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Environmentally friendly microwave ionic liquids synthesis of hybrids from cellulose and AgX (X = Cl, Br)

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ABSTRACT

The purpose of this article was to explore an environmentally friendly strategy to synthesis of biomass-based hybrids. Herein, microwave-assisted ionic liquids method was applied to fabricate the hybrids from cellulose and AgX (X = Cl, Br) using cellulose and $AgNO_3$. The ionic liquids act simultaneously as a solvent, a microwave absorber, and a reactant. Ionic liquids provided Cl^- or Br^- to the synthesis of AgCl or AgBr crystals; thus no additional reactant is needed. The products are characterized by X-ray powder diffraction (XRD), Fourier transform infrared spectrometry (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and differential thermal analysis (DTA). The cellulose–Ag/AgCl hybrid and cellulose–Ag/AgBr hybrid were also obtained by using cellulose–AgCl and cellulose–AgBr hybrids as precursors. This environmentally friendly microwave-assisted ionic liquids method is beneficial to the hybrids with high dispersion.

1. Introduction

Recently, microwave-assisted ionic liquids method has received much attention in academia and industry as an environmentally friendly synthetic strategy, combining the advantages of microwave heating and ionic liquids (Leadbeater, Torenius, & Tye, 2004; Mallakpour & Rafiee, 2011; Martinez-Palou, 2010). As we all know, ionic liquids efficiently absorb microwave energy due to its high polarity. In the literatures, microwave-assisted ionic liquids method was widely used in polymerization and modification of polymers (Mallakpour & Rafiee, 2011) and organic synthesis (Leadbeater et al., 2004). Levulinic acid was produced from cellulose via microwave-assisted synthesis in SO_3H-functionalized ionic liquids (Ren, Zhou, & Liu, 2013). There have been a few reports on the synthesis of materials and biomass-based materials by microwave-assisted ionic liquid method. A variety of iron oxide nanostructures such as α-FeOOH hollow spheres, β-FeOOH architectures, α-Fe_2O_3 hollow spheres, and Fe_3O_4 hollow spheres were synthesized by the microwave hydrothermal ionic liquids method (Cao & Zhu, 2009). Flower-like Cu_2O architectures with high photochemical activity was obtained in ionic liquid ([BMIM]BF_4) by the assistance of microwave irradiation (Li et al., 2011a). More recently, Xu and Zhu (2012) reported the synthesis of CaF_2 double-shelled hollow microspheres, MgF_2 hollow spheres, and SrF_2 hollow microspheres via microwave-assisted ionic liquids solvothermal method. It was found that ionic liquid [Bmim]BF_4 was used as both solvents, microwave absorbs, and reactants. Our group applied microwave-assisted ionic liquids method to the synthesis of cellulose-based materials such as cellulose/calcium silicate (Jia, Li, Ma, & Sun, 2011a, 2011b), cellulose/carbonated hydroxyapatite (Ma, Jia, Li, & Sun, 2011), cellulose/F-substituted hydroxyapatite (Jia, Li, Ma, & Sun, 2012), cellulose/CuO (Ma et al., 2013b), and cellulose/$CaCO_3$ (Ma, Dong, Fu, Li, & Sun, 2013a). As far as we know, the synthesis of the hybrids from cellulose and AgCl/AgBr by microwave-assisted ionic liquids method has not been reported yet.

Hybrids from cellulose and Ag have been extensively explored (Csoka et al., 2012; He, Kunitake, & Watanabe, 2005; H. Liu, Song, Shang, Song, & Wang, 2012; Wu, Zhao, Zhang, & Xu, 2012). However, there have been only few literatures reporting on the synthesis of hybrids from cellulose and AgX (X = Cl, Br). Silver chloride (AgCl) is a photosensitive material and was widely used in various applications such as photometry, plating, electrochemical, and biomedical fields. AgCl with antimicrobial activity was embedded in silica matrix on cotton fabric (Tomsic et al., 2009). AgCl nanoparticles were carried out under ambient conditions in nanoporous bacterial cellulose membranes, exhibiting high hydrophilic ability and strong antimicrobial activity (Hu

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et al., 2009). Polymer/silver bromide composites were useful as antimicrobial coating in the biomedical field (Sambhy, MacBride, Peterson, & Sen, 2006). Moreover, Ag/AgCl hybrids also exhibited high photocatalytic activity and good reusability for decomposing organic pollutants (Chen, Yoo, & Huang, 2012) and better antibacterial properties on *Escherichia coli*, *Staphylococcus aureus* and *Bacillus subtilis* (Dong, Liang, & Gong, 2012). Recently, C. Liu, et al. (2012) reported the fabrication of antimicrobial bacterial cellulose–Ag/AgCl nanocomposite using bacteria as versatile biofactory. In previous studies, cellulose–AgCl hybrids were synthesized using cellulose and $AgNO_3$ in *N*,*N*-dimethylacetamide solvent by microwave-assisted method (Li et al., 2012).

In this study, we report the synthesis of the hybrids from cellulose and AgX (X = Cl, Br) by microwave-assisted ionic liquids method. The ionic liquids act as a solvent, a microwave absorber, and a reactant. Using the cellulose–AgCl and cellulose–AgBr hybrids as precursors, cellulose–Ag/AgCl hybrids and cellulose–Ag/AgBr hybrids were obtained by adding reducing agent.

2. Experimental

Chemicals used in these experiments were analytical reagent and were purchased and used without further purification. Three types of ionic liquids including 1-butyl-3-methylimidazolium chloride ($C_8H_{15}ClN_2$, BmimCl, molecular weight of 174.67, 98.0%), 1-allyl-3-methylimidazolium chloride ($C_7H_{11}ClN_2$, AmimCl, molecular weight of 158.63, 99.0%), and 1-butyl-3-methylimidazolium bromide ($C_8H_{15}BrN_2$, BmimBr, molecular weight of 219.12, 99.0%) were used in this experiment. In a typical procedure, 0.162 g of microcrystalline cellulose was added into 8.10 g ionic liquids under vigorous stirring at 130 °C for 10 min by microwave heating to obtain a homogeneous cellulose solution. Then, 0.340 g of $AgNO_3$ was added into the above cellulose solution under vigorous magnetic stirring. The solution was continually heated to 130 °C for 15 min by microwave heating. The microwave oven used for sample fabrication 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 microwave reactor is an open reaction system. The product was filtered, washed with water and ethanol three times, dried in air at 60 °C.

X-ray powder diffraction (XRD) patterns were recorded 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) spectra was collected 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} at 4 cm^{-1} resolution and 128 scans/sample. Scanning electron microscopy (SEM) images were taken with a Hitachi 3400 N scanning electron microscope. All samples were coated with a layer of Au prior to examination by SEM. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out on a simultaneous thermal analyzer (NETZSCH STA 449F3) at a heating rate of 10 °C min^{-1} in high-purity N_2.

3. Results and discussion

It is well known that ionic liquids are the better solvent to dissolve cellulose. When the cellulose was dissolved in ionic liquids via microwave heating, the phase of cellulose changed from cellulose type I to type II. The peak intensity dramatically decreased,

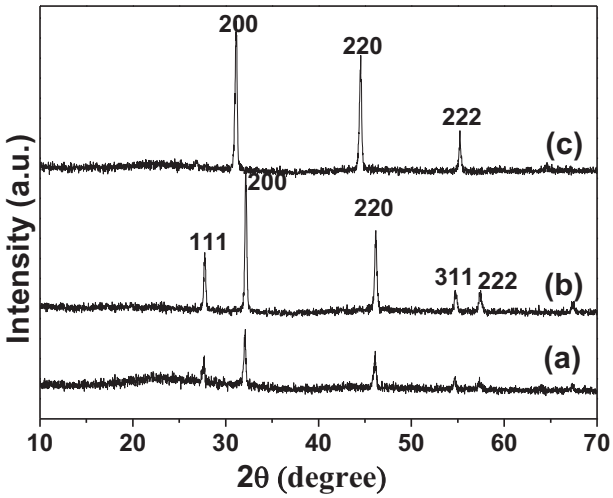

Fig. 1. XRD patterns of (a, b) the cellulose–AgCl and (c) cellulose–AgBr hybrids prepared by microwave heating using different types of ionic liquids: (a) BmimCl; (b) AmimCl; and (c) BmimBr.

indicating the decreasing crystallinity of cellulose. This result is in accord with the previous report (Ma et al., 2011). By adding the $AgNO_3$ into the above solution, the hybrids from cellulose and AgX (X = Cl and Br) were synthesized via microwave heating at 130 °C. Using BmimCl and AmimCl as solvents, the ionic liquids provided Cl^- to the synthesis of AgCl crystals. One can see that both the samples consisted of a single phase of well-crystallized AgCl with a cubic structure (JCPDS 31-1238) (Fig. 1a and b). No peaks from Ag were observed. When BmimBr was chosen as solvent, the ionic liquid provided Br^- to the synthesis of AgBr crystals. From Fig. 1c, the sample consisted of a single phase of well-crystallized AgBr with a cubic structure (JCPDS 06-0438). From Fig. 1, one can conclude that ionic liquids acted as the solvents for the dissolution of cellulose and the reactants for the synthesis of AgX (X = Cl and Br). In the literature, Xu and Zhu (2012) used ionic liquid $[Bmim]BF_4$ as reactant to synthesize CaF_2, MgF_2, and SrF_2 via microwave-assisted solvothermal method.

The sizes of AgX (X = Cl and Brhe hybrids from cellulose and AgX were synthesized via microwave heating at 130) were calculated according to the Scherrer formula

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where K is a constant, λ is 1.5418 Å, and β is half peak width. K is assigned as 0.89. The sizes of samples synthesized in ionic liquids of BmimCl, AmimCl, and BmimBr were 34.4 nm, 36.2 nm, and 32.4 nm, respectively.

The dispersion and shape of AgX (X = Cl and Br) are very important for the applications. We investigated the dispersion and shape of hybrids from cellulose and AgX (X = Cl and Br) via SEM, as shown in Fig. 2. Using BmimCl as solvent, AgCl crystals with various shapes and sizes were observed (Fig. 2a). Although some AgCl crystals were dispersed on the surface of cellulose, it is clearly observed that there were not tightly conjunction between AgCl crystals and cellulose and the AgCl crystals did not grow using cellulose as matrix. The hybrids were not fabricated by two individual phase materials. Therefore, BmimCl was not an ideal solvent for the synthesis of hybrid from cellulose and AgCl. Using AmimCl instead of BmimCl, the AgCl crystals grew using cellulose as matrix (Fig. 2b). Magnified micrograph of the hybrid was shown in Fig. 2c. The shape and size of AgCl crystals were not clearly observed. Colloidal AgCl crystals were embedded in the cellulose substrate and few individual particles were observed outside of the cellulose, demonstrating that

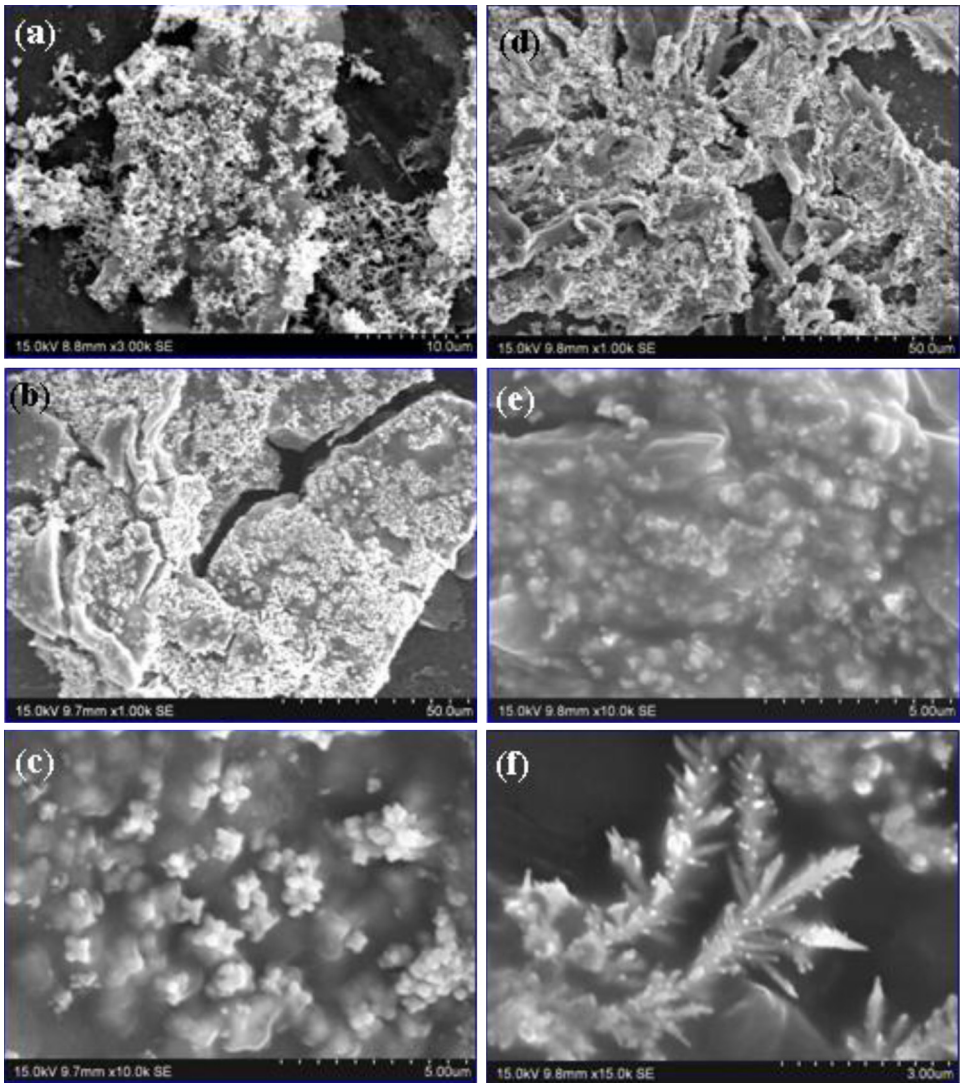

Fig. 2. SEM images of (a–c) the cellulose–AgCl and (d–f) cellulose–AgBr hybrids prepared by microwave heating using different types of ionic liquids: (a) BmimCl; (b) and (c) AmimCl; (d–f) BmimBr.

a strong bonding existed between AgCl crystals and cellulose. As indicated in Fig. 1a and b, the hybrid synthesized in AmimCl had stronger peak intensity than in BmimCl. Based on the above results, AmimCl was a better solvent to fabricate hybrid from cellulose and AgCl, compared with BmimCl. AmimCl has lower melting point (T_m = 17 °C) than that of BmimCl (T_m = 65 °C). Moreover, AmimCl has low viscosity. In this experiment, AmimCl was used as solvent for the dissolution of cellulose and fabrication of AgCl crystals. Because of high viscosity of BmimCl, the diffusion of the Ag^+ and Cl^- ions and fast nucleation were restrained. However, using AmimCl instead of BmimCl as solvent, the viscosity of the solvent decreased, conducing the formation of the AgCl crystals with a good dispersion in the cellulose matrix. Using BmimBr instead of AmimCl as solvent, similar results were obtained, as shown in Fig. 2d–f. AgBr crystals with dendrite-like shape were obvious observed in Fig. 2f. This result indicated that the hybrid from cellulose and AgBr was synthesized in ionic liquid BmimBr. Cellulose was firstly dissolved in ionic liquids of AmimCl and BmimBr. By the addition of $AgNO_3$, the synthesis of AgX (X = Cl and Br), the regeneration of cellulose, and the hybrid from cellulose and AgX (X = Cl and Br) were simultaneous carried out, inducing that the AgX (X = Cl and Br) particles were homogeneously dispersed in the cellulose matrix.

FTIR analysis is a useful tool for studying functional groups of hybrids. All the hybrids were further examined by FTIR analysis, as shown in Fig. 3. Fig. 3b and c had similar FTIR spectra, which

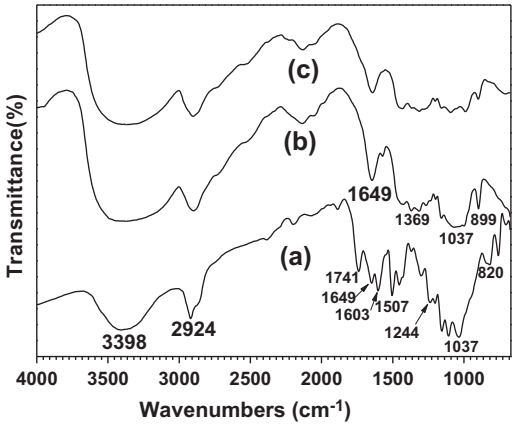

Fig. 3. FTIR spectra of (a, b) the cellulose–AgCl and (c) cellulose–AgBr hybrids prepared by microwave heating using different types of ionic liquids: (a) BmimCl; (b) AmimCl; (c) BmimBr.

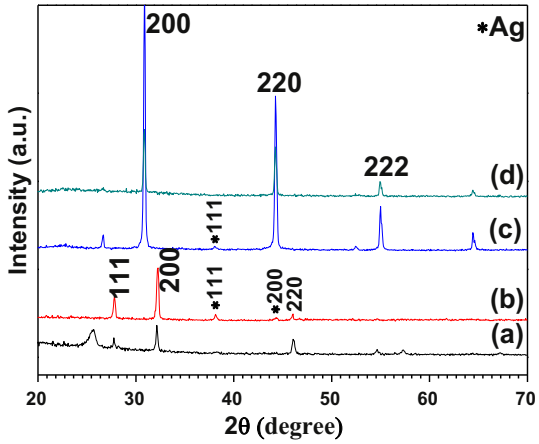

Fig. 4. XRD patterns of the cellulose–AgX/Ag hybrids prepared by microwave heating using different types of ionic liquids: (a) and (b) AmimCl; (c) and (d) BmimBr.

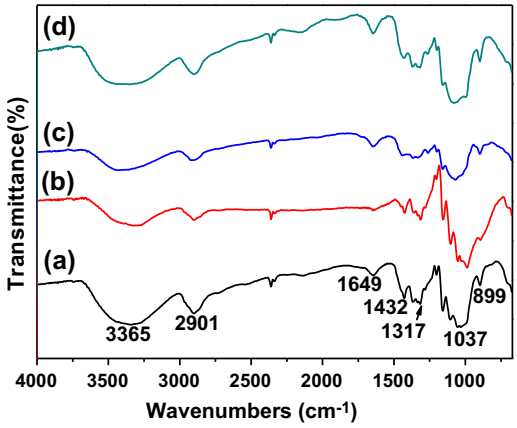

Fig. 6. FTIR spectra of the cellulose–AgX/Ag hybrids prepared by microwave heating using different types of ionic liquids: (a) and (b) BmimBr; (c) and (d) AmimCl.

displayed the characteristics of cellulose. All the peaks were in accord with the results in the literature (Ma et al., 2013b). For example, the peaks at 899, 1037, 1369, and 1649 cm^{-1} are assigned to the characteristic of β-glycosidic linkages, the C—O in cellulose, the O—H bending, and the bending mode of adsorbed water, respectively. The peaks of ionic liquids are difficult distinguished between the wide peaks at 1037 and 1369 cm^{-1} because of the overlapping. Using BmimCl as solvent, a different FTIR spectrum was observed, as shown in Fig. 3a. The characteristics of cellulose were also observed at 1037, 1244, and 2924 cm^{-1}. The peaks at 1603, 1507, 1168, and 761 cm^{-1} belonged to the stretching and bending vibrations of the C—H and the stretching vibrations of C—C and C—N in the imidazole ring of BmimCl (Jia et al., 2011b).

By adding the reducing reagent, the hybrids from cellulose and AgX can transform into cellulose–Ag hybrids or cellulose–AgX/Ag hybrids, which has widely applications in antimicrobial effects, electrical conductivity, optical properties, and oxidative catalysis. The sample was obtained using cellulose–AgCl hybrid as precursor and ascorbic acid as the reducing reagent in AmimCl via microwave heating at 130 °C for 30 min. XRD pattern of the sample was still indexed to cellulose and AgCl and no phase of Ag crystals was observed (Fig. 4a). This result implied that the obtained cellulose–AgCl hybrid had highly chemical stability. In the previous study, cellulose–Ag hybrids were obtained using ascorbic acid as the reducing reagent in LiCl/*N*,*N*-dimethylacetamide by microwave-assisted method (Li et al., 2011b). In comparison, AmimCl was used as solvent to dissolve the cellulose, and then the $AgNO_3$ and ascorbic acid were added into the ionic liquid, and the reaction was kept at 130 °C for 30 min via microwave heating. One can clearly see that the peaks of sample were indexed to mixed phases of AgCl and Ag, indicating the synthesis of cellulose–AgCl/Ag hybrids (Fig. 4b). Some Ag^+ reacted with Cl^- to form AgCl and some Ag^+ reacted with ascorbic acid to form Ag crystals during the heating procedure. However, when the cellulose–AgCl hybrid was firstly synthesized, these colloidal AgCl crystals were embedded in the

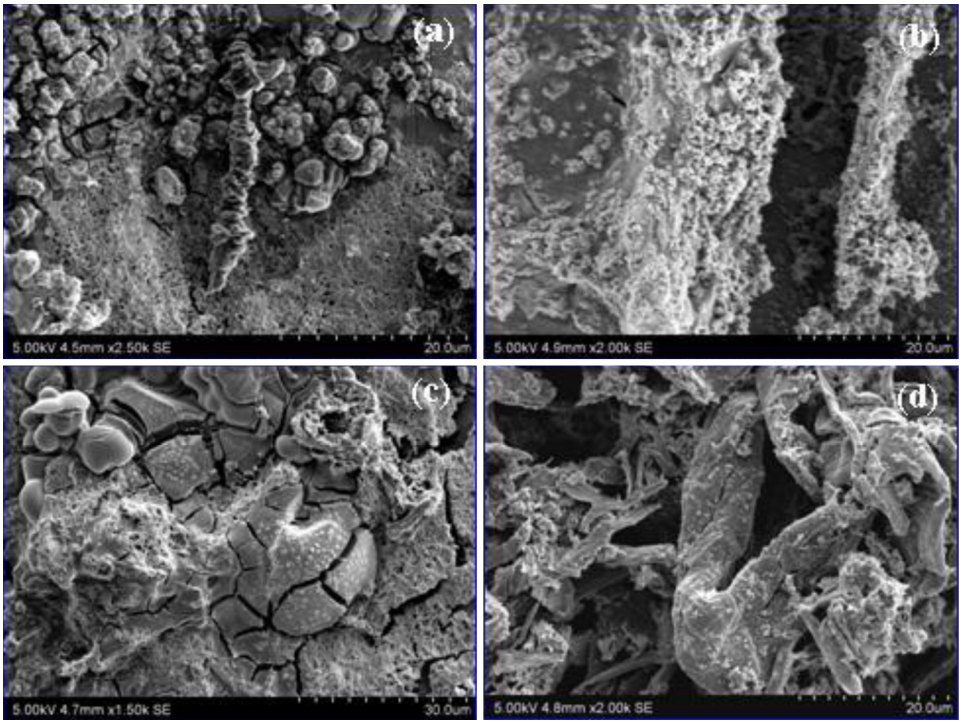

Fig. 5. SEM images of the cellulose–AgX/Ag hybrids prepared by microwave heating using different types of ionic liquids: (a) and (b) AmimCl; (c) and (d) BmimBr.

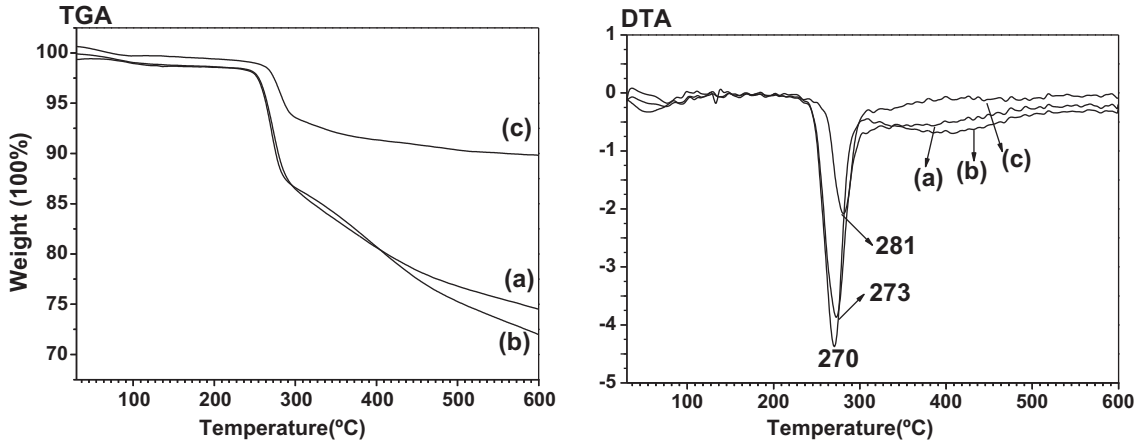

Fig. 7. TGA and DTA curves of (a, b) the cellulose–AgCl and (c) cellulose–AgBr hybrids prepared by microwave heating using different types of ionic liquids: (a) BmimCl; (b) AmimCl; and (c) BmimBr.

cellulose matrix (Fig. 2b and c), inducing that AgCl crystals did not react with ascorbic acid to form Ag crystals after adding ascorbic acid.

The chemical stability of cellulose–AgBr hybrids was further investigated. The sample was obtained using cellulose–AgBr hybrid as precursor and ascorbic acid as the reducing reagent in BmimBr via microwave heating at 130 °C for 30 min. One can obviously see that the sample consisted of the characteristic peaks of AgBr and Ag (Fig. 4c). This result indicated that the AgBr crystals were reduced to form Ag crystals by adding ascorbic acid. This result was not in accord with the results in AmimCl, indicating that the cellulose–AgCl hybrid had relative high chemical stability, compared with cellulose–AgBr hybrid. Furthermore, BmimBr was also used as solvent to dissolve the cellulose, and then the $AgNO_3$ and ascorbic acid were added simultaneously into the ionic liquid, and the reaction was kept at 130 °C for 30 min via microwave heating. The sample was indexed to AgBr and no Ag crystals were observed (Fig. 4d). The peaks intensity of AgBr dramatically decreased compared with Fig. 4c. The solubility product (*Ksp*) of AgBr is 5.0×10^{-13}, which is smaller than that of AgCl (1.8×10^{-10}). As we all know, the product is firstly obtained with low *Ksp* value under normal condition. Therefore, the AgBr crystals were fabricated when the $AgNO_3$ and ascorbic acid were added simultaneously into the ionic liquid BmimBr (Fig. 4d). Of course, the detail mechanism still need to be further explored in the near future.

Investigation has been conducted on the effect of the reducing reagent on the morphologies of the samples. When the sample was synthesized using cellulose–AgCl hybrid as precursor and ascorbic acid as the reducing reagent in AmimCl, AgCl particles were still embedded in the cellulose (Fig. 5a). However, the AgCl aggregation was also observed. The sample had similar shape and poor dispersion, compared with Fig. 2b and c. When the $AgNO_3$ and ascorbic acid were simultaneously added into the ionic liquid AmimCl, a completely different shape was observed in the cellulose–AgCl/Ag hybrids, as shown in Fig. 5b. One can clearly observe that many aggregation AgCl/Ag particles were dispersed on the surface of cellulose. These results further indicated that the Ag particles formed, inducing that the inorganic Ag particles were dispersed from inside to surface of the cellulose.

When the sample was synthesized using cellulose–AgBr hybrid as precursor and ascorbic acid as the reducing reagent in BmimBr, the cellulose–AgBr/Ag hybrids were obtained (Fig. 4c). The AgBr/Ag particles were dispersed on the surface of cellulose and AgBr/Ag aggregation was also observed (Fig. 5c). Two types of dispersion in cellulose–AgBr/Ag hybrids were observed compared with that of cellulose–AgBr hybrids (Fig. 2d–f). When the $AgNO_3$ and ascorbic acid were simultaneously added into the ionic liquid BmimBr, the cellulose–AgBr hybrids were obtained (Fig. 4c). From Fig. 5d, one can see that the AgBr particles were homogeneously dispersed in the cellulose matrix. Based on the above SEM results, one can conclude that the addition of reducing reagent dramatically changed dispersion and shape in the cellulose–AgX (X = Cl and Br) hybrids.

Investigation has been also conducted on the effect of the reducing reagent on the functional groups samples. Using ascorbic acid as the reducing reagent in BmimBr, both the FTIR spectra displayed similar characteristics of cellulose (Fig. 6a and b). However, using ascorbic acid as the reducing reagent in AmimCl, the peaks at 1037 and 1317 cm^{-1} became broader (Fig. 6c and d). This result was due to the interaction between AgCl/Ag particles and cellulose.

The thermal stability of the hybrids from cellulose and AgX (X = Cl, Br) was further explored with TGA and DTA. TGA and DTA curves for the cellulose–AgX (X = Cl, Br) hybrids synthesized in BmimCl, AmimCl, and BmimBr are shown in Fig. 7, respectively. All the samples exhibited the obvious weight loss from 230 to 300 °C, as shown in Fig. 7, which were probably caused by thermal degradation of cellulose. One can clearly see the corresponding exothermic peaks at about 273, 270, and 281 °C in the DTA curves, testifying that the TGA profiles are in good agreement with the DTA results of these cellulose–AgX (X = Cl, Br) hybrids. The total weight losses of the cellulose–AgX (X = Cl, Br) hybrids synthesized in BmimCl, AmimCl, and BmimBr were ~25.4%, 28.0%, and 10.2% from room temperature to 600 °C in the TGA curves, respectively. The cellulose–AgCl hybrids synthesized in BmimCl and AmimCl had similar total weight losses and thermal degradation temperature. However, the cellulose–AgBr hybrids synthesized in BmimBr had relatively low total weight loss and high thermal degradation temperature, compared with cellulose–AgCl hybrids. These results indicated that the cellulose–AgCl hybrids had high percent of AgCl crystals and relatively low thermal stability and cellulose–AgBr hybrids had low percent of AgBr crystals and relatively high thermal stability.

4. Conclusions

In summary, the synthesis of the cellulose–AgX (X = Cl, Br) hybrids were reported via microwave-assisted method in ionic liquids. The ionic liquids act simultaneously as a solvent, a microwave absorber, and a reactant, which provided X^- to the synthesis of AgX crystals. The cellulose–AgCl hybrids had high percent of AgCl crystals and relatively low thermal stability; meanwhile, cellulose–AgBr hybrids had low percent of AgBr crystals and relatively high thermal stability. The reducing reagent played

an important role in the phase, shape, and dispersion of the cellulose–AgX/Ag (X = Cl, Br) hybrids. This environmentally friendly microwave-assisted ionic liquids method reported here opens a new window to the high value-added applications of cellulose.

Acknowledgments

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