks were clearly observed, in which the smaller hydrodynamic radius (R_h) represents the individual cellulose chains, whereas that with lager R_h attributed to their aggregates. Obviously, with an

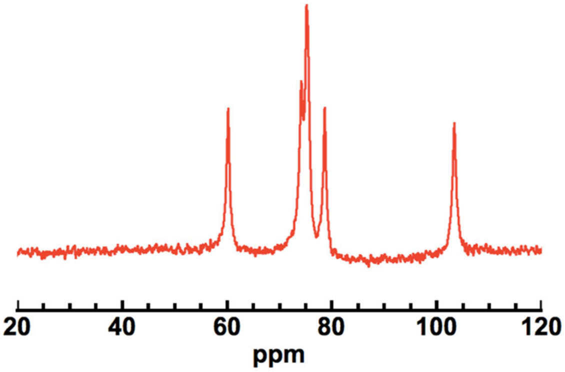


Fig. 2 The ^{13}C NMR spectra of cellulose solution dissolved in NaOH/zinc nitrate

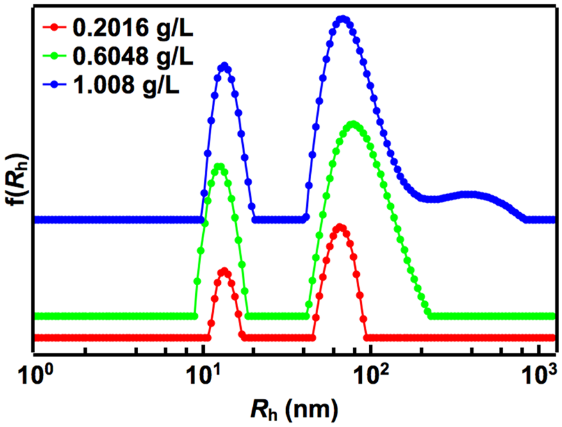


Fig. 3 The hydrodynamic distribution of dilute cellulose solution in NaOH/zinc nitrate

increase of the cellulose concentration, more aggregates appeared in the solution, similar to the LiOH/urea system, indicating the metastable properties of cellulose solution in NaOH/zinc nitrate (Lue et al. 2011). The stability of the concentrated cellulose solution was also important, especially for the fabrication of regenerated materials. Figure 4 shows the elastic storage modulus (G') and viscous loss modulus (G'') of the cellulose solution in NaOH/zinc aqueous solution as a function of time at different concentrations. Apparently, a viscous liquid behavior of 1 wt% cellulose solution appeared with the G' smaller than G'' (Fig. 4a), and the stability was maintained even at higher temperature (80 °C). For the solution of 2 wt% cellulose concentration, G' and G'' curves almost remained stable and parallel during the test, but showed a trend of crossover from 70 °C. Usually, the crossover of G' and G'' curves were chosen as a qualitative indicator of the gel point of the polymer solution (Nagarkar et al. 2010), suggesting the severe entanglement of polymer chains. The temperatures of gelation were about 76 °C and 58 °C for the cellulose solution with concentration of 3 wt% and 4 wt%, respectively (Fig. 4c, d). The rheological test results proved that cellulose solution dissolved in NaOH/zinc nitrate system was more stable at room temperature than that in NaOH/urea system (Cai and Zhang 2006). Thus NaOH/zinc nitrate system benefits commercial scale production of cellulose materials. However, the higher concentration of cellulose solution in the solvent system would obviously lead to higher possibility of the contact and entanglement of the macromolecules, and even led a sol–gel transition at higher temperatures.

Structure and morphology of cellulose/ZnO (CMZ) microspheres

As mentioned above, single cellulose chains tended to aggregate in the solution, which would self-assemble into regenerated cellulose microspheres (CM). In the specific process, cellulose solution was firstly dispersed under strong stirring to form small droplet suspension in isooctane and Span. Ice bath was then removed to increase the temperature in favor for the regeneration of cellulose. Ethylene glycol was subsequently added to the emulsion, which will destroy the cellulose solvent systems, thus facilitate the regeneration of cellulose and at the same time, ethylene glycol will also lead to the transformation of zinc salts to ZnO during the regeneration process (Ashoka et al. 2009). Due to porous structure induced by the assembly of the polymer, ZnO could be embedded simultaneously in the cellulose matrix to form composites microspheres. Figure 5a shows the XRD spectra of the CMZ5, CMZ6 and CM microspheres. All the microspheres displayed typical diffraction signals at 2θ = 12°, 20° and 22°, ascribed to the cellulose II (Yang et al. 2011; French 2014). For the CMZ5 and CMZ6, several new peaks appeared at 2θ = 31.9°, 34.5°, 36.4°, 47.6°, 56.6°, 63.0°, 66.4°, 67.8° and 68.9° corresponding to (110), (002), (101), (102), (110), (103), (200), (112) and (201) of hexagonal wurtzite zinc oxide, respectively. The results confirmed that ZnO were well crystallized and the composite microspheres were successfully fabricated directly from the cellulose solution in NaOH/zinc nitrate aqueous solution. The average diameter of hexagonal wurtzite zinc oxide was approximately 12 nm calculated with Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos\left(\frac{\theta}{2}\right)} \qquad (3)$$

where D is the average thickness of the grain perpendicular to the grain surface, K the Scherrer constant, λ the wavelength of X-ray, which is adopted as 0.154056 nm, β the half-height width of the diffraction peak, θ the diffraction angle of the particle. No peaks related to zinc hydroxide could be observed, indicating the complete transformation of $Zn(OH)_4^{2-}$

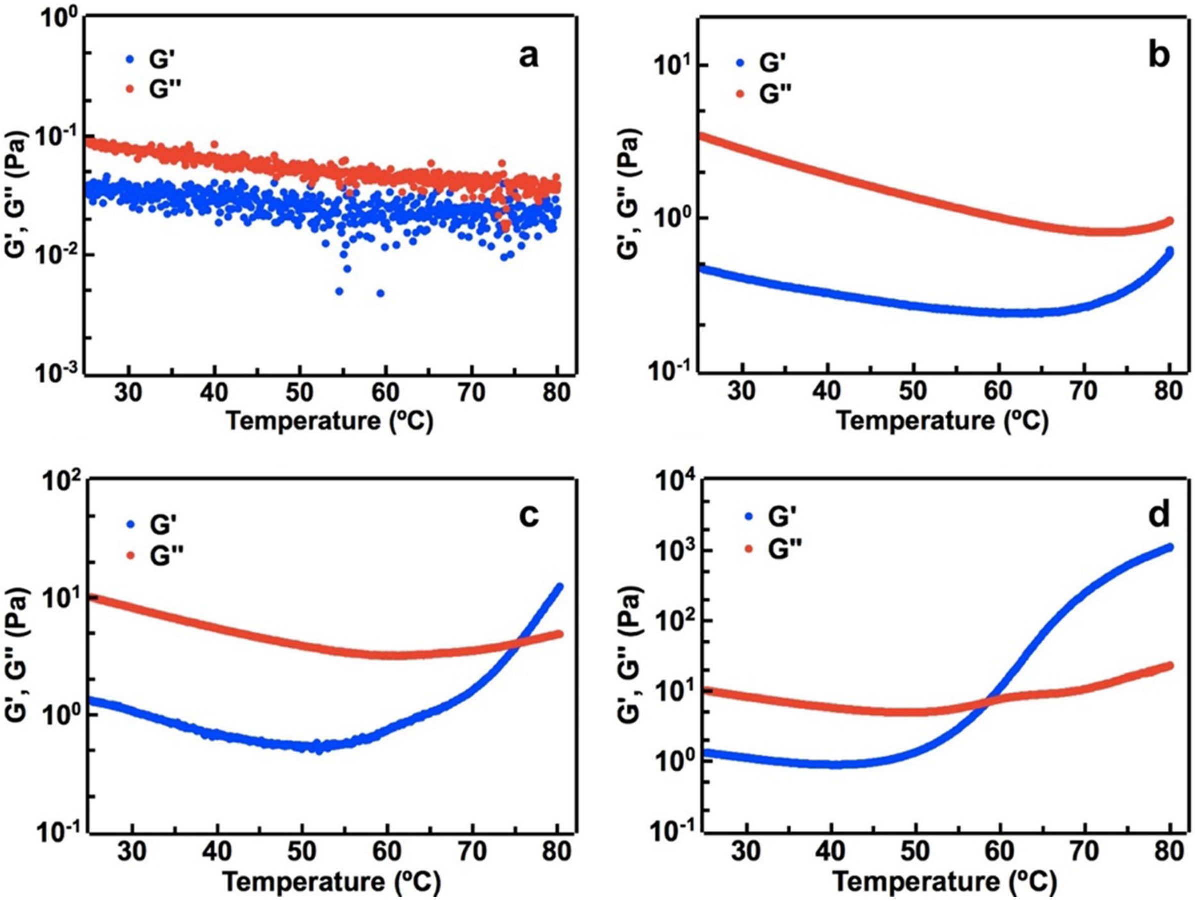


Fig. 4 Elastic storage modulus (G′) and viscous loss modulus (G″) of the cellulose solution in NaOH/zinc as a function of temperature at different concentrations, **a** 1 wt%, **b** 2 wt%, **c** 3 wt%, **d** 4 wt%

to ZnO in the composite microspheres. Furthermore, the intensity of ZnO peaks in CMZ6 was stronger than that of CMZ5, indicating the higher ZnO content in CMZ6, due to the higher concentration of zinc ions in the solvent. The XRD results were also supported by the IR spectra of CMZ5, CMZ6 and CM (Fig. 5b). Compared with the pure cellulose absorption of CM, the Zn–O absorption band at 520 cm^{-1} appeared clearly for both CMZ5 and CMZ6, and the intensity of CMZ6 was also stronger (Kondo 1997; Sangeetha et al. 2011). These results further confirmed that ZnO existed in the cellulose composite microspheres, and the desired organic/inorganic hybrid material was successfully constructed. Figure 5c, d shows the TG and DTG curves of CM, CMZ5 and CMZ6 in air atmosphere, respectively. The pyrolysis of CM exhibited a two-step process, in which the first one at about 320 °C was attributed to the onset of cellulose decomposition, and the second one at 450 °C to the full decomposition of cellulose (Jia et al. 2012). From the data, the residue weight of CM was calculated to be nearly zero after 700 °C, proving that CM was composed of pure cellulose. And the ZnO contents were 12.3%, 16.3%, 21.1% and 26.2% for the CMZ4, CMZ5, CMZ6 and CMZ7 composites, respectively. Obviously, the more precursor in the solvent will result in the higher content of ZnO embedded in the microspheres. The CMZ5 and CMZ6 displayed similar two-step pyrolysis process, but the corresponding temperature moved lower, as a result of the catalytic function of ZnO, which facilitated the breakdown of the carbon skeleton of cellulose (Bagheri and Rabieh 2013). Especially, the pyrolysis temperature of CMZ6 was even lower than that of CMZ5, due to its higher ZnO content, which was also demonstrated by its higher residue weight than that of CMZ5 after 700 °C.

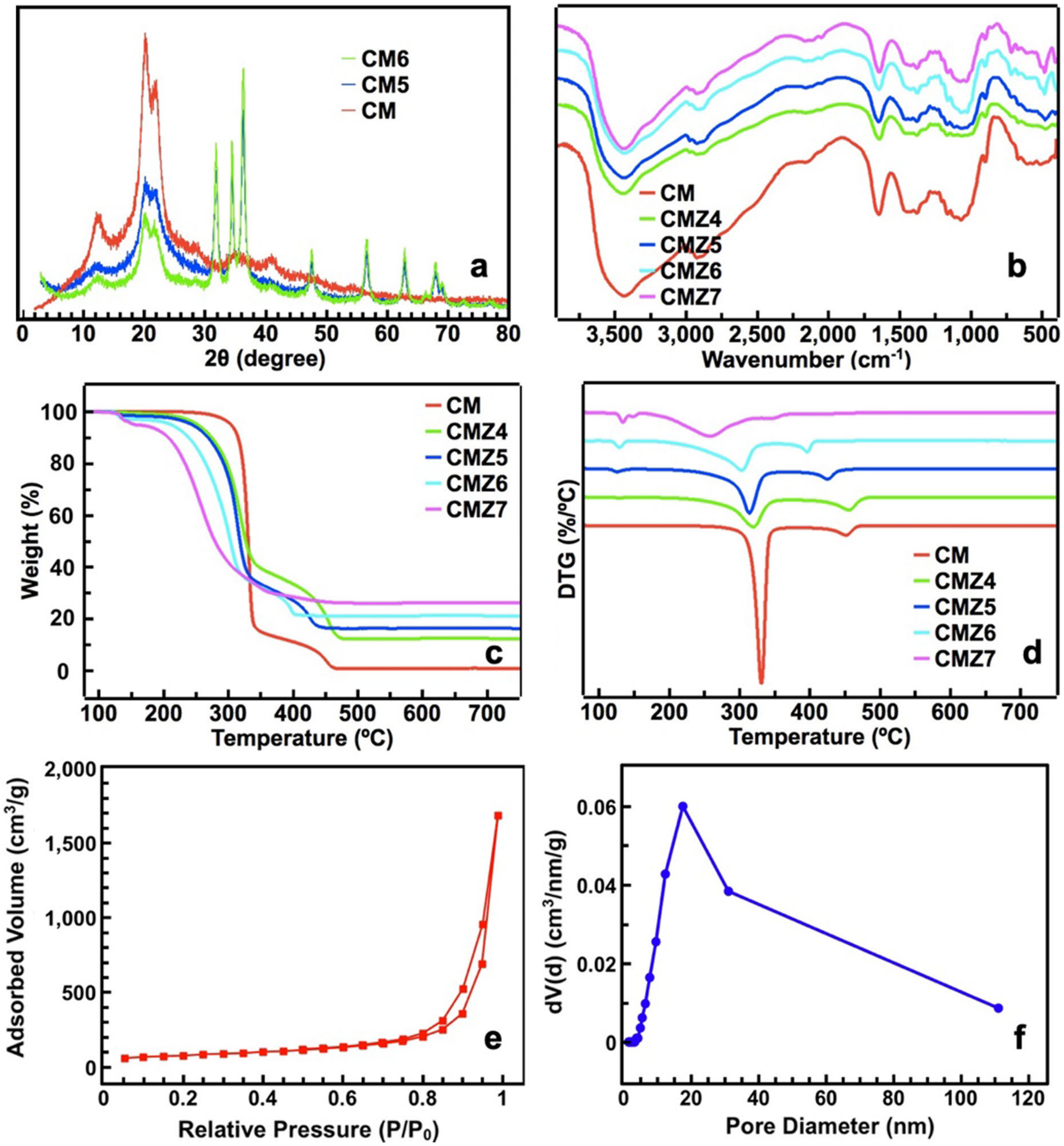


Fig. 5 XRD (**a**), IR (**b**), TG (**c**), DTG (**d**) spectra, nitrogen adsorption and desorption isotherms (**e**) and Barrett-Joyner-Halendar (BJH) pore size distribution (**f**) of composite cellulose/ZnO microspheres

Nitrogen adsorption/desorption results (Fig. 5e, f) indicated that the CMZ microspheres had the surface area of 275.86 m^2/g and the average pore diameter of 17.58 nm. Figure 6 shows the SEM images of the CMZ5 microspheres, indicating a dense and porous network structure. The ZnO of a cluster structure were evenly embedded on the microspheres with an average diameter of about 12 nm, which can be clearly observed in TEM images. More importantly, the cellulose/ZnO composites were obtained directly via a

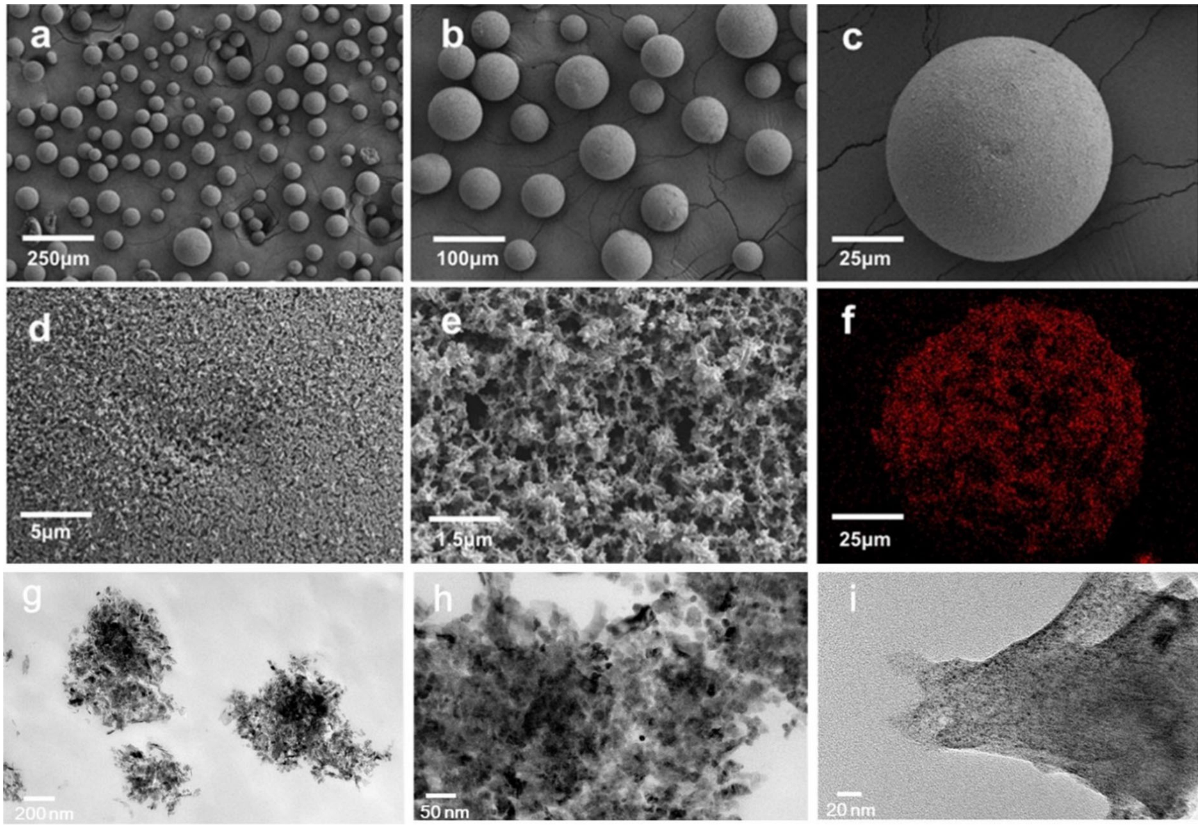


Fig. 6 SEM images of the composite cellulose/ZnO microspheres (**a**–**e**) and the EDS mapping of Zn element (**f**), TEM images of the CMZs (**g**–**i**)

one-step method from cellulose solution, and this architecture is of great use, significantly broadening the application of the cellulose biomass.

Antibacterial properties

To evaluate the application as biomedical materials, antibacterial properties of the cellulose/ZnO composites were performed. Figure 7 shows the cellulose microspheres (CM) without ZnO had no inhibition effect on the microorganism growth for *E. coli* and *S. aureus*. The viable bacteria number went up obviously in CM without ZnO within 3 h to nearly 10^6 CFU/mL. In contrast, a significant antibacterial effect could be observed for CMZ.

The viable bacteria number was an obvious 1 log reduction after the first 1 h contact time against both *E. coli* and *S. aureus*. After 2 h, the CMZ exhibited a more significant inhibition effect against *S. aureus* than *E. coli*, since the viable bacteria number of *S. aureus* quickly went down below 10^2 CFU/mL, less than that of *E. coli*. Meanwhile, both of *S. aureus* and *E. coli* were completely killed by the composite cellulose/ZnO microspheres within 3 h, showing good antibacterial properties.

Basically, the antibacterial mechanism is still controversial, but some agreements have been made (Sirelkhatim et al. 2015). Aquatic ZnO can produce reactive oxygen species (ROS) by photocatalytic reaction, such as superoxide anion, hydrogen peroxide and hydroxide, which may be the major cause of nanotoxicity (Huang et al. 2008; Xia et al. 2008). The species involve in the destruction of cellular components such as lipids, DNA, and proteins, as a result of their internalization into the bacteria cell membrane. The peptidoglycan layer of the *S. aureus* cell wall is composed of networks with plenty of pores, which make them more susceptible to the attack. On the other hand, the cell wall of *E. coli* is made up of thin membrane of peptidoglycan and an outer membrane

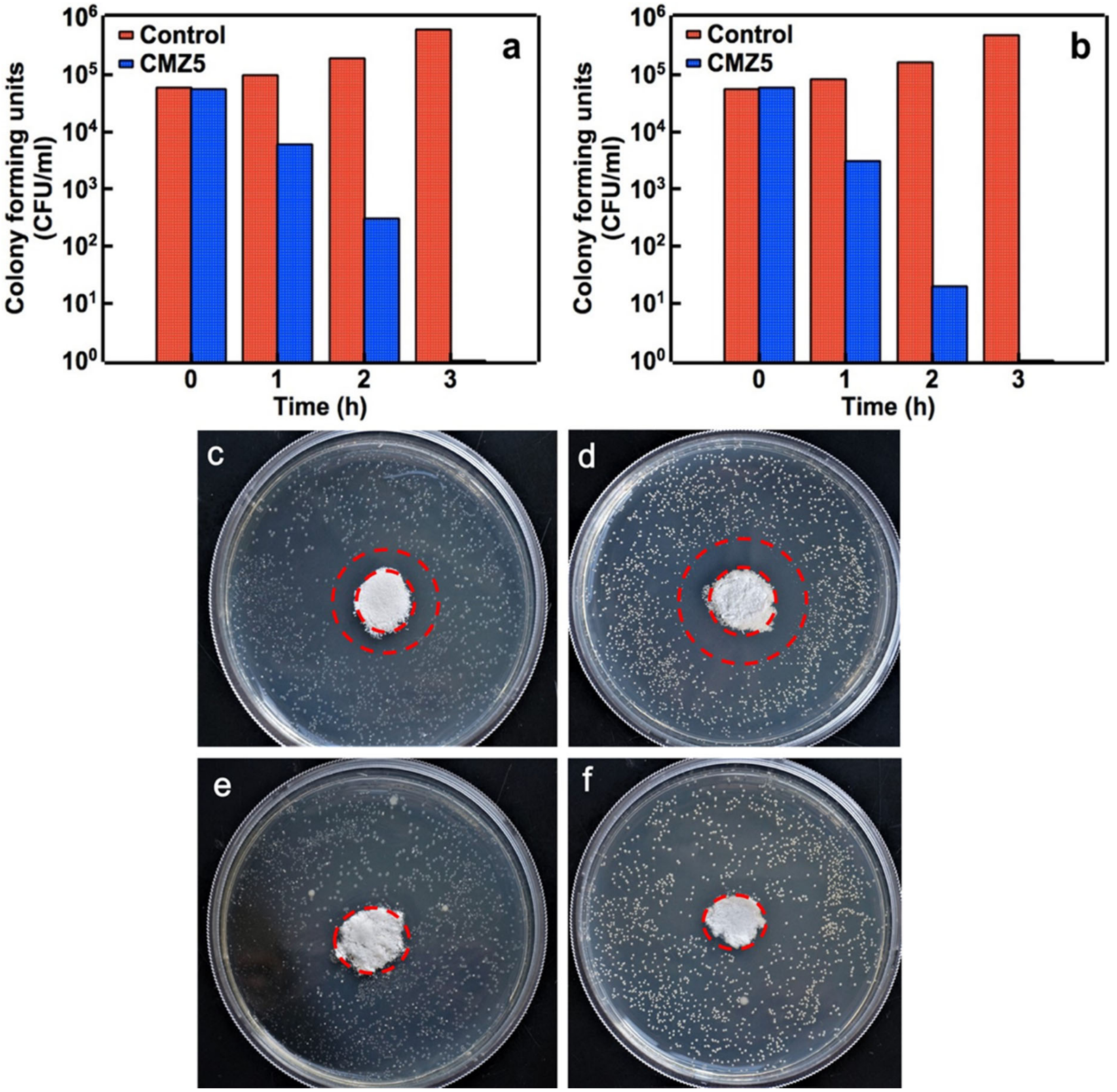


Fig. 7 Time-kill tests of the composite cellulose/ZnO microspheres against *E. coli* (**a**) and *S. aureus* (**b**). Inhibition zone test of the composite cellulose/ZnO microspheres and cellulose microspheres against (**c**, **e**) *E. coli* and (**d**, **f**) *S. aureus*

composed of lipopolysaccharide, lipoprotein, and phospholipids (Inphonlek et al. 2010) which would be less vulnerable. Therefore, the CMZ had higher antibacterial activity against *S. aureus* than *E. coli*. What's more, the zinc ions released from ZnO could also have significant effect in the active transport inhibition as well as in the amino acid metabolism and enzyme system disruption. This mechanism is somewhat under debate due to the low solubility of ZnO, although it has been adopted and accepted (Aydin Sevinç and Hanley 2010). Moreover, the CMZ prepared by this method was homogenous and the ZnO can keep good stability and distribution in the environment protected by cellulose matrix, which can avoid the decrease of antibacterial activity led by the aggregation of the ZnO. This antibacterial property would greatly expand the application of the cellulose materials. Compared to other antibacterial materials based on cellulose, the CMZ could be prepared more easily in aqueous solutions via a one-pot process from dissolution to construction. However, most of others are prepared through multi-steps methods, including intermediate reactions such as reduction of the metals or derivatization of the polymers (Cen et al. 2003; Mary et al. 2009).

Conclusion

A novel solvent, NaOH/zinc nitrate aqueous solution, was developed to dissolve cellulose. In this system, the solubility of cellulose and stability of the solution were obviously improved. The cellulose dissolution was a physical process without derivatization. The cellulose solution was meta-stable, and single cellulose chains and their aggregates co-existed in the solution. The precipitation of ZnO could occur in the cellulose solution, and the composite microspheres (CMZ) containing ZnO having hexagonal wurtzite structure were constructed, which evenly embedded in cellulose matrix to form organic/inorganic hybrid materials. The cellulose/ZnO composites displayed good antibacterial properties against both *E. coli* and *S. aureus*. This work provided a new pathway to utilize a water-based and eco-friendly solvent for the green conversion of cellulose into environmentally friendly and sustainable materials.

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References

Abe M, Kuroda K, Sato D et al (2015) Effects of polarity, hydrophobicity, and density of ionic liquids on cellulose solubility. Phys Chem Chem Phys 17:32276–32282. https://doi.org/10.1039/C5CP05808B

Ashoka S, Nagaraju G, Tharamani CN, Chandrappa GT (2009) Ethylene glycol assisted hydrothermal synthesis of flower like ZnO architectures. Mater Lett 63:873–876. https://doi.org/10.1016/j.matlet.2009.01.054

Aydin Sevinç B, Hanley L (2010) Antibacterial activity of dental composites containing zinc oxide nanoparticles. J Biomed Mater Res B Appl Biomater 94B:22–31. https://doi.org/10.1002/jbm.b.31620

Bagheri M, Rabieh S (2013) Preparation and characterization of cellulose–ZnO nanocomposite based on ionic liquid ([C4mim] Cl). Cellulose 20:699–705

Bergmann M, Tekman MB, Gutow L (2017) Sea change for plastic pollution. Nature 544:297

Cai J, Zhang L (2005) Rapid dissolution of cellulose in LiOH/urea and NaOH/urea aqueous solutions. Macromol Biosci 5:539–548. https://doi.org/10.1002/mabi.200400222

Cai J, Zhang L (2006) Unique gelation behavior of cellulose in NaOH/urea aqueous solution. Biomacromolecules 7:183–189. https://doi.org/10.1021/bm0505585

Cai J, Zhang L, Liu S et al (2008) Dynamic self-assembly induced rapid dissolution of cellulose at low temperatures. Macromolecules 41:9345–9351

Cen L, Neoh K, Kang E (2003) Surface functionalization technique for conferring antibacterial properties to polymeric and cellulosic surfaces. Langmuir 19:10295–10303

Chang H-C, Zhang R-L, Hsu D-T (2015) The effect of pressure on cation–cellulose interactions in cellulose/ionic liquid mixtures. Phys Chem Chem Phys 17:27573–27578. https://doi.org/10.1039/C5CP04607F

Costa SV, Gonçalves AS, Zaguete MA et al (2013) ZnO nanostructures directly grown on paper and bacterial cellulose substrates without any surface modification layer. Chem Commun 49:8096–8098. https://doi.org/10.1039/C3CC43152E

Daneshvar N, Salari D, Khataee A (2004) Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO2. J Photochem Photobiol Chem 162:317–322. https://doi.org/10.1016/S1010-6030(03)00378-2

Fink HP, Weigel P, Purz HJ, Ganster J (2001) Structure formation of regenerated cellulose materials from NMMO-solutions. Prog Polym Sci 26:1473–1524

French AD (2014) Idealized powder diffraction patterns for cellulose polymorphs. Cellulose 21:885–896. https://doi.org/10.1007/s10570-013-0030-4

Gimenez AJ, Yanez-Limon JM, Seminario JM (2013) ZnO–cellulose composite for UV sensing. IEEE Sens J 13:1301–1306. https://doi.org/10.1109/JSEN.2012.2231067

Gonçalves G, Marques PAAP, Neto CP et al (2009) Growth, structural, and optical characterization of ZnO-coated cellulosic fibers. Cryst Growth Des 9:386–390. https://doi.org/10.1021/cg800596z

Huang Z, Zheng X, Yan D et al (2008) Toxicological effect of ZnO nanoparticles based on bacteria. Langmuir 24:4140–4144. https://doi.org/10.1021/la7035949

Inphonlek S, Pimpha N, Sunintaboon P (2010) Synthesis of poly(methyl methacrylate) core/chitosan-mixed-polyethyleneimine shell nanoparticles and their antibacterial property. Colloids Surf B Biointerfaces 77:219–226. https://doi.org/10.1016/j.colsurfb.2010.01.029

Isogai A (1997) NMR analysis of cellulose dissolved in aqueous NaOH solutions. Cellulose 4:99–107. https://doi.org/10.1023/A:1018471419692

Isogai A, Atalla RH (1998) Dissolution of cellulose in aqueous NaOH solutions. Cellulose 5:309–319

Jia B, Mei Y, Cheng L et al (2012) Preparation of copper nanoparticles coated cellulose films with antibacterial properties through one-step reduction. ACS Appl Mater Interfaces 4:2897–2902

John A, Ko H-U, Kim D-G, Kim J (2011) Preparation of cellulose–ZnO hybrid films by a wet chemical method and their characterization. Cellulose 18:675–680. https://doi.org/10.1007/s10570-011-9523-1

Jouault N, Xiang Y, Moulin E et al (2012) Hierarchical supramolecular structuring and dynamical properties of water soluble polyethylene glycol-perylene self-assemblies. Phys Chem Chem Phys 14:5718–5728. https://doi.org/10.1039/C2CP23786E

Katepetch C, Rujiravanit R, Tamura H (2013) Formation of nanocrystalline ZnO particles into bacterial cellulose pellicle by ultrasonic-assisted in situ synthesis. Cellulose 20:1275–1292

Khatri V, Halász K, Trandafilović LV et al (2014) ZnO-modified cellulose fiber sheets for antibody immobilization. Carbohydr Polym 109:139–147. https://doi.org/10.1016/j.carbpol.2014.03.061

Kondo T (1997) The assignment of IR absorption bands due to free hydroxyl groups in cellulose. Cellulose 4:281–292. https://doi.org/10.1023/A:1018448109214

Kumar A, Gullapalli H, Balakrishnan K et al (2011) Flexible ZnO–cellulose nanocomposite for multisource energy conversion. Small 7:2173–2178. https://doi.org/10.1002/smll.201100458

Lue A, Liu Y, Zhang L, Potthast A (2011) Light scattering study on the dynamic behaviour of cellulose inclusion complex in LiOH/urea aqueous solution. Polymer 52:3857–3864. https://doi.org/10.1016/j.polymer.2011.06.034

MacArthur E (2017) Beyond plastic waste. Science 358:843. https://doi.org/10.1126/science.aao6749

Mary G, Bajpai S, Chand N (2009) Copper(II) ions and copper nanoparticles-loaded chemically modified cotton cellulose fibers with fair antibacterial properties. J Appl Polym Sci 113:757–766

Matsumoto T, Tatsumi D, Tamai N, Takaki T (2001) Solution properties of celluloses from different biological origins in LiCl·DMAc. Cellulose 8:275–282. https://doi.org/10.1023/A:1015162027350

McCormick CL, Callais PA, Hutchinson BH (1985) Solution studies of cellulose in lithium chloride and *N*,*N*-dimethylacetamide. Macromolecules 18:2394–2401. https://doi.org/10.1021/ma00154a010

Morgenstern B, Kammer H-W (1996) Solvation in cellulose–LiCl–DMAc solutions. Trends Polym Sci 4:87–92

Nagarkar S, Nicolai T, Chassenieux C, Lele A (2010) Structure and gelation mechanism of silk hydrogels. Phys Chem Chem Phys 12:3834–3844. https://doi.org/10.1039/B916319K

Özgür Ü, Alivov YI, Liu C et al (2005) A comprehensive review of ZnO materials and devices. J Appl Phys 98:041301. https://doi.org/10.1063/1.1992666

Rochman CM, Browne MA, Halpern BS et al (2013) Classify plastic waste as hazardous. Nature 494:169

Rosenau T, Potthast A, Sixta H, Kosma P (2001) The chemistry of side reactions and byproduct formation in the system NMMO/cellulose (Lyocell process). Prog Polym Sci 26:1763–1837

Rosenau T, Potthast A, Adorjan I et al (2002) Cellulose solutions in *N*-methylmorpholine-*N*-oxide (NMMO)—degradation processes and stabilizers. Cellulose 9:283–291

Sangeetha G, Rajeshwari S, Venckatesh R (2011) Green synthesis of zinc oxide nanoparticles by aloe barbadensis miller leaf extract: structure and optical properties. Mater Res Bull 46:2560–2566. https://doi.org/10.1016/j.materresbull.2011.07.046

Sirelkhatim A, Mahmud S, Seeni A et al (2015) Review on zinc oxide nanoparticles: antibacterial activity and toxicity mechanism. Nano Micro Lett 7:219–242. https://doi.org/10.1007/s40820-015-0040-x

Swatloski RP, Spear SK, Holbrey JD, Rogers Robin D (2002) Dissolution of cellulose with ionic liquids. J Am Chem Soc 124:4974–4975

Wang S, Lu A, Zhang L (2016) Recent advances in regenerated cellulose materials. Prog Polym Sci 53:169–206. https://doi.org/10.1016/j.progpolymsci.2015.07.003

Wang S, Lyu K, Sun P et al (2017a) Influence of cation on the cellulose dissolution investigated by MD simulation and experiments. Cellulose 24:4641–4651. https://doi.org/10.1007/s10570-017-1456-x

Wang S, Sun P, Liu M et al (2017b) Weak interactions and their impact on cellulose dissolution in an alkali/urea aqueous system. Phys Chem Chem Phys 19:17909–17917. https://doi.org/10.1039/C7CP02514A

Wang S, Sun P, Zhang R et al (2017c) Cation/macromolecule interaction in alkaline cellulose solution characterized with pulsed field-gradient spin-echo NMR spectroscopy. Phys Chem Chem Phys 19:7486–7490. https://doi.org/10.1039/C6CP08744B

Xia T, Kovochich M, Liong M et al (2008) Comparison of the mechanism of toxicity of zinc oxide and cerium oxide nanoparticles based on dissolution and oxidative stress properties. ACS Nano 2:2121–2134. https://doi.org/10.1021/nn800511k

Yang Q, Qin X, Zhang L (2011) Properties of cellulose films prepared from NaOH/urea/zincate aqueous solution at low temperature. Cellulose 18:681–688

Zhang C, Liu R, Xiang J et al (2014) Dissolution mechanism of cellulose in *N*,*N*-dimethylacetamide/lithium chloride: revisiting through molecular interactions. J Phys Chem B 118:9507–9514. https://doi.org/10.1021/jp506013c