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Compare study cellulose/Ag hybrids using fructose and glucose as reducing reagents by hydrothermal method

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ABSTRACT

The primary objective of this work was to evaluate the effect of reducing reagents on the hybrids from cellulose and Ag, which have been successfully synthesized by using fructose and glucose as reducing reagents via a hydrothermal method, respectively. The hybrids were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and differential thermal analysis (DTA). The influences of the various reaction parameters including the heating time, heating temperature, and types of reducing reagents on the hybrids were investigated. Silver particles can be better dispersed in the cellulose matrix by adjusting reaction parameters. Experimental results demonstrated that the types of reducing reagents played an important role in the shape and dispersion of silver particles in hybrids.

1. Introduction

Recently, lignocelluloses were attracting much attention as a sustainable alternative of fossil feedstocks to face the challenges about increasing demand of energy, chemicals, and materials (Corma, Iborra, & Velty, 2007; Huber, Iborra, & Corma, 2006; Mosier et al., 2005). The major components of lignocelluloses were cellulose, hemicellulose, and lignin. As the main component of plant cell walls, cellulose composed of glucose molecules is one of the most abundant polysaccharides in the nature. Up to now, there were many reports on the research of cellulose/silver hybrids by using cellulose as matrix (Ifuku, Tsuji, Morimoto, Saimoto, & Yano, 2009; Maneerung, Tokura, & Rujiravanit, 2008; Sureshkumar, Siswanto, & Lee, 2010). The cellulose/silver hybrids have potential applications as biomedical device, active wound dressing, bio-films, and the coating of biomedical materials. It was found that cellulose/silver hybrids displayed strong antimicrobial activity and good performance as surface-enhanced Raman scattering substrates (Maneerung et al., 2008; Marques, Nogueira, Pinto, Neto, & Trindade, 2008). In recent years, our group mainly focused on the research of cellulose/silver hybrids (Li, Jia, Ma, et al., 2011; Li, Jia, Zhu, et al., 2011), cellulose/AgCl hybrids (Li et al., 2012), cellulose/AgX (X = Cl, Br) hybrids (Dong et al., 2013), and cellulose/Ag/AgCl hybrids (Dong et al., 2014). Experimental results revealed that the matrix had a remarkable effect on the fabrication of hybrids. In the previous literature, it was reported that the lignin was difficult to be obtained from lignocelluloses via a hydrothermal method (Ma et al., 2012). Therefore, the holocellulose was chosen as the reactant in this work so as to suppress interference of lignin. It is widely known that holocellulose consists of cellulose and hemicelluloses. Hemicelluloses belong to a group of heterogeneous polysaccharides including D-xylose, L-arabinose, D-glucose, D-galactose, D-mannose, D-glucuronic acid, 4-o-methyl-α-D-glucuronic acid, and D-galacturonic acid, etc. Very few studies on the hybrids from cellulose and silver have been published using holocellulose as the reactant based on present knowledge.

As we all know, it is very important to choose an appropriate reducing reagent during the preparation of noble silver nanostructures. Until now, various chemicals including fructose (Mehta, Chaudhary, Bharti, & Gradzielski, 2012), glucose (Mehta, Chaudhary, & Gradzielski, 2010), $NaBH_4$ (Metraux & Mirkin, 2005), ascorbic acid (Sondi, Goia, & Matijevic, 2012), apiin (Kasthuri, Veerapandian, & Rajendiran, 2009), glycolaldehyde (Skrabalak, Wiley, Kim, Formo, & Xia, 2008), poly(N-vinyl-2-pyrrolidone) (Hoppe, Lazzari, Pardinas-Blanco, & Lopez-Quintela, 2006), and ethylene glycol (Sun & Xia, 2002) have been employed as reducing reagents in the synthesis of silver crystals. The types of reducing reagents played a crucial role in the shape, size, size-distribution, and dispersion of silver crystals. For example, when ethylene glycol

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was used as reducing reagent, silver particles with diameters about 100 nm were homogeneously dispersed in the cellulose substrate (Li, Jia, Ma, et al., 2011). However, ascorbic acid was employed as reducing reagent, polyhedral silver particles with diameters about 250 nm displayed a relative poor dispersion in the cellulose substrate (Li, Jia, Zhu, et al., 2011), compared with ethylene glycol as reducing reagent. Therefore, compare study about the influences of different reducing reagents on the hybrids is of great importance for the understanding of the growth mechanism of silver crystals.

In this study, hybrids from cellulose and silver have been successfully fabricated via the hydrothermal method by using (holo)cellulose as reactant, and fructose and glucose as reducing reagents, respectively. The effects of three reaction parameters including heating times, heating temperatures, and types of reducing reagents (fructose and glucose) on the hybrids were investigated in detail. It was expected that cellulose was obtained using holocellulose as the reactant by the hydrothermal method. It was believed that these hybrids were a promising antimicrobial material for the potential application in the biomedical field.

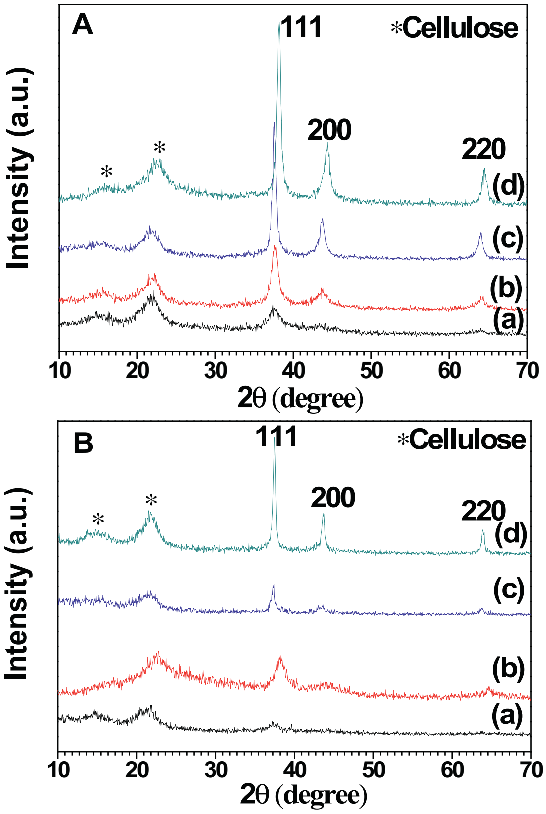

Fig. 1. XRD patterns of the hybrids from cellulose and silver using (A) fructose at 120 °C for (a) 3 h, (b) 6 h, (c) 9 h, (d) 12 h; using (B) glucose at (a) 100 °C, (b) 120 °C, (c) 140 °C, (d) 160 °C for 6 h by a hydrothermal method.

2. Experimental

2.1. Preparation of hybrids from cellulose and silver

All chemical materials and solvents used in the experiments were analytical grade reagents, and were used without further purification. In a typical synthesis of hybrids, (holo)cellulose (1.50 g) was added immediately into water (30 mL) under vigorous stirring. Then, $AgNO_3$ (0.34 g) and fructose (1.80 g) were added into the above obtained solution under vigorous stirring. The mixture solution was transferred into a 50-mL Teflon-lined stainless steel autoclave. The autoclave was maintained at 120 °C for a certain time (3, or 6, or 9, or 12 h). The product was separated from the solution by centrifugation, washed by water and ethanol three times, and dried at 60 °C for further characterization.

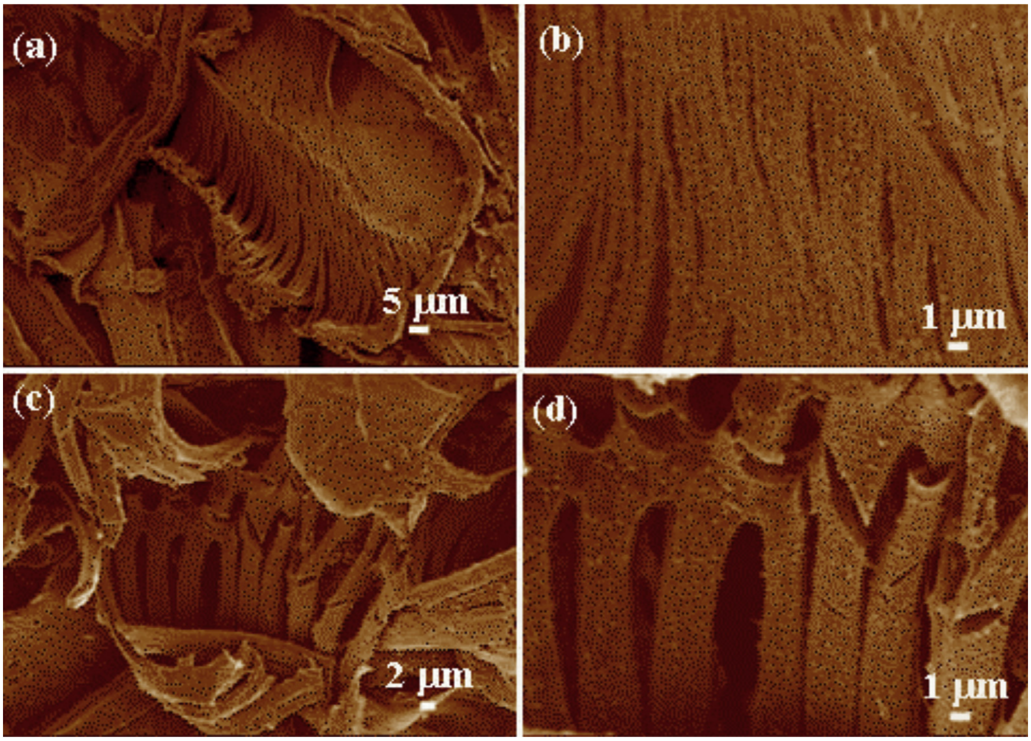

Fig. 2. SEM images of the hybrids from cellulose and silver using fructose by a hydrothermal method at 120 °C for 6 h.

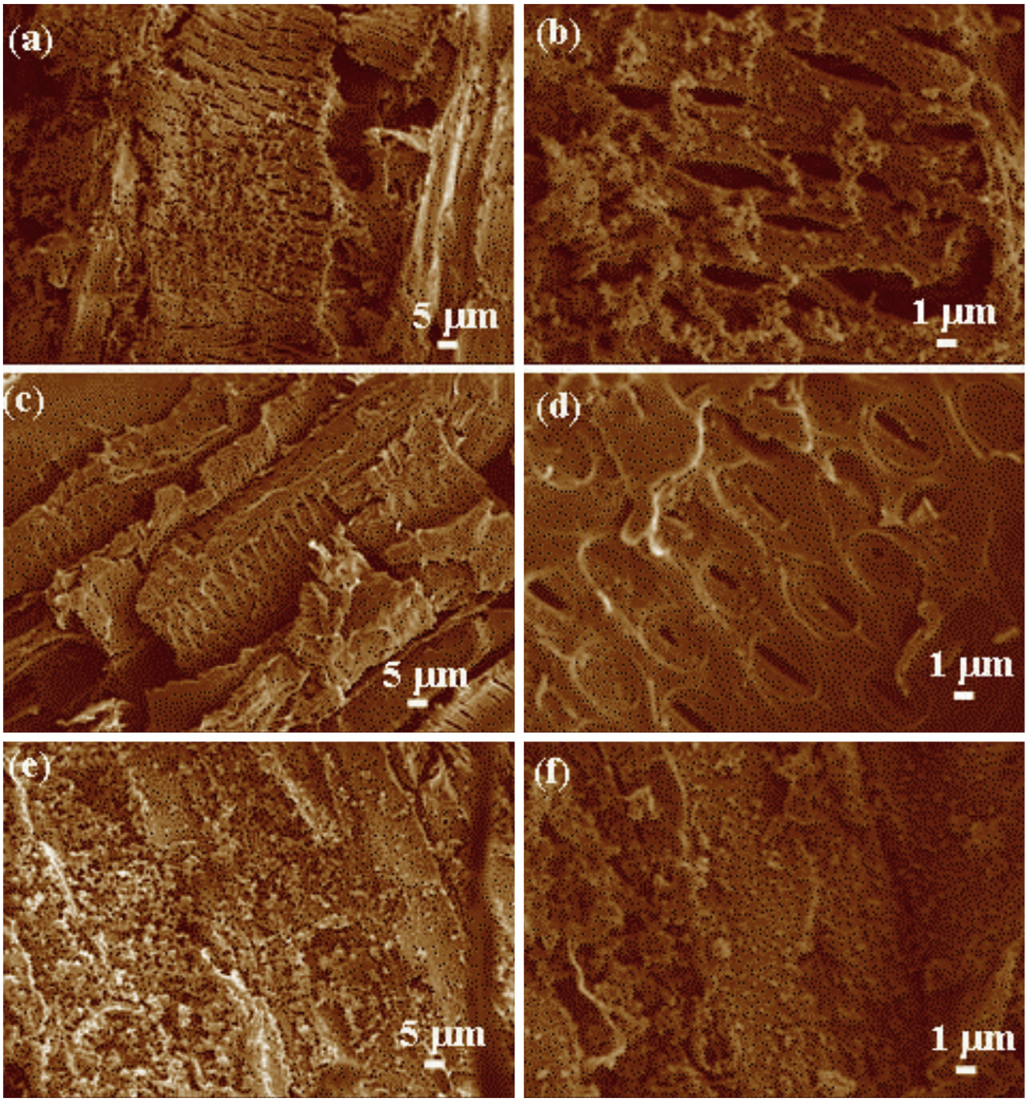

Fig. 3. SEM images of the hybrids from cellulose and silver using fructose by a hydrothermal method at 120 °C for different times: (a and b) 3 h; (c and d) 9 h; (e and f) 12 h.

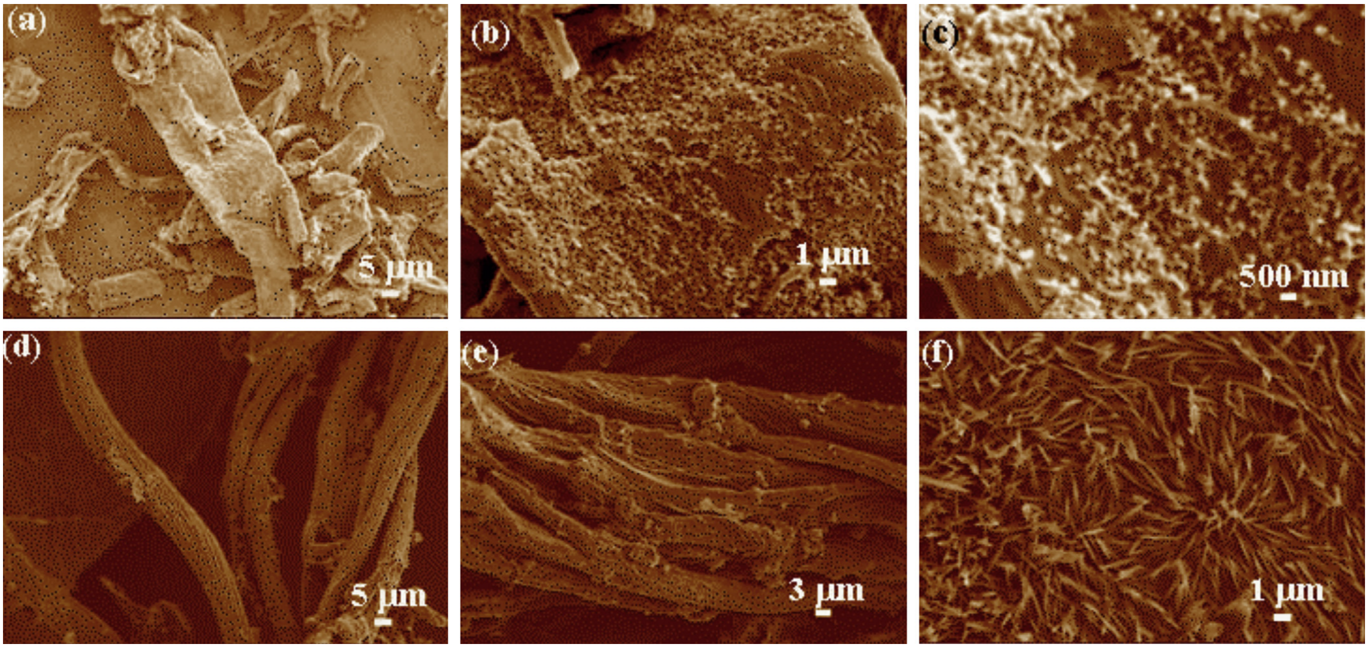

Fig. 4. SEM images of the hybrids using fructose by hydrothermal method at 120 °C for 6 h: (a–c) using microcrystalline cellulose; (d–f) using NaOH/urea.

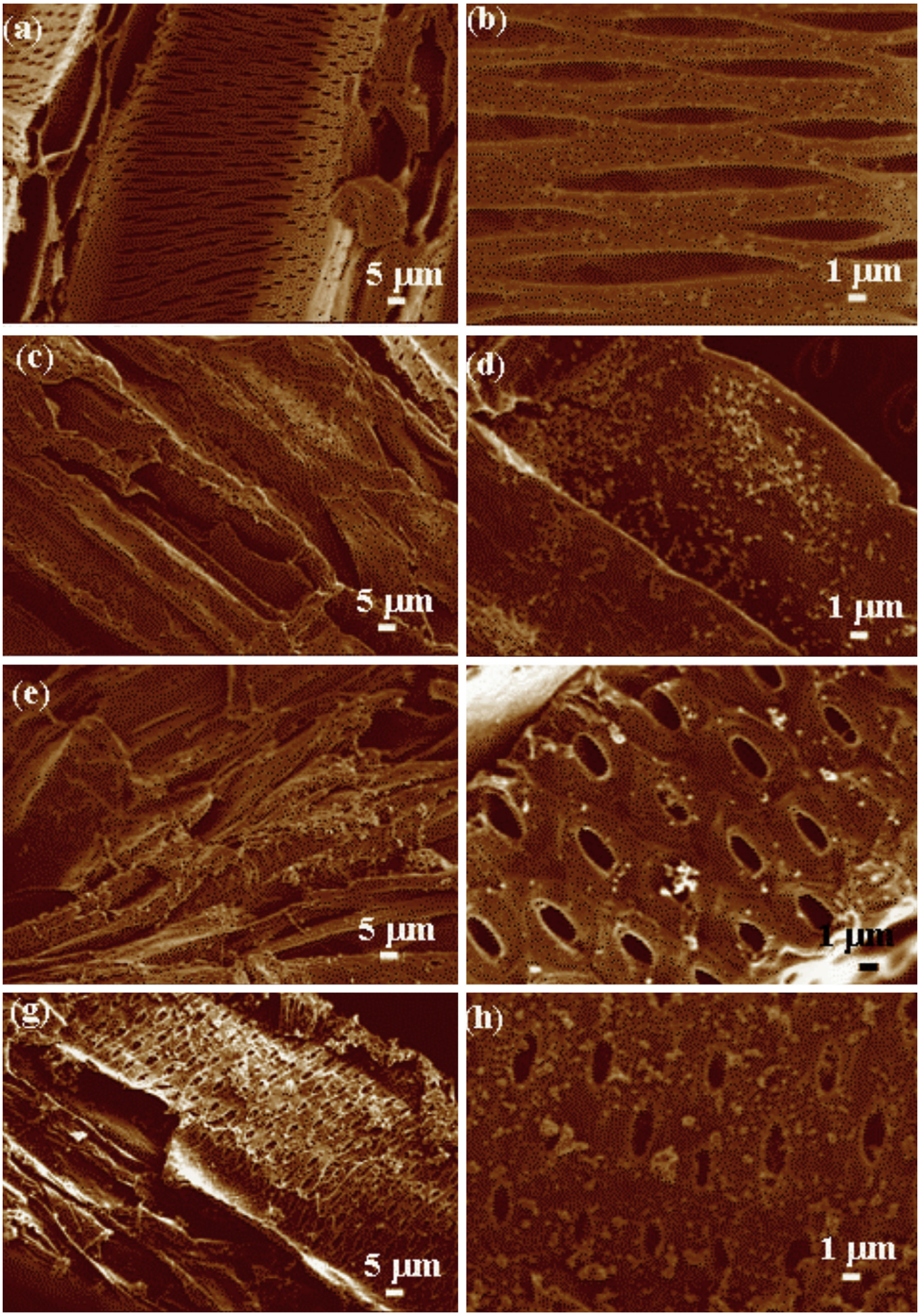

Fig. 5. SEM images of the hybrids from cellulose and silver using glucose by a hydrothermal method at different temperatures for 6 h: (a and b) 100 °C; (c and d) 120 °C; (e and f) 140 °C; (g and h) 160 °C.

2.2. *Characterization*

X-ray powder diffraction (XRD) patterns of the hybrids were carried out by using a Rigaku D/Max 2200-PC diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm) and graphite monochromator at ambient temperature. The images of hybrids were achieved by using a Hitachi 3400 N scanning electron microscopy (SEM) operating at 5 kV. All samples were Au coated prior to examination by SEM. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were taken with a heating rate of 10 °C min^{-1} from room temperature to 600 °C in flowing air with a simultaneous thermal analyzer (Netzsch, STA449F3, Germany).

3. Results and discussion

In this article, the hybrids from cellulose and silver were achieved by using fructose as reducing agent and (holo)cellulose as reactant via the hydrothermal method. Fig. 1A showed the

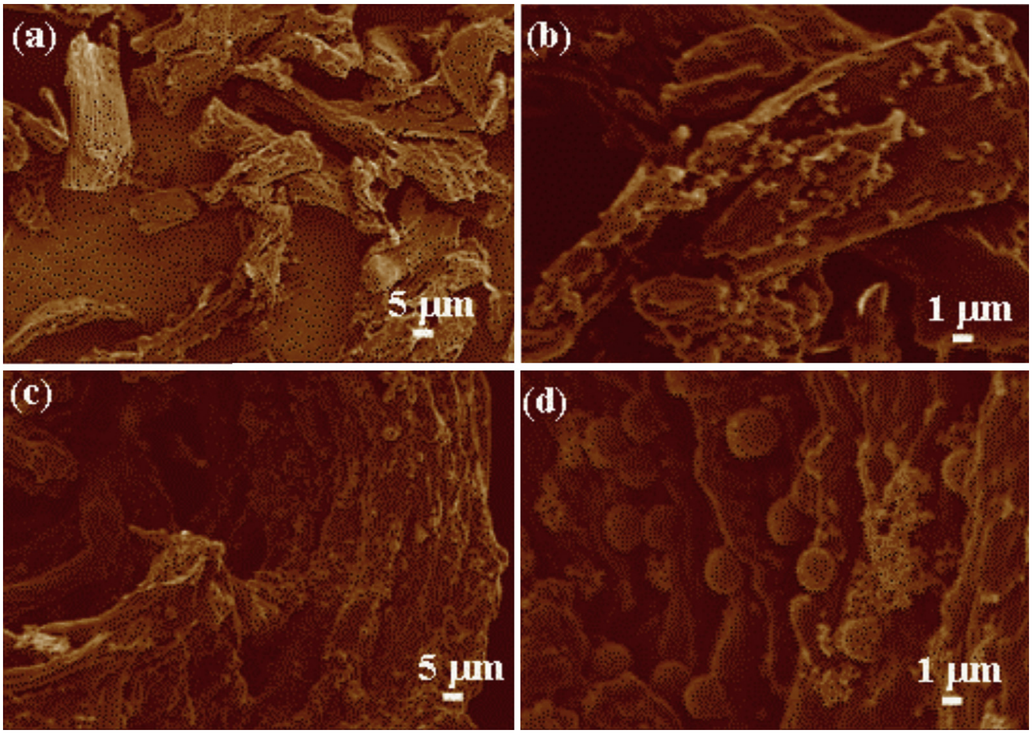

Fig. 6. SEM images of the hybrids using glucose by a hydrothermal method at 120 °C for 6 h: (a and b) using microcrystalline cellulose; (c and d) using NaOH/urea.

XRD patterns of the hybrids prepared at 120 °C for 3, 6, 9, and 12 h, respectively. One can see that all the samples consisted of the mixed phases of cellulose and well-crystallized silver with a cubic structure (JCPDS 04-0783). It is well known that (holo)cellulose consisted of cellulose and hemicelluloses, and only cellulose had crystallized phase. During the hydrothermal process, the hemicelluloses decomposed and cellulose was obtained at high temperature. The peaks of cellulose were located at $2\theta = 16.0^\circ$ and 22.6° (Marked with * in Fig. 1A). The peaks of silver were indexed to typical planes of (1 1 1), (2 0 0), and (2 2 0). No other impurities were observed in the XRD patterns of the hybrids. From Fig. 1A, one can observe that the peaks intensities of (1 1 1) and (2 0 0) planes obviously increased with increasing heating time, demonstrating the increasing crystallinity of silver crystals. Moreover, the peaks intensities of cellulose also had slightly changed. Furthermore, the sizes of silver crystals have been calculated according to Scherrer formula:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where K is constant, λ is1.5405 Å, and β is half peak width. The peak of (1 1 1) was chosen as to calculate the sizes of silver crystals. Here, K is assigned as 0.89. The sizes of silver crystals in hybrids synthesized for 3, 6, 9, and 12 h, were 9.7, 11.2, 16.8, and 16.3 nm, respectively, implying that the sizes of silver in hybrids slightly increased with increasing heating time.

The hybrids were also synthesized by using glucose instead of fructose as reducing reagent via the hydrothermal method at 100, 120, 140, and 160 °C for 6 h, respectively. The corresponding XRD patterns of the hybrids were shown in Fig. 1B. In all the samples, one can see the peaks of cellulose in hybrids at 14.9° and 21.7° (Marked with * in Fig. 1B). When the heating temperature was 100 °C, only a small weak peak was observed, belonging to the (1 1 1) plane of silver crystals (Fig. 1B(a)). When the heating temperature was increased to 120 and 140 °C, the peak intensity of (1 1 1) plane increased and the peaks of (2 0 0) and (2 2 0) planes appeared (Fig. 1B(b) and (c)). Increasing the heating temperature to 160 °C, the peaks intensities of (1 1 1), (2 0 0), and (2 2 0) planes were dramatically increased (Fig. 1B(d)), compared with Fig. 1B(a–c), indicating the better crystallinity of silver crystals. Obviously, the heating temperature favored the increasing crystallinity of silver crystals in hybrids. The sizes of silver crystals were also calculated according to the above mentioned Scherrer formula. The sizes of silver crystals synthesized at 100, 120, 140, and 160 °C were 17.3, 11.3, 22.9, and 23.9 nm, respectively. These results indicated that the sizes of silver nanostructures first decreased and then increased with increasing heating temperature. It is well known that the size of metal crystals increase with increasing heating temperature due to the growth of inorganic particles. The synthesis of inorganic particles involved the nucleation, growth, ripening, or agglomeration processes. When the heating temperature is increased from 100 to 120 °C, nucleation is the key step, inducing the decreasing sizes of silver crystals. On the contrary, when the heating temperature is increased from 120 to 140 and 160 °C, growth is the key step, inducing the increasing sizes of silver crystals in the hybrids. Of course, the intrinsic mechanism still needs to be further explored in the near future.

The images and dispersion of hybrids were further investigated with SEM. Fig. 2 displayed the SEM images of hybrids synthesized using fructose as reducing agent at 120 °C for 6 h, from which one can see the fiber-like cellulose with pore structure (Fig. 2a and c). Thousands and hundreds of silver particles abounded on the surface of cellulose (Fig. 2b and d). The silver particles displayed a better dispersion in the cellulose matrix. Decreasing the heating time to 3 h, cellulose with a similar shape was observed, as shown in Fig. 3a. Besides silver particles abounded on the surface of cellulose, congregated particles were also observed in the cellulose matrix (Fig. 3b). When the heating time was increased to 9 h, cellulose with uniform pore structure and clear surface was obtained (Fig. 3c). The number of silver particles decreased and no congregated particles were found (Fig. 3d). Increasing the heating time to 12 h, congregated particles were obviously observed on the cellulose matrix

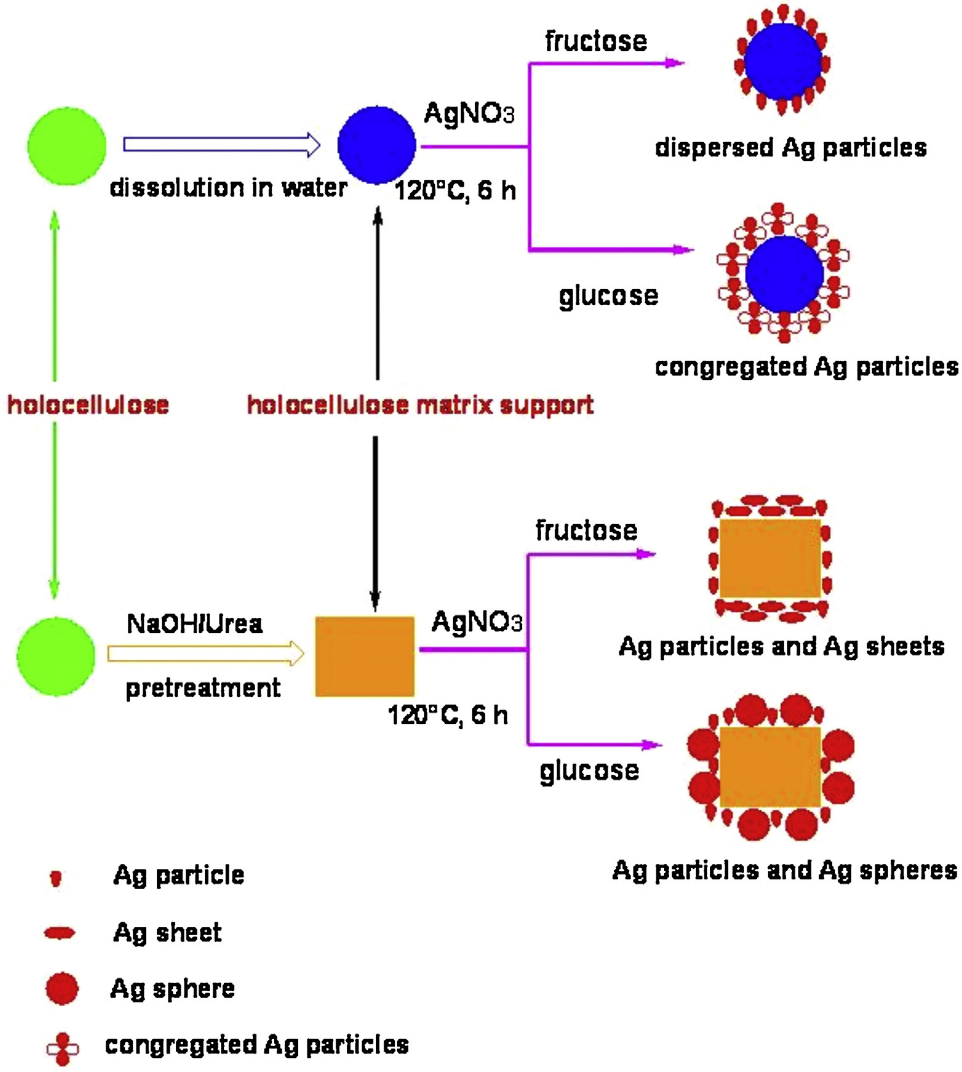

Fig. 7. Schematic illustration of formation process of hybrids from cellulose and silver using fructose and glucose as reducing agent, respectively.

(Fig. 3e and f). From Figs. 2 and 3, one can see the dispersion and congregate degree of silver particles in hybrids. Based on the results of Figs. 2 and 3, when the heating time was 6 h, silver particles had better dispersion on the cellulose matrix, compared with the others. Therefore, choosing appropriate time is important for the preparation of hybrids with good dispersion.

The influence of types of cellulose and pretreatment of (holo)cellulose on the hybrids was also investigated. The hybrids were synthesized via the hydrothermal method at 120 °C for 6 h by using microcrystalline cellulose instead of (holo)cellulose, keeping the other conditions the same. One can see that microcrystalline cellulose displayed irregular fiber-like shape (Fig. 4a). Silver particles were dispersed on the surface of cellulose (Fig. 4b and c). Compared to Fig. 2, the size of silver particles was obviously increased, ascribing that the microcrystalline cellulose had an effect on the size of silver particles. In addition, the (holo)cellulose was previously dispersed in the NaOH/urea solution, favoring for the growth of silver particles in the cellulose matrix. (Holo)cellulose (1.50 g) was added immediately into the NaOH/urea aqueous solution (37.13 g, 7:12 in wt%) under vigorous stirring at room temperature, and then the suspension solution was cooled down to −12 °C for 12 h. The obtained solution was applied to fabricate the hybrids of cellulose and silver. The corresponding SEM images were shown in Fig. 4d–f. One can observe that cellulose had fiber-like shape and several micrometers size (Fig. 4d and e). Silver sheets were also observed at the surface of fiber-like cellulose, as shown in Fig. 4f. In view of the SEM results, one can conclude that hybrids synthesized by using microcrystalline cellulose or by the pretreatment of (holo)cellulose in NaOH/urea solution had completely different shapes, demonstrating that reaction parameters were very important for the synthesis of hybrids with good size, shape, and dispersion.

The influences of glucose on the shape of hybrids of cellulose and silver were also explored. Fig. 5 displayed the SEM images of hybrids synthesized by using glucose as reducing reagent via the hydrothermal method at 100, 120, 140, and 160 °C for 6 h, respectively. From Fig. 5, one can still see similar cellulose with fiber-like shape and uniform pore structure, implying that the glucose had slight effect on the shape of cellulose. When the heating temperature was 100 °C, the silver particles were homogeneously dispersed in the cellulose matrix (Fig. 5a and b). When the heating temperature was increased to 120 °C, the congregate degree of silver particles increased (Fig. 5c and d). Increasing the heating temperature to 140 and 160 °C, the uniform pore structures were clearly observed (Fig. 5e–h). Especially, when the heating temperature was 160 °C, the highly congregated silver particles were obtained and

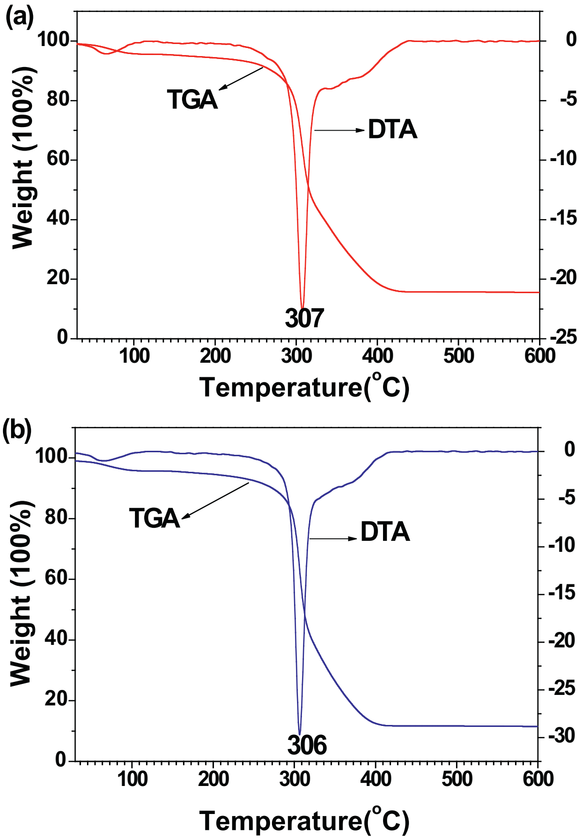

Fig. 8. TGA and DTA curves of the hybrids prepared by a hydrothermal method at 120 °C for 6 h: (a) using fructose; (b) using glucose.

the size of silver particles was obviously increased, compared with the others. In view of these results, one can conclude that the heating temperature played an important role in the dispersion of silver particles in hybrids.

The influences of types of cellulose and pretreatment of (holo)cellulose on the hybrids were also investigated by using glucose as reducing reagent. The hybrids were synthesized via the hydrothermal method at 120 °C for 6 h by using microcrystalline cellulose instead of (holo)cellulose, keeping the other conditions the same. One can see that microcrystalline cellulose still displayed irregular fiber-like shape (Fig. 6a and b). But the size of silver particles was obviously bigger than that using fructose as reducing reagent (Fig. 4a–c). Moreover, compared to Fig. 4a–c, the silver particles had badly dispersion in hybrids. These results further indicated that the types of reducing reagents had a big effect on the dispersion of silver particles in hybrids. In addition, the (holo)cellulose was previously dispersed in the NaOH/urea solution. The hybrids synthesized by using glucose as reducing reagent also displayed a different shape, as shown in Fig. 6c and d. Congregated cellulose fibers were observed (Fig. 6c). Beside silver particles, the spheres with micrometer size were also obtained on the surface of congregated cellulose fibers (Fig. 6d). No silver sheets existed. Only using glucose instead of fructose as reducing reagent, keeping the other conditions the same, the shape of cellulose and silver crystals changed, demonstrating that reducing reagent was the key reaction parameter in the synthesis of hybrids.

Fig. 7 displays the schematic illustration of formation process of hybrids from cellulose and silver using fructose and glucose as reducing agents, respectively. One can clearly see that dispersed silver particles were observed using fructose as reducing agent in water; meanwhile, congregated silver particles were obtained using glucose as reducing agent in water. Moreover, it was found that silver with particles and sheets were observed using fructose as reducing agent in NaOH/urea solution; meanwhile, silver with particles and spheres were obtained using glucose as reducing agent in NaOH/urea solution. These experimental results demonstrated that the solvents and reducing agents played a crucial role in the morphologies and dispersion of silver in hybrids. It was supposed that the reducing ability of glucose induced the congregated silver particles, compared with that of fructose. When the (holo)cellulose was pretreated in NaOH/urea solution by the hydrothermal method, hemicellulose was released easily, displaying a reducing ability and inducing the synthesis of silver with complex shapes. Moreover, as described above, it seems that the cellulose from (holo)cellulose displayed different shapes, compared with the microcrystalline cellulose.

Thermal stability is very important for the applications of polymer-based hybrids. The thermal stability of the hybrids from cellulose and silver was further explored with TGA and DTA (Fig. 8). Using fructose as reducing reagent, the hybrids had obvious weight loss and were measured to be 84.1% from 220 to 426 °C in the TGA curve (Fig. 8a). The weight loss was assigned to the thermal decomposition of cellulose. The DTA curve in Fig. 8a displays an obvious endothermic peak at 307 °C, which fits well with that of weight loss in the TGA curve. However, using glucose instead of fructose as reducing reagent, the hybrids were measured to be 88.2% from 220 to 410 °C in the TGA curve (Fig. 8b). These results indicated that the high percent of cellulose and low percent of silver were obtained in the hybrids. The DTA curve in Fig. 8b displays a similar endothermic peak at 306 °C. In view of the TGA and DTA results, one can see that the reducing reagents had an effect on the weight loss and had a slight effect on the weight loss zone.

4. Conclusions

In summary, the synthesis of hybrids from cellulose and silver was carried out using fructose or glucose as reducing reagent by the hydrothermal method. The silver particles displayed a better dispersion in the cellulose matrix. The reaction parameters including the heating time, heating temperature and types of reducing reagents played an important role in the shape and dispersion of silver structures in hybrids. It was found that dispersed silver particles and silver with particles and sheets were observed using fructose as reducing agent in water and NaOH/urea solution, respectively; meanwhile, congregated silver particles and silver with particles and spheres were obtained using glucose as reducing agent in water and NaOH/urea solution, respectively. Using glucose instead of fructose as reducing reagent, the high percent of cellulose and low percent of silver were obtained in the hybrids. It is expected that these hybrids might be a promising antibacterial candidate for the applications in biomedical field. This green synthetic strategy reported here opens a new window to the high value-added applications of biomass.

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References

Corma, A., Iborra, S., & Velty, A. (2007). Chemical routes for the transformation of biomass into chemicals. *Chemical Reviews*, *107*, 2411–2502.

Dong, Y. Y., Deng, F., Zhao, J. J., He, J., Ma, M. G., Xu, F., et al. (2014). Environmentally friendly ultrosound synthesis and antibacterial activity of cellulose/Ag/AgCl hybrids. *Carbohydrate Polymers*, *99*, 166–172.

Dong, Y. Y., He, J., Sun, S. L., Ma, M. G., Fu, L. H., & Sun, R. C. (2013). Environmentally-friendly microwave ionic liquids synthesis of hybrids from cellulose and AgX (X = Cl, Br). *Carbohydrate Polymers*, *98*, 168–173.

Hoppe, C. E., Lazzari, M., Pardinas-Blanco, I., & Lopez-Quintela, M. A. (2006). One-step synthesis of gold and silver hydrosols using poly(N-vinyl-2-pyrrolidone) as a reducing agent. *Langmuir*, *22*, 7027–7034.

Huber, G. W., Iborra, S., & Corma, A. (2006). Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering. *Chemical Reviews*, *106*, 4044–4098.

Ifuku, S., Tsuji, M., Morimoto, M., Saimoto, H., & Yano, H. (2009). Synthesis of silver nanoparticles templated by TEMPO-mediated oxidized bacterial cellulose nanofibers. *Biomacromolecules*, *10*, 2714–2717.

Kasthuri, J., Veerapandian, S., & Rajendiran, N. (2009). Biological synthesis of silver and gold nanoparticles using apiin as reducing agent. *Colloids and Surfaces B: Biointerfaces*, *68*, 55–60.

Li, S. M., Fu, L. H., Ma, M. G., Zhu, J. F., Sun, R. C., & Xu, F. (2012). Simultaneous microwave-assisted synthesis, characterization, thermal stability, and antimicrobial activity of cellulose/AgCl nanocomposites. *Biomass and Bioenergy*, *47*, 516–521.

Li, S. M., Jia, N., Ma, M. G., Zhang, Z., Liu, Q. H., & Sun, R. C. (2011). Cellulose-silver nanocomposites: microwave-assisted synthesis, characterization, their thermal stability, and antimicrobial property. *Carbohydrate Polymers*, *86*, 441–447.

Li, S. M., Jia, N., Zhu, J. F., Ma, M. G., Xu, F., Wang, B., et al. (2011). Rapid microwave-assisted preparation and characterization of cellulose–silver nanocomposites. *Carbohydrate Polymers*, *83*, 422–429.

Ma, M. G., Jia, N., Zhu, J. F., Li, S. M., Peng, F., & Sun, R. C. (2012). Isolation and characterization of hemicelluloses extracted by hydrothermal pretreatment. *Bioresource Technology*, *114*, 677–683.

Maneerung, T., Tokura, S., & Rujiravanit, R. (2008). Impregnation of silver nanoparticles into bacterial cellulose for antimicrobial wound dressing. *Carbohydrate Polymers*, *72*, 43–51.

Marques, P. A. A. P., Nogueira, H. I. S., Pinto, R. J. B., Neto, C. P., & Trindade, T. (2008). Silver-bacterial cellulosic sponges as active SERS substrates. *Journal of Raman Spectroscopy*, *39*, 439–443.

Mehta, S. K., Chaudhary, S., Bharti, B., & Gradzielski, M. (2012). Correspondence via electron and charge carrier dynamics of silver nanoparticles with organic dyes. *Science of Advanced Materials*, *4*, 78–92.

Mehta, S. K., Chaudhary, S., & Gradzielski, M. (2010). Time dependence of nucleation and growth of silver nanoparticles generated by sugar reduction in micellar media. *Journal of Colloid and Interface Science*, *343*, 447–453.

Metraux, G. S., & Mirkin, C. A. (2005). Rapid thermal synthesis of silver nanoprisms with chemically tailorable thickness. *Advanced Materials*, *17*, 412.

Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y. Y., Holtzapple, M., et al. (2005). Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology*, *96*, 673–686.

Skrabalak, S. E., Wiley, B. J., Kim, M., Formo, E. V., & Xia, Y. N. (2008). On the polyol synthesis of silver nanostructures: Glycolaldehyde as a reducing agent. *Nano Letters*, *8*, 2077–2081.

Sondi, I., Goia, D. V., & Matijevic, E. (2003). Preparation of highly concentrated stable dispersions of uniform silver nanoparticles. *Journal of Colloid and Interface Science*, *260*, 75–81.

Sun, Y. G., & Xia, Y. N. (2002). Shape-controlled synthesis of gold and silver nanoparticles. *Science*, *298*, 2176–2179.

Sureshkumar, M., Siswanto, D. Y., & Lee, C. K. (2010). Magnetic antimicrobial nanocomposite based on bacterial cellulose and silver nanoparticles. *Journal of Materials Chemistry*, *20*, 6948–6955.