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Environmentally-friendly sonochemistry synthesis of hybrids from lignocelluloses and silver

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ABSTRACT

The purpose of this study was to explore a green strategy about the high value-added applications of biomass. Hybrids from lignocelluloses and silver have been successfully prepared using $NaBH_4$ as reducing reagent by an environmentally-friendly sonochemistry method. The phase, microstructure, and morphology of 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 reaction time, lignocelluloses concentration, and types of reducing reagents on the products were investigated in detail. Silver particles can be better dispersed on the lignocelluloses matrix by adjusting reaction parameters. These hybrids may be a promising antimicrobial material for their applications in the biomedical field. This environmentally-friendly synthetic strategy reported here opens a new window to the high value-added applications of lignocelluloses.

1. Introduction

Recently, green strategies have received much more attention in the materials fields due to its green, environmentally-friendly, and economically-friendly characteristics (Anastas & Eghbali, 2010; Anastas & Kirchhoff, 2002; Clark, 2006; Lenardao, Freitag, Dabdoub, Batista, & Silveira, 2003; Sheldon, 2012). It was noted that these green strategies included using green synthesis methods (Polshettiwar & Varma, 2008; Raveendran, Fu, & Wallen, 2006), green solvents (Gu & Jerome, 2010; Swatloski, Spear, Holbrey, & Rogers, 2002), green reactants (Toda et al., 2005), etc. Until now, some green synthesis methods such as microwave-assisted method (Loupy, 2004; Polshettiwar & Varma, 2008), sonochemistry method (Kardos & Luche, 2001; Xu, Zeiger, & Suslick, 2013), room-temperature synthesis method, photochemistry (Albini & Fagnoni, 2004), and hydrothermal/solvothermal method (Liu et al., 2012) were employed for the preparation of functional materials. Among these green synthesis methods, it is found that sonochemistry method has unique notable chemical, physical, and biological effects due to the existence of acoustic cavitation, and widely applications in organic synthesis, organometallic chemistry, and functional materials (Dhas & Suslick, 2005; Gedanken, 2004; Kardos & Luche, 2001). In recent years, rapid progress has been made in the preparation of functional materials including metal (Zhang et al., 2006), alloys (Anandan, Grieser, & Ashokkumar, 2008), carbides (Hyeon, Fang, & Suslick, 1996), metal sulfides (Mdleleni, Hyeon, & Suslick, 1998; Zhu, Xu, Wang, Zhu, & Chen, 2003), and metal oxides (Yin, Wang, Pang, Koltypin, & Gedanken, 2002; Zhou et al., 2006) via the sonochemistry method. Moreover, it was reported that sonochemistry method was also used in the degradation, polymerization, and surface modification of polymers (Jing, Wang, Wu, & Qiang, 2007; Price, 2003). Hybrids combined the advantages of individual components. There have been a few reports on the synthesis of hybrids with core–shell structure and hetero-structure (Anandan et al., 2008; Gao, Li, & Wang, 2005). However, as far as we all know, the synthesis of hybrids from lignocelluloses and silver by a sonochemistry method has not been reported yet. In our earlier studies, the synthesis of vaterite spheres was carried out by using cellulose as matrix via the sonochemistry method (Fu, Dong, Ma, Li, & Sun, 2013) and cellulose/Ag/AgCl hybrids with desirable antimicrobial activities were obtained by using the cellulose solution,

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$AgNO_3$, $AlCl_3{\cdot}6H_2O$ with ultrasound agitation method (Dong et al., 2014).

As a typical low-cost and sustainable biomass, it is widely known that lignocelluloses consisted of three main polymeric components of cellulose, hemicelluloses and lignin, and provided the numerous productions including fuels, chemicals, and materials (Anderson & Akin, 2008; Zaldivar, Nielsen, & Olsson, 2001). Compared to the petroleum-based polymers, the applications of lignocelluloses had the advantages of reducing greenhouse gas emissions, enhancing existing energy fuels, making use of solid waste, and improving air quality (Lange, 2007; Zhang, 2008). It is well known that silver and silver compounds have potential applications in various fields such as electrical conductivity (Ma, Tang, & Kim, 2008; Wiley et al., 2006), oxidative catalysis (Ahamed et al., 2010; Kim et al., 2009), antibacterial filters (Rai, Yadav, & Gade, 2009; Sharma, Yngard, & Lin, 2009), biomedical field (Atiyeh, Costagliola, Hayek, & Dibo, 2007; Evanoff & Chumanov, 2005; Percival, Bowler, & Russell, 2005), etc. It was reported that silver had strong antimicrobial activity against nearly 650 types of bacteria (Sharma et al., 2009). In previous studies, our group developed the synthesis of cellulose/silver nanocomposites with high antibacterial activity by microwave-assisted method (Li, Jia, Zhu, Ma, Xu, et al., 2011; Li, Jia, Zhu, Ma, Zhang, et al., 2011).

In this study, the sonochemistry method was applied to the synthesis of hybrids from lignocelluloses and silver by using $NaBH_4$ as reducing reagent. The influences of reaction parameters including reaction time, lignocelluloses concentration, and types of reducing reagents on the phase, microstructure, morphology, size, and dispersion of silver crystals in the hybrids were investigated in detail. In comparison with previous reports, this environmentally-friendly synthetic strategy utilizes all the main components of lignocelluloses, opens a new window to the high value-added applications of lignocelluloses, and favors for the large-scale industrial applications of this hybrids.

2. Experimental

2.1. Preparation of hybrids from lignocelluloses and silver

All chemical materials were of analytical grade, and used as received without further purification. In a typical synthesis, 3.00 g dewaxed cotton straw powder was added immediately into the 50.00 g NaOH/urea aqueous solution (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.

For the synthesis of hybrids, $AgNO_3$ (0.34 g) and $NaBH_4$ (0.38 g) were added into the above lignocelluloses solution under vigorous stirring. The above solution was subjected to sonication (Xin-Zhi, JY92-2D, Ti-horn, 20 kHz, 80 W/cm^2) at ambient condition with a high-density ultrasonic probe immersed directly in the solution. During the ultrasonic irradiation, the reaction solution was kept for a certain time. 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. Characterization

X-ray powder diffraction (XRD) patterns were carried out using a Rigaku D/Max 2200-PC diffractometer with Cu Kα radiation (λ = 0.15418 nm) and graphite monochromator at ambient temperature. The morphologies of hybrids were obtained using a Hitachi 3400N scanning electron microscopy (SEM) operating at 15 kV. All samples were Au coated prior to examination by SEM. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were worked out 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).

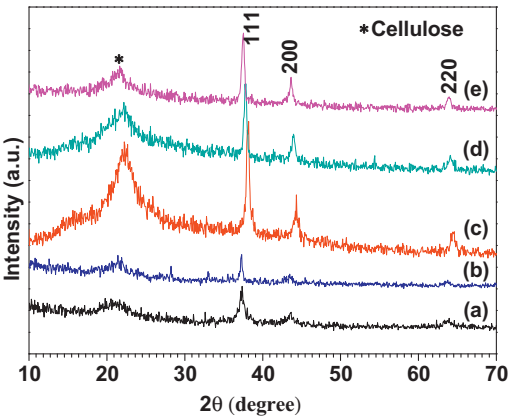

Fig. 1. XRD patterns of the hybrids prepared using $NaBH_4$ by ultrasound agitation method for different times: (a) the control; (b) 10 min; (c) 20 min; (d) 40 min; (e) 60 min.

3. Results and discussion

The hybrids were carried out using $NaBH_4$ as reducing agent and lignocelluloses as matrix by the environmentally-friendly sonochemistry method. Fig. 1b–e displays the XRD patterns of the hybrids prepared by ultrasound agitation method for 10, 20, 40, and 60 min, respectively. One can see that all the samples are indexed to crystallized silver with a cubic structure (JCPDS 04-0783). It is shown that the peak of cellulose is also observed at $2\theta = 21.5°$ (marked with * in Fig. 1). As we all know, lignocelluloses consisted of cellulose, hemicelluloses, and lignin, and only cellulose had crystallized phase. It was found that the peaks intensities of silver crystals increased and the peak intensity of cellulose decreased with increasing reaction time. Moreover, the peaks of silver crystals slight moved to low value of 2θ with increasing reaction time. For comparison, the XRD pattern of the control sample prepared without $NaBH_4$ by ultrasound agitation method for 60 min was also provided, as shown in Fig. 1a, which was also indexed to crystallized silver. The peaks intensities of silver were obviously lower than that in Fig. 1e. Furthermore, in comparison with Fig. 1b–e, the peak of (1 1 1) became broader, demonstrating the small size of silver. It is noted that hemicelluloses are typical polysaccharides containing different heterogeneous polymers mainly consisted of xylose, arabinose, galactose, mannose, 4-O-methyl-D-glucuronic acid, etc., which can be applied as reducing agents for the synthesis of silver crystals from $AgNO_3$. The addition of reducing reagent favored for the increasing crystallinity of silver. Therefore, the $NaBH_4$ was chosen as reducing reagent in this article.

As we all know, the sizes of silver nanostructures can be calculated according to Scherrer formula:

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

where K is constant, λ is 0.15418 Å, and β is half peak width. Ag nanostructures are observed in this article. Therefore, K is assigned as 0.89. The sizes in Fig. 1a, b, c, d, and e were 17.3, 18.2, 27.7, 21.6, and 22.7 nm, respectively. These results demonstrated that the hybrids synthesized using $NaBH_4$ as reducing reagent had bigger size, compared with the control sample. Moreover, using $NaBH_4$ as reducing reagent, the hybrids synthesized by ultrasound agitation

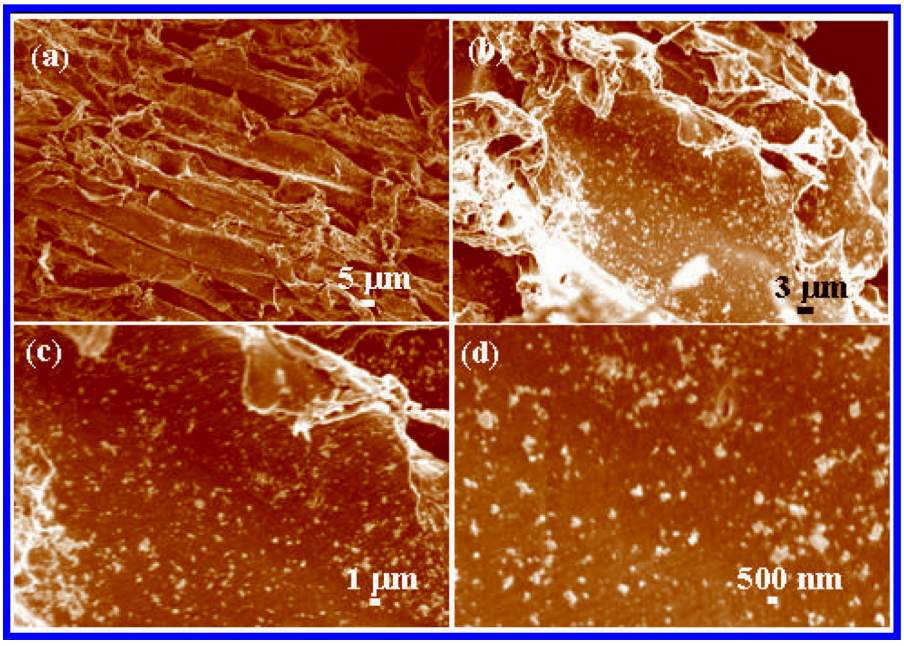

Fig. 2. SEM images of the sample prepared by ultrasound agitation method for 60 min (the control).

method for 20 min had relatively bigger size, compared with the others. It is suggested that the $NaBH_4$ is a relatively strong reducing reagent with high reduction ability, compared with hemicelluloses. With the assistance of $NaBH_4$, silver crystals could nucleation and growth rapidly, inducing relatively high crystallinity and big size.

The morphologies and dispersion of hybrids were further investigated with SEM. The control sample was obtained without using $NaBH_4$ as reducing agent by ultrasound agitation method for 60 min, the lignocelluloses displayed long fibers shape (Fig. 2a). Some rolling sheets were also observed. The microspore structure was clearly displayed on the sheets. Silver nanoparticles were abounded on the surface of lignocelluloses (Fig. 2b–d). From Fig. 2, one can see that the silver nanoparticles had better dispersion on the lignocelluloses matrix.

Using $NaBH_4$ as reducing agent, when the reaction time was 10 min, lignocelluloses with long fibers shape were still clearly observed (Fig. 3a), compared with the control sample. The lignocelluloses had clean surface and only a few silver nanoparticles were observed (Fig. 3b). This result was in accord with the XRD result, in which relatively weak peaks of silver crystals were obtained. Increasing the reaction time to 20 min, the pore, hole, and tube structures were observed on the lignocelluloses (Fig. 3c). Silver nanosheets grow by using lignocelluloses as matrix (Fig. 3d). When the reaction time was increased to 40 min, most silver nanosheets were observed at the surface of lignocelluloses (Fig. 3e and f). It is interesting to find that silver nanostructures grow firstly from the pore of lignocelluloses. These results implied that the lignocelluloses with pore microstructures favored for the growth of silver nanostructures. When the reaction time was prolonged to 60 min, irregular pores were observed on the surface of lignocelluloses (Fig. 3g). However, only silver nanoparticles were observed and no silver nanosheets were obtained (Fig. 3h). From Fig. 3, one can observe the evolution process of morphology of silver nanostructures on the lignocelluloses matrix with increasing reaction time. The size of silver nanosheets dramatically increased on the lignocelluloses matrix with increasing reaction time. However, the over longer reaction time did not make the silver nanosheets grow bigger. Therefore, choosing appropriate reaction time is important for the obtained hybrids with good shape and better dispersion. In comparison with the control sample, the addition of $NaBH_4$ favored for the synthesis of silver crystals with different shape, size, and dispersion.

The influence of lignocelluloses concentrations on the hybrids was also carried out. When the lignocelluloses concentration was 1.0 g, lignocelluloses displayed fiber-like shape with pore structure (Fig. 4a) and agglomerated silver nanoparticles were dispersed on the surface of lignocelluloses (Fig. 4b). Increasing the lignocelluloses concentration to 2.0 g, lignocelluloses with a similar shape were obtained (Fig. 4c) and the silver nanoparticles still existed (Fig. 4d). The nanosheets were also observed at the surface of the lignocelluloses. As was mentioned above, when the lignocelluloses concentration was increased to 3.0 g, the silver nanosheets grew on the surface of lignocelluloses (Fig. 3c and d). In the hybrids from lignocelluloses and silver, the silver crystals concentration did not increase on the lignocelluloses matrix as the decreasing lignocelluloses concentration. These results indicated that both the reactant concentration and reaction time had an effect on the hybrids from lignocelluloses and silver.

Although the hybrids from lignocelluloses and silver were also obtained without using $NaBH_4$ as reducing reagent, the existence of reducing reagents played an important role in the shape, size, and dispersion of silver crystals in the hybrids. To further explore the influences of reducing reagents on the morphologies and microstructure of hybrids, a list of reducing reagents including fructose, $C_6H_{12}O_6$, and ascorbic acid were applied in the reaction. Using fructose instead of $NaBH_4$ as reducing agent, silver needles were dispersed on the surface of lignocelluloses with pore structure (Fig. 5a and b). Using $C_6H_{12}O_6$ as reducing agent, a similar shape was obtained (Fig. 5c and d). However, using ascorbic acid as reducing agent, the sheets with dramatically big size were observed (Fig. 5e and f), which were completely different from the results using other reducing agents. When $C_6H_{12}O_6$ was applied as reducing agent and the reaction time was increased to 60 min, the silver with various shapes including nanosheets, nanowires, and nanorods grew on the lignocelluloses matrix (Fig. 6), which was similar with that of ascorbic acid. From Figs. 2, 3, 5 and 6, one can conclude that the reducing reagents had dramatically effects on the shape,

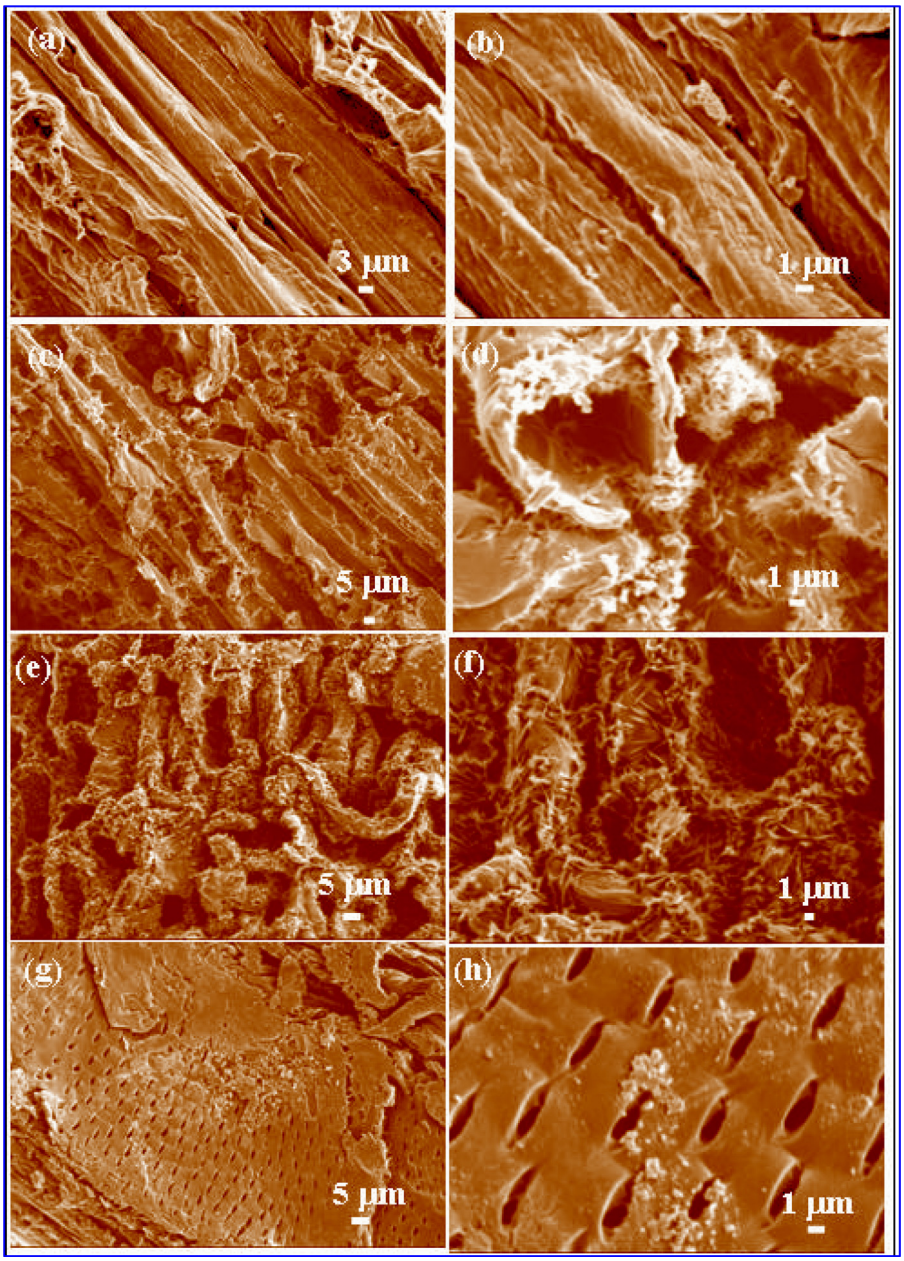

Fig. 3. SEM images of the hybrids prepared using $NaBH_4$ by ultrasound agitation method for different times: (a and b) 10 min; (c and d) 20 min; (e and f) 40 min; (g and h) 60 min.

size, and dispersion of silver crystals in the hybrids and favored for the growth of silver nanostructures on the lignocelluloses matrix.

Schematic illustration of the formation process of hybrids from lignocelluloses and silver with different ultrasonic time and with different reducing agents was shown in Fig. 7. As shown in Fig. 7, one can see that lignocelluloses were pretreated by NaOH/urea solution. It is found that hybrids from lignocelluloses and Ag are carried out by addition of $AgNO_3$ via sonochemistry method. As a promising green methodology, the sonochemical method has characteristics of intense local heating, high pressures, and extremely rapid cooling rates, which favors the synthesis of Ag crystals at relatively short time and does not destroy the structure of lignocelluloses. Obviously, Ag with different shapes is achieved by using different reducing reagents. Using $NaBH_4$ as reducing reagent, Ag nanoparticles and nanosheets are achieved. Without $NaBH_4$, Ag nanoparticles with small size are observed. It seems that Ag needles are observed with the addition of fructose or $C_6H_{12}O_6$, and Ag sheets are obtained with the addition of ascorbic acid.

Thermal stabilities of the hybrids were investigated with TGA and DTA, as shown in Fig. 8. Without the addition of $NaBH_4$, the hybrids had three stages of weight loss from TGA curve (Fig. 8a). The first weight loss was observed and measured to be 6.5% from room temperature to 110 °C, which was corresponded to the loss of absorbed water molecule. Then, the second and the last weight losses were measured to be 77.1% and probably caused by thermal degradation and thermal decomposition of lignocelluloses. The DTA curve in Fig. 8a displays three obvious endothermic peaks located at about 78, 272, and 411 °C, respectively, which

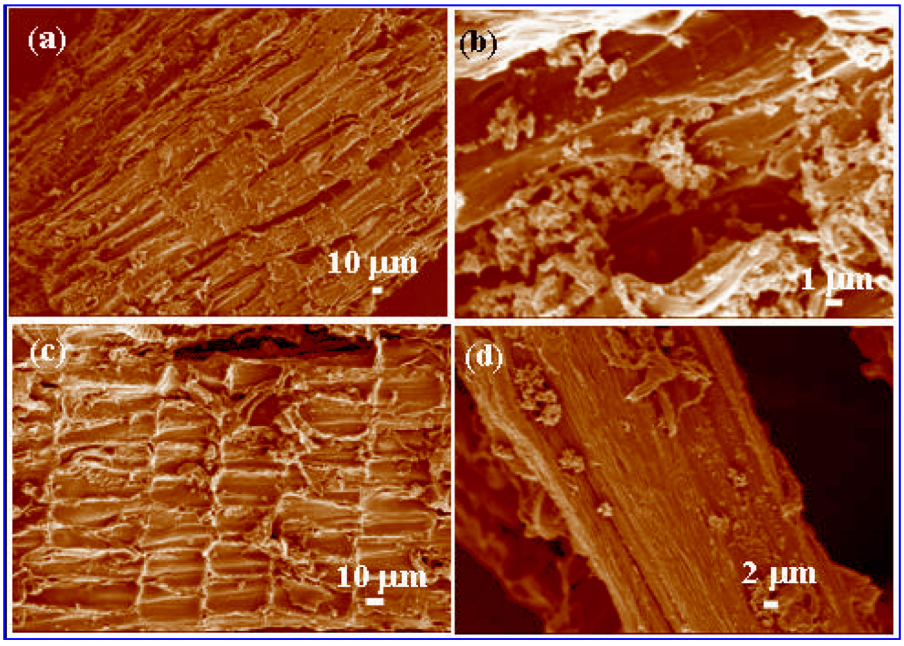

Fig. 4. SEM images of the hybrids prepared using $NaBH_4$ by ultrasound agitation method for 20 min using different cotton straw powder concentrations: (a and b) 1.0 g; (c and d) 2.0 g.

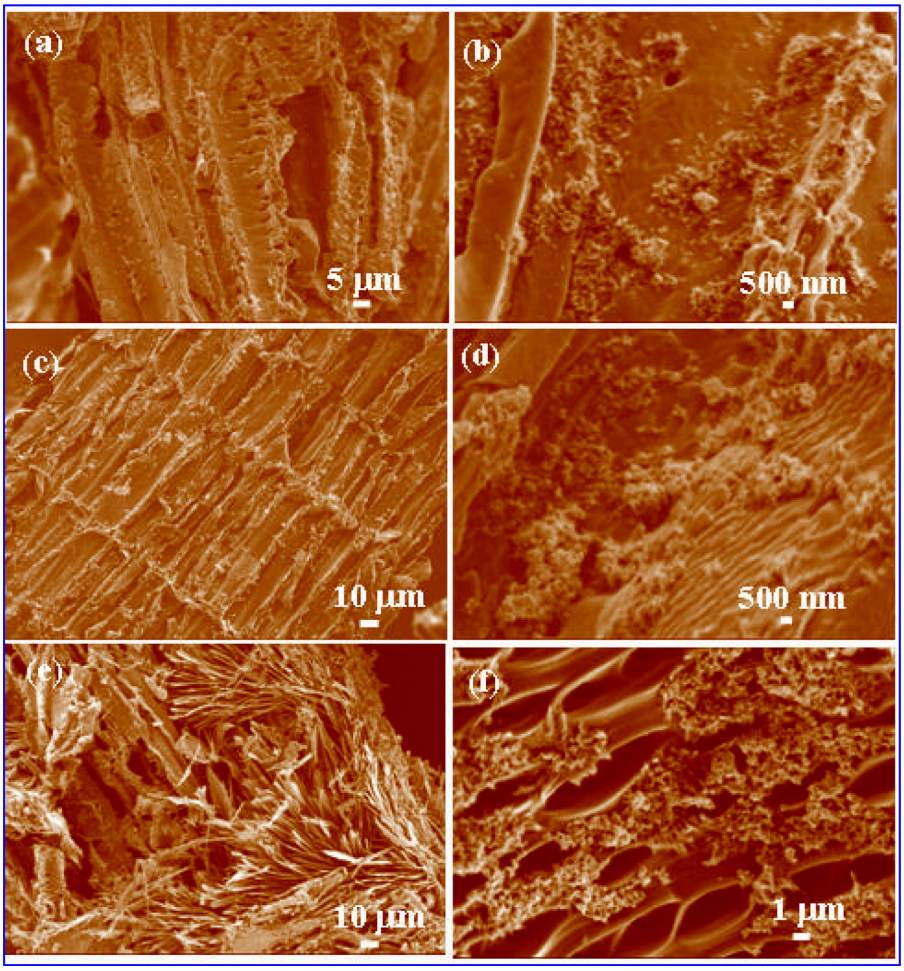

Fig. 5. SEM images of the samples prepared by ultrasound agitation method for 20 min using different reducing agents: (a and b) fructose; (c and d) $C_6H_{12}O_6$; (e and f) ascorbic acid.

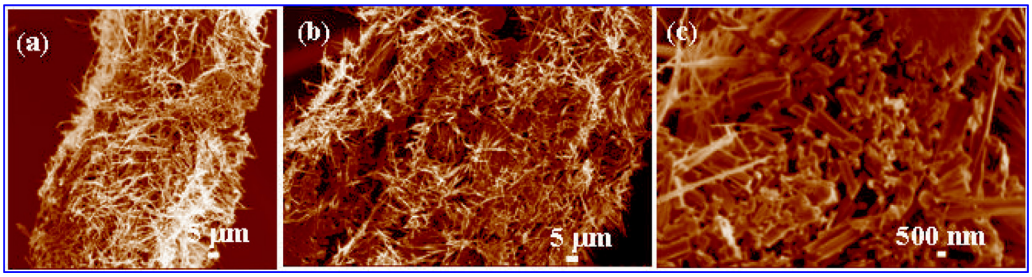

Fig. 6. SEM images of the sample prepared using $C_6H_{12}O_6$ by ultrasound agitation method for 60 min.

fit well with that of weight loss in the TGA curve. Using $NaBH_4$ as reducing reagent, the first weight loss was observed and measured to be 9.5% from room temperature to 118 °C (Fig. 8b). Two endothermic peaks located at 72 and 97 °C were observed from the DTA curve. Second weight loss was observed at around 174 °C (Fig. 8b). The last weight loss was obtained from 200 to 600 °C. The corresponding endothermic peak was observed at 262 °C in DTA curve. Compared with Fig. 8a, no obvious endothermic peak was observed at around 411 °C. The total weight loss of the hybrids synthesized without the addition of $NaBH_4$ was 83.6% from room temperature to 456 °C, while the total weight loss of the hybrids synthesized using $NaBH_4$ as reducing reagent was 67.0% from room temperature to 600 °C. The weight loss was due to the thermal decomposion of lignocelluloses and the residue was assigned to silver crystals. Therefore, in view of the TGA results, one can conclude that the addition of $NaBH_4$ favored for the increasing the silver concentration in hybrids (from 16.4% to 33.0%).

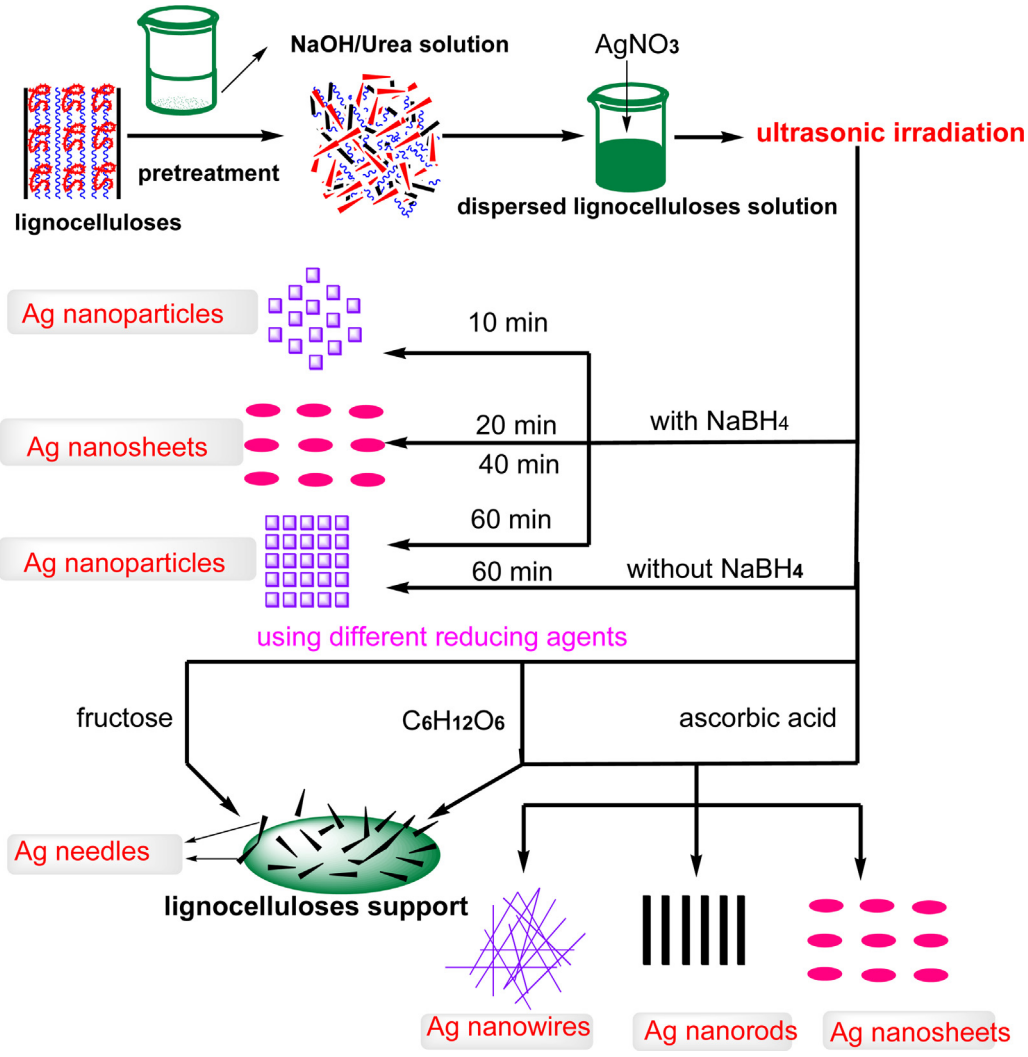

Fig. 7. Schematic illustration of the formation process of hybrids from lignocelluloses and Ag with different ultrasonic time and with different reducing agents.

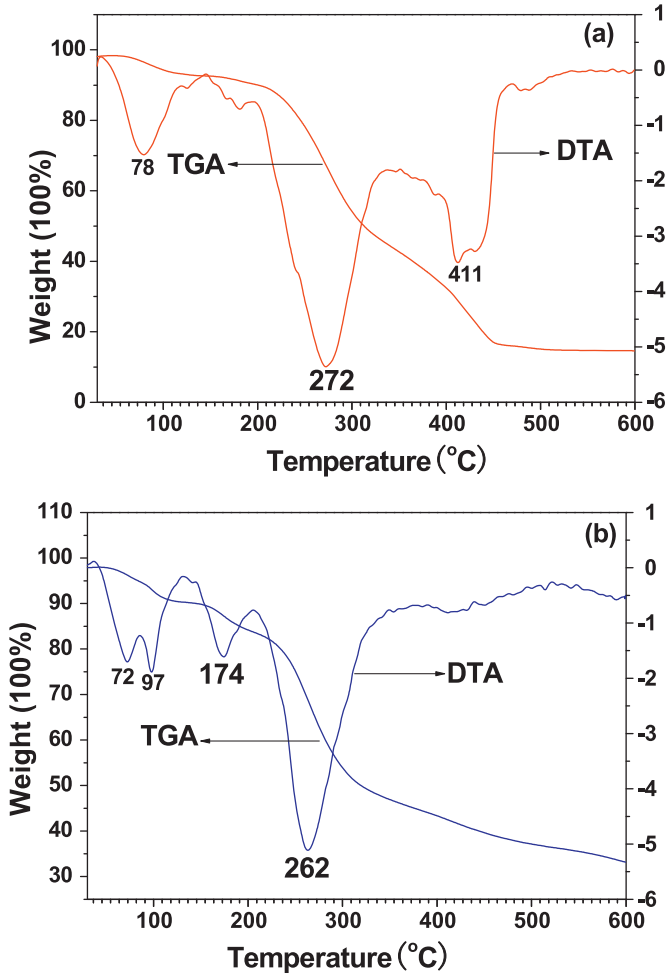

Fig. 8. TGA and DTA curves of the hybrids prepared by ultrasound agitation method for 60 min: (a) without the addition of $NaBH_4$; (b) using $NaBH_4$ as reducing reagent.

4. Conclusions

In summary, the synthesis of hybrids from lignocelluloses and silver was reported by the environmentally-friendly sonochemistry method. The reaction parameters including reaction time, lignocelluloses concentration, and types of reducing reagents played an important role in the phase and shape of silver crystals in hybrids. 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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