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Microwave synthesis of cellulose/CuO nanocomposites in ionic liquid and its thermal transformation to CuO

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ABSTRACT

The purpose of this study is to develop a green strategy to synthesize the cellulose-based nanocomposites and open a new avenue to the high value-added applications of biomass. Herein, we reported a microwave-assisted ionic liquid route to the preparation of cellulose/CuO nanocomposites, which combined three major green chemistry principles: using environmentally friendly method, greener solvents, and sustainable resources. The influences of the reaction parameters including the heating time and the ratio of cellulose solution to ionic liquid on the products were discussed by X-ray powder diffraction, Fourier transform infrared spectrometry, and scanning electron microscopy. The crystallinity of CuO increased and the CuO shape changed from nanosheets to bundles and to particles with increasing heating time. The ratio of cellulose solution to ionic liquid also affected the shapes of CuO in nanocomposites. Moreover, CuO crystals were obtained by thermal treatment of the cellulose/CuO nanocomposites at 800 °C for 3 h in air.

1. Introduction

Microwave-assisted method is a rapid and green methodology (Polshettiwar, Nadagouda, & Varma, 2009), and has unique effects including rapid volumetric heating, high reaction rate, short reaction time, enhanced reaction selectivity, environmental friendliness, and energy saving (Zhu, Wang, Qi, & Hu, 2004). Ionic liquids is well known as the solvent for the dissolution of cellulose due to its advantages of high fluidity, low melting temperature, low toxicity, nonflammability, high ionic conductivity, and importantly no measurable vapor pressure (Plechkova & Seddon, 2008; Welton, 1999), compared with other solvents. As a promising green technology, microwave-assisted ionic liquid method has been received more and more attention due to combining the advantages of both microwave heating and ionic liquids (Bilecka, Djerdj, & Niederberger, 2008; Cao & Zhu, 2009; Li et al., 2011a). In the literatures, microwave-assisted ionic liquid method was widely applied for the synthesis of inorganic nanomaterials such as tellurium nanorods and nanowires (Zhu et al., 2004), $PbCrO_4$ and Pb_2CrO_5 rods (Wang & Zhu, 2005), $ZnFe_2O_4$ nanoparticles (Cao, Zhu, Cheng, & Huang, 2009), TiO_2 nanocrystals (Ding et al., 2007), and CaF_2, MgF_2 and SrF_2 hollow microspheres (Xu & Zhu, 2012).

It is well known that cellulose is the most abundant renewable material and natural polysaccharide found on the earth (Klemm, Heublein, Fink, & Bohn, 2005). Cellulose-based nanocomposites have become a fast-growing research field of biomass thanks to their interesting optical, electrical, and mechanical properties and many promising potential applications in optics, biological labels, biomedical fields, water treatment, etc. (Eichhorn et al., 2010). However, there have been few reports by microwave-assisted ionic liquid method on the synthesis of cellulose-based nanocomposites. Recently, the applications of microwave-assisted ionic liquid method in the synthesis of cellulose-based nanocomposites including cellulose/calcium silicate nanocomposites (Jia, Li, Ma, & Sun, 2011a; Jia, Li, Ma, Sun, & Zhu, 2011b), cellulose/carbonated hydroxyapatite (Ma, Jia, Li, & Sun, 2011), and cellulose/F-substituted hydroxyapatite nanocomposites (Jia, Li, Ma, & Sun, 2012) have been reported by our groups.

As a transition metal oxide with a narrow band gap (E_g = 1.2 eV), CuO is one of the most important functional materials due to its unique properties such as electronic, photoconductive and photochemical properties and promising novel applications in photovoltaic thin film solar cells, negative-electrode material for lithium-ion batteries, a photocatalyst for water splitting, high-temperature superconductors, and magnetoresist materials (Gao et al., 2004; Maruyama, 1998; Wu et al., 1987; Zheng et al., 2000). Xu, Chen, and Jiao (2005) reported the fabrication of CuO pricky microspheres with tunable size via hydrothermal method by using

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$CuCl_2{\cdot}2H_2O$, $Na_2(C_4H_4O_6){\cdot}3H_2O$, and NaOH as starting materials. More recently, the rapid synthesis of flower-like Cu_2O architectures was reported in the presence of ionic liquid 1-n-butyl-3-methyl imidazolium tetrafluoroborate ([Bmim]BF_4) with the assistance of microwave irradiation (Li et al., 2011b). As far as we know, the synthesis of cellulose/CuO nanocomposites by a microwave-assisted ionic liquid method has not been reported yet.

In this study, we report the microwave-assisted ionic liquid route for the synthesis of the cellulose/CuO nanocomposites. CuO crystals with different shapes were obtained by thermal treatment of the cellulose/CuO nanocomposites at 800 °C for 3 h in air. The influences of the reaction parameters including the heating time and the ratio of cellulose solution to ionic liquid on the products were discussed in detail.

2. Experimental

2.1. Preparation of cellulose/CuO nanocomposites

All chemicals were of analytical grade and used as received without further purification. All experiments were conducted under ambient atmosphere. The preparation of cellulose solution followed our previous report (Jia et al., 2010). In a typical synthesis, 7.00 g of NaOH and 12.00 g of urea were added into 81 mL of distilled water under vigorous stirring to form NaOH-urea aqueous solution. Then, 3.24 g of microcrystalline cellulose was added into the above solution under vigorous stirring. The above solution was cooled to −12 °C for 12 h. The obtained cellulose solution was used for the preparation of cellulose/CuO nanocomposites.

For the synthesis of cellulose/CuO nanocomposites, 0.34 g of $CuCl_2{\cdot}2H_2O$ was added into the mixed solution of the cellulose solution (10 mL) and ionic liquid ($BmimBF_4$, 10 mL) under vigorous stir. The mixture solution was heated to 100 °C by microwave heating and kept at this temperature for 10 min, 20 min, and 30 min, respectively, and then air cooled to room temperature naturally. The microwave oven used for sample preparation was purchased from Beijing Xiang-Hu Science and Technology Development Reagent Co., Ltd., which was equipped with the magnetic stirring system and a water-cooled condenser outside the microwave cavity. The product was separated from the solution by centrifugation, washed by deionized water and ethanol three times, and dried at 60 °C for further characterization.

2.2. Preparation of the CuO crystals

The CuO samples were obtained by thermal decomposition of the as-prepared cellulose/CuO nanocomposites, which were put into an alumina crucible in a furnace, heated to 800 °C in air with a heating rate of 1 °C/min, and kept at 800 °C for 3 h.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were obtained in 2θ range from 10° to 70° on a Rigaku D/Max 2200-PC diffractometer with Cu Kα radiation (λ = 0.15418 nm) and graphite monochromator at ambient temperature. Fourier transform infrared (FTIR) spectroscopy was carried out on Thermo Scientific Nicolet iN10 FTIR Microscope (Thermo Nicolet Corporation, Madison, WI, USA), which was equipped with a liquid nitrogen cooled MCT detector. Dried samples were ground and pelletized with BaF_2, and the spectra were recorded in the range of 4000–670 cm^{-1} with 4 cm^{-1} resolution and 128 scans/sample. Scanning electron microscopy (SEM) images were recorded with a Hitachi 3400 N scanning electron microscopy. All samples were Au coated prior to examination by SEM. Thermogravimetric analysis (TG) and differential scanning calorimetric analysis (DSC) were performed on a STA-409PC/4/H Luxx simultaneous TG/DSC apparatus (Netzsch Co., Selb, Germany) at a heating rate of 10 °C/min from room temperature to 800 °C under air atmosphere.

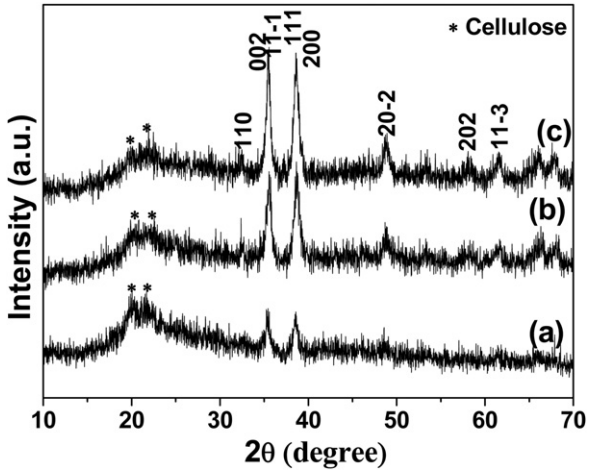

Fig. 1. XRD patterns of the cellulose/CuO nanocomposites prepared in ionic liquid by microwave heating at 100 °C for different times: (a) 10 min; (b) 20 min; (c) 40 min.

3. Results and discussion

Fig. 1a shows the XRD pattern of a typical sample prepared in the mixed solution of ionic liquid (10 mL)/cellulose solution (10 mL) by microwave heating at 100 °C for 10 min. One can see that the sample consisted of the mixed phases of well-crystallized CuO with a monoclinic structure (JCPDS 48-1548) and cellulose (marked with * in Fig. 1a). No peaks from impurities such as $Cu(OH)_2$ or Cu_2O were observed. The cellulose/CuO nanocomposites have been successfully fabricated for only 10 min via microwave-assisted ionic liquid method, confirming the high reaction efficiency of this methodology. The other samples prepared for 20 min and 40 min, had similar XRD patterns (Fig. 1b and c), compared with Fig. 1a. When the heating time was 10 min, only the peaks of (0 0 2, 1 1 −1) and (1 1 1, 2 0 0) of CuO were observed (Fig. 1a), indicating the low crystallinity of CuO in the cellulose/CuO nanocomposites. When the heating time was increased from 10 min to 20 min, and 40 min, more peaks of CuO appeared (Fig. 1b and c). Moreover, the peaks intensity of CuO obviously increased with increasing heating time. These results indicated a better crystallinity of CuO in the cellulose/CuO nanocomposites, which was in accordance with those reported in the literature (Ma et al., 2012). These results also demonstrated that the increased heating time favored the synthesis and crystallization of cellulose/CuO nanocomposites.

The morphologies and microstructures of the cellulose/CuO nanocomposites were investigated with SEM. The SEM images of the typical sample synthesized in ionic liquid (10 mL)/cellulose solution (10 mL) by microwave heating at 100 °C for 20 min were shown in Fig. 2. One can observe that the CuO crystals grow on cellulose substrate (Fig. 2a). Magnified micrographs of the cellulose/CuO nanocomposites were shown in Fig. 2b–d. The CuO crystals displayed the irregular sheet-like shape (Fig. 2b). CuO with bundle-like shape consisted of nanosheets was also observed (Fig. 2c). From Fig. 2d, one can clearly see that CuO nanosheets were absorbed on the surface of cellulose. In view of the SEM results, one can conclude that the cellulose/CuO nanocomposites with CuO nanosheets dispersed in the cellulose matrix were successfully synthesized.

The effect of the heating time on the shapes of cellulose/CuO nanocomposites was investigated. When the heating time was decreased to 10 min, and kept the other condition the same, the CuO crystals were also dispersed on the cellulose matrix (Fig. 3a).

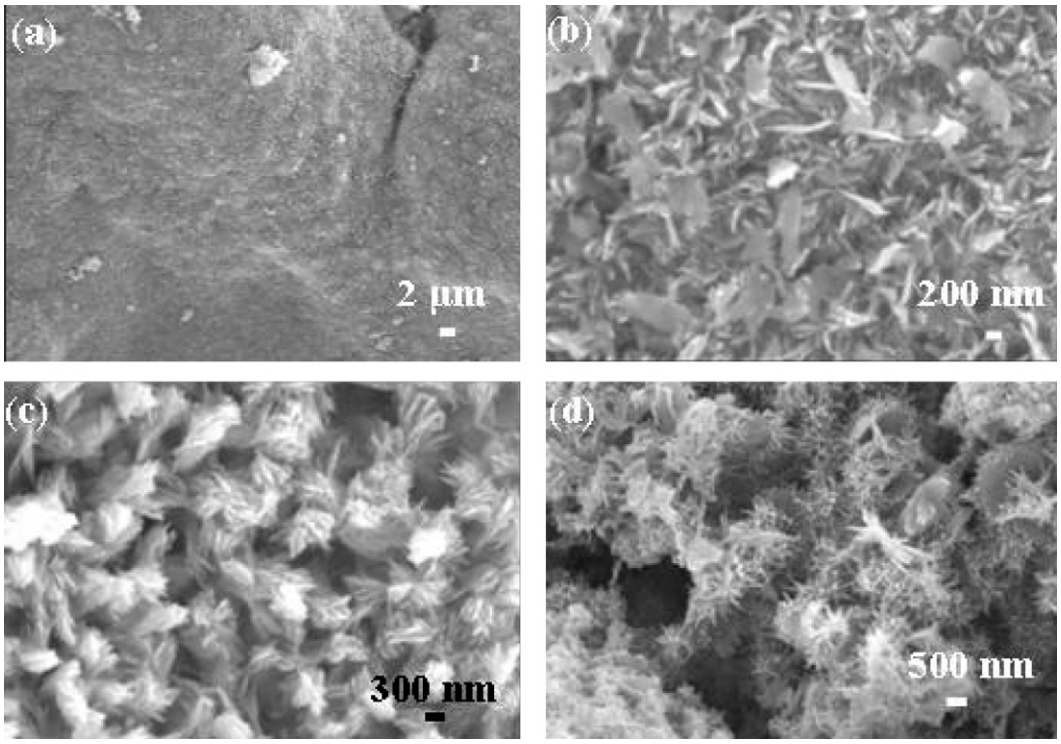

Fig. 2. SEM images of the cellulose/CuO nanocomposites prepared in ionic liquid (10 mL)/cellulose solution (10 mL) by microwave heating at 100 °C for 20 min.

Magnified image of the sample was shown in Fig. 3b, from which one can see the CuO owns relatively uniform size, and consists of regular nanosheets, compared with Fig. 2. When the heating time was increased to 40 min, the CuO aggregation on the surface of cellulose was observed (Fig. 3c). The CuO particles with diameters of about 300 nm were displayed from the magnified image (Fig. 3d). From Figs. 2 and 3, one can clearly see the change process of the CuO morphologies from the regular nanosheets to the bundles consisted of irregular nanosheets, and to the particles. Therefore, choosing the appropriate heating time is important for the formation of the cellulose/CuO nanocomposites with desirable morphologies. Moreover, the size of CuO crystals was obviously increased with increasing

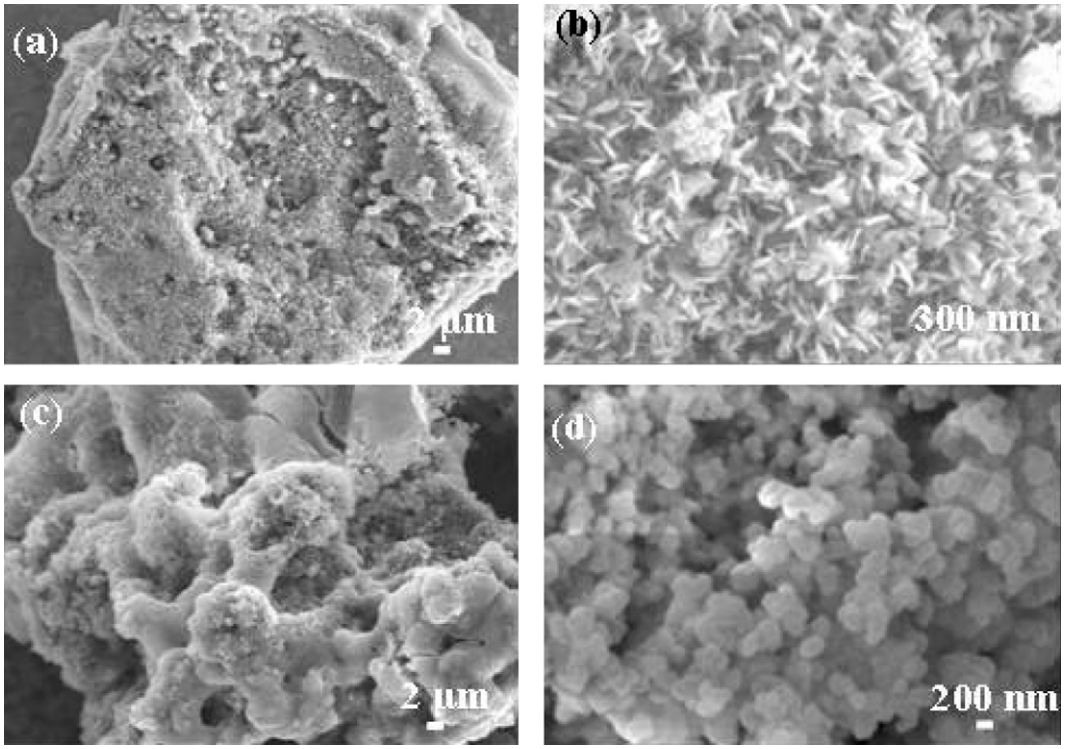

Fig. 3. SEM images of the cellulose/CuO nanocomposites prepared in ionic liquid (10 mL)/cellulose solution (10 mL) by microwave heating at 100 °C for different times: (a and b) 10 min; (c and d) 40 min.

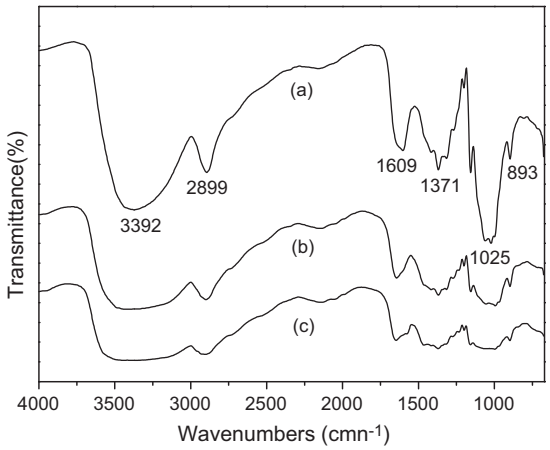

Fig. 4. FTIR spectra of the cellulose/CuO nanocomposites prepared by microwave heating using different ratio of ionic liquid to cellulose solution at 100 °C for 20 min: (a) ionic liquid (5 mL)/cellulose solution (15 mL); (b) ionic liquid (10 mL)/cellulose solution (10 mL); and (c) ionic liquid (15 mL)/cellulose solution (5 mL).

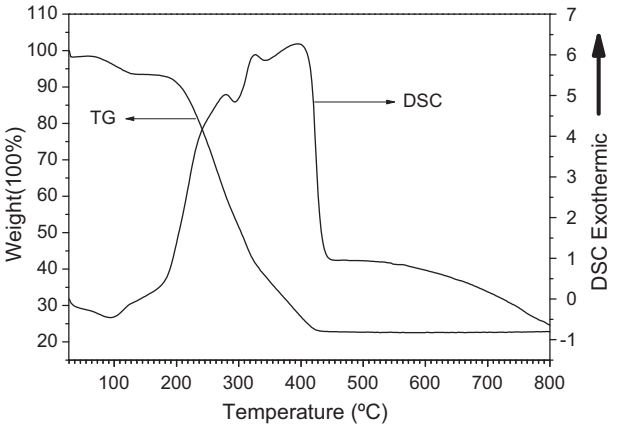

Fig. 6. TG and DSC curves of the cellulose/CuO nanocomposites prepared in ionic liquid (10 mL)/cellulose solution (10 mL) by microwave heating method at 100 °C for 20 min.

heating time, which is in agreement with the results in the literatures (Jia, Chen, Jiao, & Zhai, 2009; Zheng et al., 2006). These results demonstrated that the heating time not only played an important role on the crystallinity of CuO crystals, but also had a significant influence on the morphologies and sizes of CuO crystals in the nanocomposites.

The influence of the ratio of ionic liquid to cellulose solution on the microstructure of samples was also studied. When the ratio of ionic liquid to cellulose solution was 1:3, the FTIR spectrum of the sample was shown in Fig. 4a. The sharp peak at 893 cm^{-1} is characteristic of β-glycosidic linkages between the glucose units. The band at 1025 cm^{-1} can be assigned to the C—O in cellulose. The band at ~1371 cm^{-1} is assigned to the O—H bending. The band at ~1609 cm^{-1} is due to the bending mode of adsorbed water. The band at ~2899 cm^{-1} belongs to the asymmetrical stretching vibration of C—H in pyranoid ring. The band at ~3392 cm^{-1} is indicative of stretching vibration in OH group. When the ratio of ionic liquid to cellulose solution was increased from 1:3 to 1:1 or 3:1, the FTIR spectra of samples were shown in Fig. 4b and c, respectively. Both of the samples had similar FTIR spectra, compared with Fig. 4a, indicating the synthesis of similar materials. However, with the ratio of ionic liquid to cellulose solution was increased, the peak intensity at 1025 and 3392 cm^{-1} dramatically decreased (Fig. 4), indicating the decreasing cellulose concentration in the cellulose/CuO nanocomposites. Moreover, the band at ~3392 cm^{-1} in Fig. 4b and c became broader with increasing ionic liquid concentration, compared with Fig. 4a. This phenomenon was due to the interaction between the cellulose and CuO crystals. A similar phenomenon that the peak of FTIR at high wavenumber in cellulose-based nanocomposites

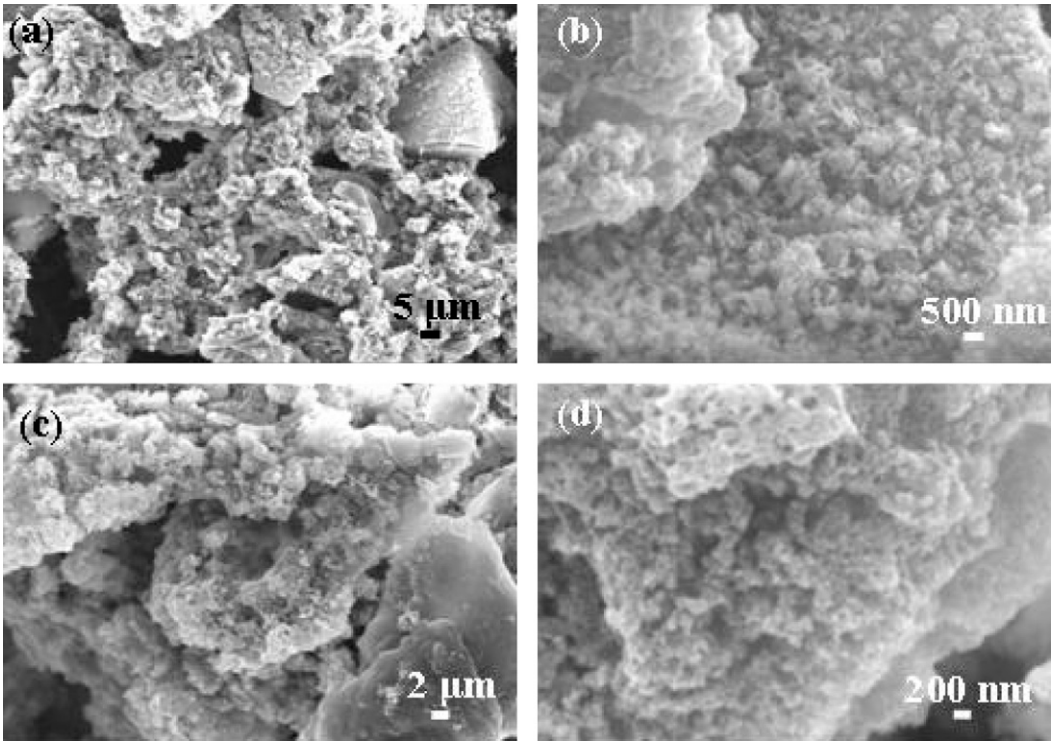

Fig. 5. SEM images of the cellulose/CuO nanocomposites prepared by microwave heating using different ratio of ionic liquid to cellulose solution at 100 °C for 20 min: (a and b) ionic liquid (5 mL)/cellulose solution (15 mL); (c and d) ionic liquid (15 mL)/cellulose solution (5 mL).

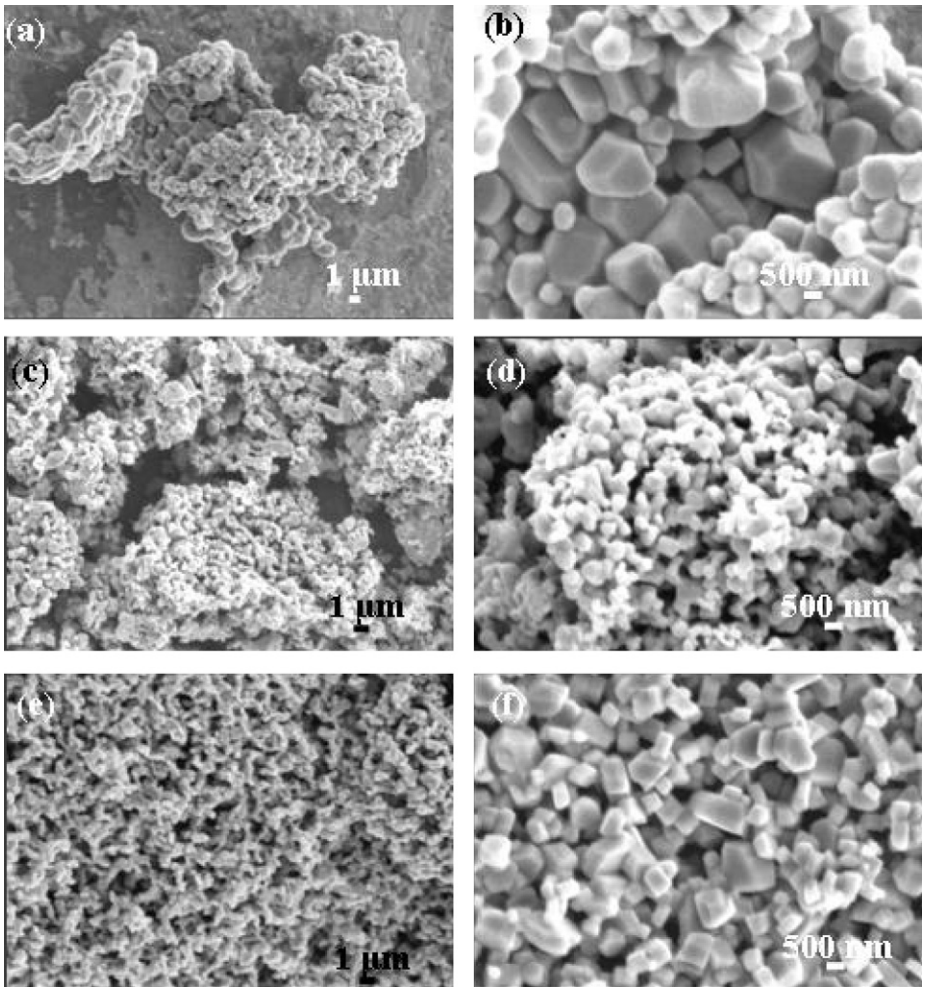

Fig. 7. SEM images of the CuO crystals by calcination of the samples at 800 °C for 3 h, which were prepared in ionic liquid (10 mL)/cellulose solution (10 mL) by microwave heating at 100 °C for different times: (a and b) 10 min; (c and d) 20 min; (e and f) 40 min.

became broader was reported for cellulose/calcium silicate (Li, Jia, Zhu, Ma, & Sun, 2010), cellulose/Fe_2O_3 nanocomposite fibers (Liu, Zhang, Zhou, & Wu, 2008), and cellulose/hydroxyapatite nanocomposites (Ma et al., 2010). This result indicated that the cellulose/CuO samples were not mechanical mixtures but composites of cellulose and CuO crystals. Of course, the growth mechanism of composition between cellulose and CuO crystals still needs to be explored.

The effect of the ratio of ionic liquid to cellulose solution on the shape of samples was displayed in Fig. 5. When the ratio of ionic liquid to cellulose solution was 1:3, the CuO bundles consisted of nanosheets were dispersed on the surface of cellulose (Fig. 5a and b). When the ratio of ionic liquid to cellulose solution was 1:1, the cellulose/CuO nanocomposites consisted of CuO irregular nanosheets, as shown in Fig. 2. When the ratio of ionic liquid to cellulose solution was 3:1, the CuO nanoparticles were dispersed on the surface of cellulose (Fig. 5c and d). From Figs. 2 and 5, one can observe the morphology varies with ionic liquid concentration, indicating that the ratio of ionic liquid to cellulose solution played an important role in the shapes of CuO in cellulose/CuO nanocomposites. In view of the above results, one can conclude that the CuO nanosheets were obtained at low ionic liquid concentration and/or short heating time; meanwhile, CuO nanoparticles were obtained at high ionic liquid concentration and/or long heating time.

The thermal behavior of cellulose/CuO nanocomposites synthesized in the mixed solution of ionic liquid (10 mL)/cellulose solution (10 mL) by microwave heating at 100 °C for 20 min, was investigated with TG and DSC (Fig. 6). TG curve shows that the major weight loss took place from 180 °C to 436 °C, which was due to the thermal decomposition of cellulose in the cellulose/CuO nanocomposites. The total weight loss of the composites was measured to be 77.3%. The DSC curve shows an endothermic peak located between 180 °C and 448 °C. The temperature range of the endothermic peak in the DSC curve fits with that of weight loss in the TG curve. Cellulose was usually used as a template for the synthesis of inorganic materials by thermal treatment of the cellulose-based composites. The mesoporous titania networks consisting of anatase nanowires were fabricated by using bacterial cellulose membranes as template (Zhang & Qi, 2005). In view of the results of TG and DSC, the temperature of 800 °C was chosen to ensure the complete decomposition of cellulose and the thermal transformation of the precursor (cellulose/CuO nanocomposites) to CuO crystals.

CuO samples prepared by thermal treatment of precursors (cellulose/CuO nanocomposites) at 800 °C for 3 h in air were investigated with SEM, as shown in Fig. 7. CuO crystals with different morphologies and sizes were obtained by thermal transformation of different precursors (cellulose/CuO nanocomposites), which were synthesized in ionic liquid (10 mL)/cellulose solution (10 mL) by microwave heating at 100 °C for 10 min, 20 min, and 40 min, respectively. When the cellulose/CuO nanocomposites synthesized at 100 °C for 10 min, 20 min, and 30 min were used as precursor, CuO crystals with polyhedral-like shape (Fig. 7a and b), irregular

particle-like shape (Fig. 7c and d), and cube-like shape (Fig. 7e and f) were obtained, respectively. The CuO crystals with big size were observed from the precursor synthesized at 100 °C for 10 min (Fig. 7a and b), however, the CuO crystals with small size and narrow size distribution were obtained from the precursor synthesized at 100 °C for 20 min and 40 min (Fig. 7c–f). The polyhedron and cube were the typical morphologies of CuO crystals. The obtained CuO crystals presented different morphologies including polyhedral, irregular particles, and cubes via thermal treatment of the cellulose/CuO nanocomposites with irregular nanosheets, nanosheets, and nanoparticles of CuO in cellulose matrix, respectively. The morphologies of precursors were not preserved after decomposition of precursors to the CuO crystals. In general, the product can be obtained through the thermal decomposition of the precursor; its morphology can be preserved during dehydration process (Liu, Wang, Xu, & Wang, 2002). However, the calcination also induced the lost of water, phase transformation, and morphology transformation during the heating procedure. CuO crystals were obtained by the growth and sintering of the cellulose/CuO nanocomposites. The shape of inorganic crystals was related to the relative growth rates of different crystal facets. The CuO nanosheets were obtained in the existence of cellulose. During the decomposition process of cellulose, the relative growth rates of different crystal facets were changed, the structure of CuO nanosheets is not stable, and chooses to aggregate and further grow to big particles, to minimize the surface energy. The CuO grain size increased as increasing annealing temperature, inducing the formation of CuO crystals with various morphologies. In the literature, nanoporous Mn_2O_3 was obtained by thermal treatment of $MnCO_3$ submicrocubes at 600 °C for 3 h in air (Yang, Zhu, Tong, & Wang, 2007). The morphology of ZnO nanocrystals evolved from nanorod to nanoparticle with an increase in the annealing temperature (Zheng et al., 2007). Hollow ZnO nanospheres were obtained by thermal treatment of ZnO nanofibers precursor (Zhu, Lu, Su, Xie, & Lan, 2012).

4. Conclusions

In summary, we report the synthesis of the cellulose/CuO nanocomposites via microwave-assisted ionic liquid method. The microwave-assisted ionic liquid method for the synthesis of cellulose-based nanocomposites combined three major green chemistry principles: using environmentally friendly method, greener solvents, and sustainable resources. The cellulose solution was obtained by the dissolution of microcrystalline cellulose in NaOH-urea aqueous solution. XRD results indicated that the crystallinity of CuO increased with increasing microwave-heating time. SEM micrographs indicated that the CuO shape changed from nanosheets to bundles consisted of irregular nanosheets, and to particles with increasing microwave-heating time. The ratio of ionic liquid to cellulose solution played an important role in the shape and microstructure of CuO in nanocomposites. The CuO with polyhedral-like shape, particles, cube-like shape were obtained by thermal transformation of different precursors (cellulose/CuO nanocomposites). This synthetic strategy reported here opens a new window to the high value-added applications of cellulose.

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