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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).

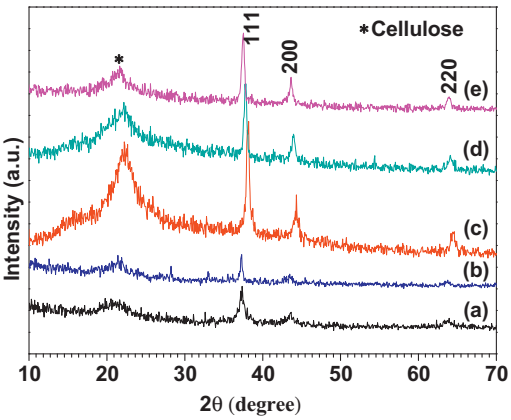

Fig. 1. XRD patterns of the hybrids prepared using $NaBH_4$ by ultrasound agitation method for different times: (a) the control; (b) 10 min; (c) 20 min; (d) 40 min; (e) 60 min.

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