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Cellulose–silver nanocomposites: Microwave-assisted synthesis, characterization, their thermal stability, and antimicrobial property

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ABSTRACT

A facile microwave-assisted method was developed to fabricate cellulose–silver nanocomposites by reducing silver nitrate in ethylene glycol (EG). EG acts as a solvent, a reducing reagent, and a microwave absorber in the whole system, thus no additional reductant is needed. The influences of the heating time and heating temperature on the products were investigated. The products were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), and scanning electron microscope (SEM). The thermal stability of cellulose–silver nanocomposites in nitrogen and air was studied using thermogravimetric analysis (TG) and differential scanning calorimetric analysis (DSC). Also, the cellulose–silver nanocomposites possess a high antimicrobial activity against the model microbes *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive). It is expected that the cellulose–silver nanocomposites are a promising material for the application in the biomedical field.

1. Introduction

In recent years, nanocomposites have been received considerable attention because of their excellent properties and broad applications (Habibi et al., 2008; Hubbe, Rojas, Lucia, & Sain, 2008; Miyamoto, Takahashi, Ito, Inagaki, & Noishiki, 1989). Among of all nanocomposites, antimicrobial polymer–metallic nanocomposites have excellent antimicrobial properties and potential applications in public health care and biomedical field (Rhim & Ng, 2007; Sharma, Yngard, & Lin, 2009; Yang, Wang, & Wang, 2007). Until now, the synthesis of the antimicrobial polymer–metallic nanocomposites including polyester/clay silver nanocomposites (Konwar, Karak, & Mandal, 2010), polymer/silver bromide composites (Sambhy, MacBride, Peterson, & Sen, 2006), chitosan/Ag nanocomposite films (Rhim, Hong, Park, & Ng, 2006), poly(vinyl alcohol)/Ag nanofibers (Hong, Park, Sul, Youk, & Kang, 2006), and poly(methyl methacrylate)/Ag nanofibers (Kong & Jang, 2008) has been tried.

Cellulose–silver nanocomposite consists of cellulose and Ag nanoparticles. It is well known that cellulose is the most abundant component of biomass in nature (Klemm, Heublein, Fink, & Bohn, 2005; Klemm et al., 2006). Silver ions and silver compounds have been known to have strong antimicrobial activity (Sharma et al., 2009) against nearly 650 types of bacteria and have potential applications in various fields like antibacterial filters, wound dressing materials, etc. Cellulose fiber was used as a template for the fabrication of antimicrobial materials such as silver nanoparticles (Ferraria, Boufi, Battaglini, do Rego, & ReiVilar, 2010; He, Kunitake, & Nakao, 2003; Zhu, Xue, & He, 2009), porous and nonporous Ag nanostructures (He, Kunitake, & Watanabe, 2005), and gold–silver alloy nanoparticles (Shin, Bae, Arey, & Exarhos, 2008). There have been few reports on the fabrication of the cellulose–silver nanocomposites (Klemencic, Simoncic, Tomsic, & Orel, 2010; Li et al., 2011; Maneerung, Tokura, & Rujiravanit, 2008; Maria et al., 2009; Pinto et al., 2009; Son, Youk, & Park, 2006; Sureshkumar, Siswanto, & Lee, 2010). For example, Maneerung et al. (2008) succeeded in impregnating silver nanoparticles into bacterial cellulose with a strong antibacterial activity for antimicrobial wound dressing. Cellulose/Ag nanocomposites with antibacterial activity against *Bacillus subtilis*, *Staphylococcus aureus* and *Klebsiella pneumoniae* were prepared using two distinct methodologies and two cellulose substrates: vegetable and bacterial cellulose (Pinto et al., 2009). Bacterial cellulose/colloidal silver nanocomposites were also fabricated using different reductants (hydrazine, hydroxylamine or ascorbic acid) together with gelatin or polyvinylpyrrolidone (Maria et al., 2009). Recently, Sureshkumar et al. (2010) reported the synthesis of magnetic antimicrobial nanocomposite based on bacterial cellulose and silver nanoparticles by a high speed blender using polydopamine as reducing reagent. We reported the synthesis of cellulose–silver nanocomposites using cellulose solution, $AgNO_3$

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and ascorbic acid in *N*,*N*-dimethylacetamide at 150 °C for 40 min (Li et al., 2011).

Recently, microwave-assisted method was employed for the synthesis of the cellulose–silver nanocomposites (Li et al., 2011), cellulose–carbonated hydroxyapatite nanocomposites (Jia et al., 2010), and cellulose–hydroxyapatite nanocomposites (Ma et al., 2010) due to its unique effects such as rapid volumetric heating, high reaction rate, short reaction time, enhanced reaction selectivity, and energy saving. The polyol, such as EG, is a polar solvent which also has a reducing ability. The polyol process was applied for the large-scale synthesis of silver nanowires with uniform diameters (Sun, Mayers, Herricks, & Xia, 2003). Microwave–polyol method has been widely utilized in preparation of Ag nanoparticles using polyol as both reducing agent and solvent (Katsuki & Komarneni, 2003; Komarneni, Li, Newalkar, Katsuki, & Bhalla, 2002; Tsuji et al., 2008). Moreover, microwave–polyol method also was used to the synthesis of nanocomposites (Zhu & Zhu, 2006; Zhu, Zhu, Ma, Yang, & Gao, 2007).

In this paper, we reported a facile microwave-assisted synthesis of cellulose–silver nanocomposites using microcrystalline cellulose and silver nitrate in EG. The Ag nanoparticles were formed *in situ* on the surface of cellulose. EG acted as a solvent, a reducing reagent, and a microwave absorber, thus no additional reductant was needed. Compared to the previously report (Li et al., 2011), this method is more simple for the synthesis of cellulose–silver nanocomposites. Investigation has been conducted on the effect of reaction parameters, such as heating time and heating temperature. Moreover, the inhibition zone experiment was applied to evaluate the antimicrobial activity of cellulose–silver nanocomposites by using the model microbes *Escherichia coli* (Gram-negative) and *S. aureus* (Gram-positive), respectively.

2. Experimental

2.1. Materials

Microcrystalline cellulose (MCC) (molecular weight of 34, 843-38, 894, with a degree of polymerization of 215–240) was obtained from Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China. Ethylene glycol and silver nitrate were purchased from Beijing Chemical Works. All chemical materials and solvents used in the experiments were analytical grade reagents, and were used without further purification.

2.2. Preparation of the cellulose–silver nanocomposites

MCC (1.000 g) and silver nitrate (0.340 g) were mixed with ethylene glycol (EG, 50 mL) under vigorous magnetic stirring to form a uniform dispersed suspension. After that, the mixture was stirred and heated to a certain temperature and kept at this temperature for a certain time by microwave heating, and then air cooled to room temperature naturally. The microwave oven used for specimen preparation was purchased from Beijing Xiang-Hu Science and Technology Development Reagent Co., Ltd., which was equipped with the vigorous magnetic stirring system and a water-cooled condenser outside the microwave cavity. The product was filtered, washed three times by ethanol and dried in vacuum at 60 °C for 5 h.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were recorded in the range of $2\theta = 10–90°$ on an X'Pert PRO MPD diffractometer operating at 40 kV with Cu Kα (λ = 1.5405 Å) radiation. Fourier transform infrared (FT-IR) spectra of the cellulose–silver nanocomposites were obtained by a Fourier transform infrared spectrophotometer (Nicolet 510) in a range of wavenumber from 4000 to 400 cm^{-1}, using the KBr disk method. Thermogravimetric analysis (TG) and differential scanning calorimetric analysis (DSC) were carried out with a STA-409PC/4/H Luxx simultaneous TG/DSC apparatus (Netzsch Co., Selb, Germany) at a scan rate of 10 °C/min from room temperature to 800 °C under air and nitrogen atmosphere, respectively. The morphology of cellulose–silver nanocomposites was examined using a Hitachi 3400N scanning electron microscopy (SEM) operating at 15 kV. All samples were Au coated prior to examination by SEM.

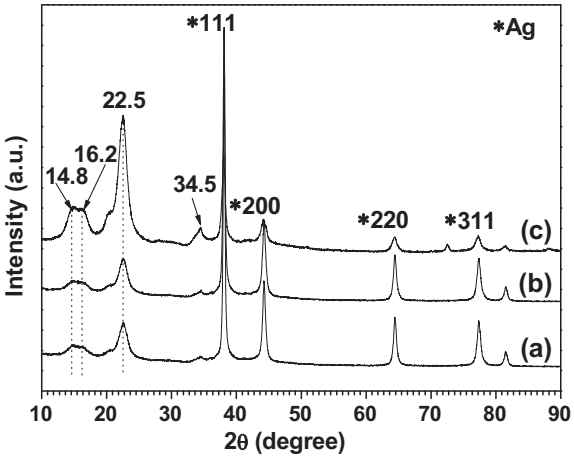

Fig. 1. XRD patterns of the cellulose–Ag nanocomposites prepared using microcrystalline cellulose and 0.338 g of $AgNO_3$ by microwave heating in EG at 140 °C for different heating times: (a) 10 min; (b) 30 min; (c) 60 min.

2.4. Antimicrobial activity studies

The antimicrobial activities of cellulose–silver nanocomposites have been investigated against *E. coli* as the model Gram-negative bacteria and *S. aureus* as the model Gram-positive bacteria by the disc diffusion method. In the inhibition zone experiment, nutrient agar was poured into disposable sterilized Petri dish and solidified. Then 100 μL of *E. coli* and 100 μL of *S. aureus* were streaked over the dish and spread uniform. After that, circular pieces of the control and the test samples were gently placed on Petri dishes. This was done for both the bacterial strains (*E. coli* ATCC 25922 and *S. aureus* ATCC 25923). The cellulose–silver nanocomposites were cut into a disc shape with 1.4 cm diameter, sterilized by autoclaving at

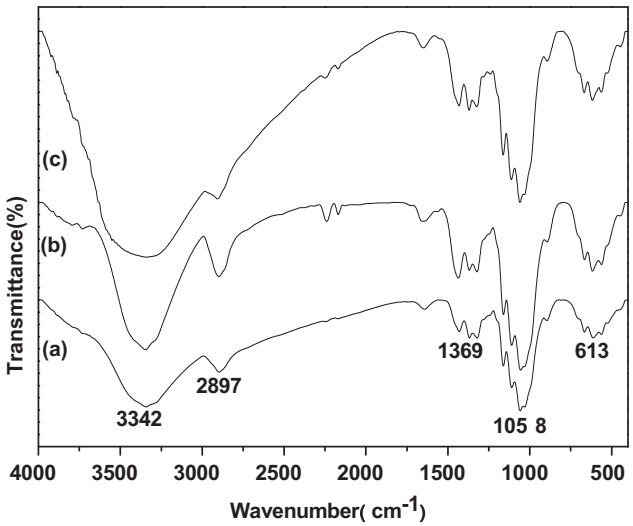

Fig. 2. FT-IR spectra of the same samples as in Fig. 1.

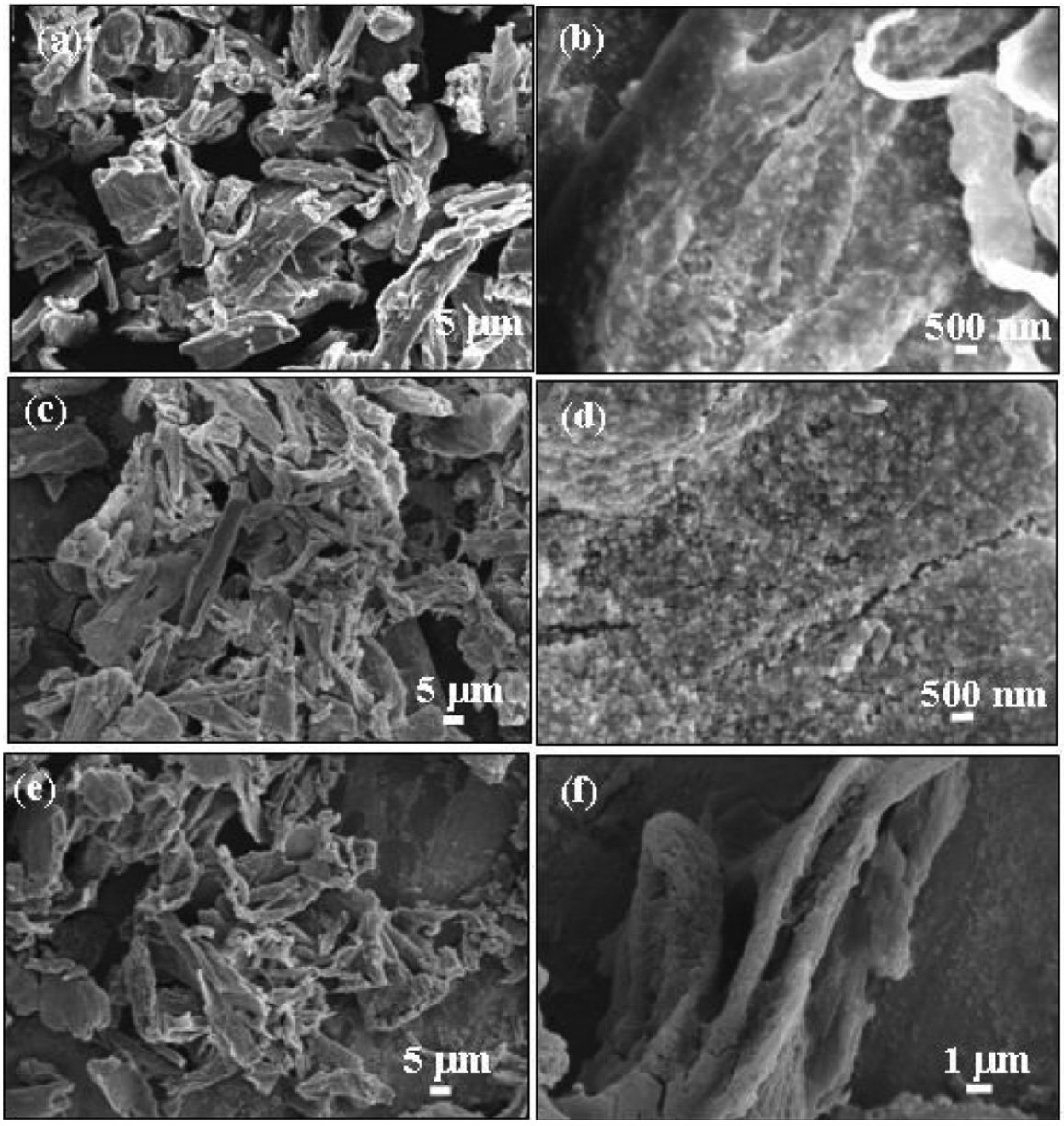

Fig. 3. SEM micrographs of the cellulose–Ag nanocomposites prepared by microwave heating at 140 °C for different heating times: (a and b) 10 min; (c and d) 30 min; (e and f) 60 min.

120 °C for 20 min, and were placed on *E. coli*-cultured and *S. aureus*-cultured agar plates, which were then incubated at 37 °C for 24 h. Finally, the inhibition zone was monitored.

3. Results and discussion

3.1. Phase, microstructure, and morphology of the cellulose–silver nanocomposites

The phases of the cellulose–silver nanocomposites were characterized by XRD. Fig. 1 shows the XRD patterns of the typical samples prepared using microcrystalline cellulose and $AgNO_3$ by microwave heating in ethylene glycol at 140 °C for 10, 30, and 60 min, respectively. All of the samples have similar diffraction peaks. One can see that the diffraction peaks were attributed to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes of the crystallized silver with a cubic structure (JCPDS 04-0783), suggesting the successful synthesis of silver using EG as a reducing reagent. The samples have also the diffraction peaks at around $2\theta = 14.8°$, 16.2°, 22.5°, and 34.5° corresponding to the typical diffraction patterns of crystalline cellulose type I (Oh et al., 2005). These results indicated that all of the samples consisted of the mixed phase of the microcrystalline cellulose and silver. However, slight differences are observed among the XRD patterns. It is clear that the intensity of diffraction peak at around $2\theta = 22.5°$ increased with the increasing heating time, implying that a longer heating time decreased the crystallinity of cellulose (Fig. 1c).

In this work, cellulose–silver nanocomposites were obtained in EG. EG has high viscosity at room temperature and a high dielectric loss constant to absorb microwave efficiently. Moreover, EG also acts as a reducing reagent for the formation of Ag under MW heating. With the help of the microwave heating, the Ag particles can be synthesized in the cellulose matrix by the following chemical reactions (Fievet, Lagier, Blin, Beaudoin, & Fiflarz, 1989), leading to rapid fabrication of cellulose–silver nanocomposites:

$$CH_2OH\text{–}CH_2OH \rightarrow CH_3CHO + H_2O \quad (1)$$

$$2CH_3CHO + 2Ag^+ \rightarrow 2Ag + 2H^+ + CH_3COCOCH_3 \quad (2)$$

Fig. 2 shows the FT-IR spectra of cellulose–silver nanocomposites obtained at 140 °C for 10, 30, and 60 min, respectively. Obviously, all the FT-IR spectra of cellulose–silver nanocomposites display the typical bands of cellulose (Surflet, Chitanu, & Popa, 2006; Uesu, Pineda, & Hechenleitner, 2000). For the cellulose–silver nanocomposites, the band centered at around 3342 cm^{-1} can be attributed to the stretching vibration of hydroxyl group; the band at about 2897 cm^{-1} is assigned to the C–H group; the band at around 1369 cm^{-1} is corresponded to the C–H bending mode; the absorption band at 1058 cm^{-1} is ascribed to C–O–C stretching mode from the glucosidic units (Surflet et al., 2006); the peak at 894 cm^{-1} was related to the C–H rocking vibration of cellulose (Alemdar & Sain, 2008). It is important to note that the broad peak at around 3342 cm^{-1} became broader in Fig. 2c, compared with that in Fig. 2a. A similar phenomenon in cellulose-based nanocomposites was reported for cellulose–calcium silicate nanocomposites (Li, Jia, Zhu, Ma, & Sun, 2010) and cellulose–Fe_2O_3 nanocomposites (Liu, Zhang, Zhou, & Wu, 2008).

The morphology of the cellulose–silver nanocomposites was investigated with SEM. Fig. 3 shows the SEM micrographs of the cellulose–silver nanocomposites prepared by microwave heating the EG solution of 0.338 g of $AgNO_3$ and microcrystalline cellulose at 140 °C for 10 min, 30 min, and 60 min, respectively. There were no significant differences in the morphology of cellulose. The cellulose has flake-like morphology (Fig. 3a, c, and e). As can be seen from the magnified micrographs of the cellulose–silver nanocomposites in Fig. 3b, d and f, silver particles with diameters about 100 nm were homogeneously dispersed in the cellulose substrate. It is worth mentioning that no individual silver particles were observed outside the cellulose, indicating the strong interaction between the cellulose and silver particles.

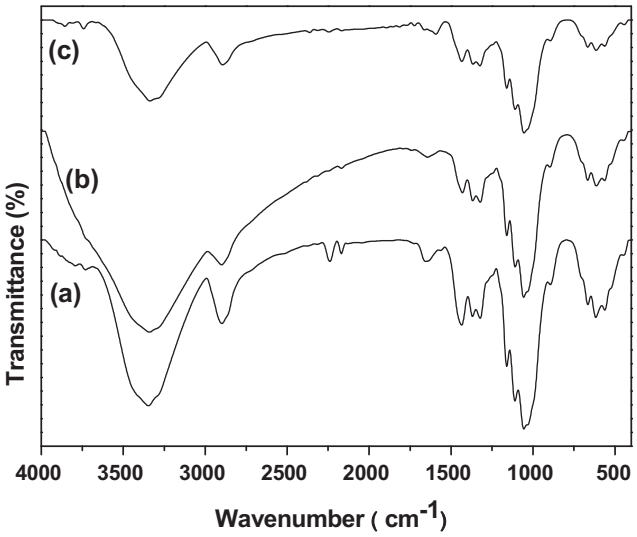

Fig. 4. FT-IR spectra of the cellulose–Ag nanocomposites prepared by microwave heating at different temperatures for 30 min: (a) 140 °C; (b) 160 °C; (c) 180 °C.

Investigation has also been conducted on the effect of heating temperature on the cellulose–silver nanocomposites. The cellulose–silver nanocomposites were prepared at 140 °C, 160 °C, and 180 °C for 30 min, respectively, while other reaction conditions were kept the same. Fig. 4 shows the corresponding FT-IR spectra of the cellulose–silver nanocomposites prepared at different temperatures, which are similar to those in Fig. 2. In addition, their slight difference is observed about the intensity of the peaks for different samples. The intensity of the peaks decreased with the increasing heating temperature.

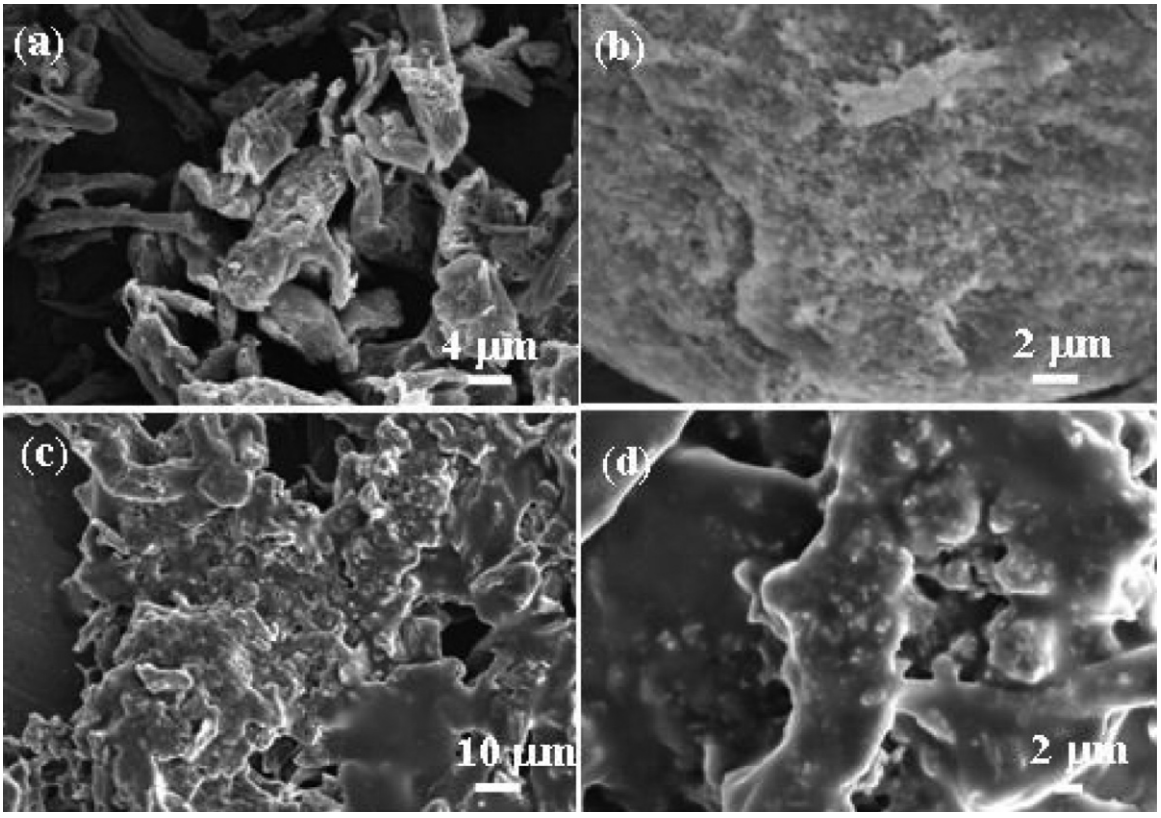

Fig. 5. SEM micrographs of the cellulose–Ag nanocomposites prepared by microwave heating at different temperatures for 30 min: (a and b) 160 °C; (c and d) 180 °C.

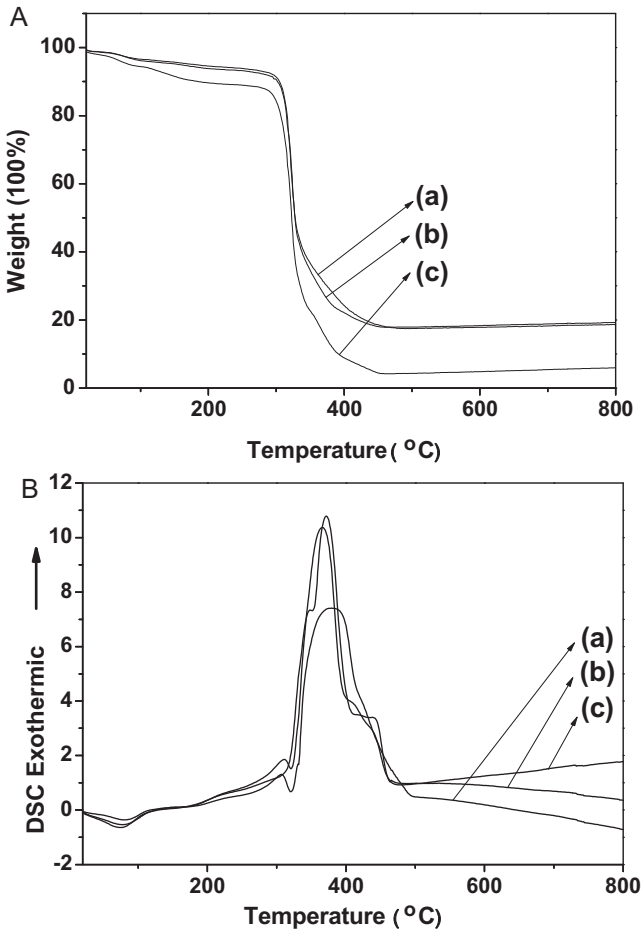

Fig. 6. (A) TG and (B) DSC curves of the typical cellulose–Ag nanocomposites obtained by testing in air at heating rate of 10 °C/min. The samples were prepared for: (a) 10 min; (b) 30 min; (c) 60 min.

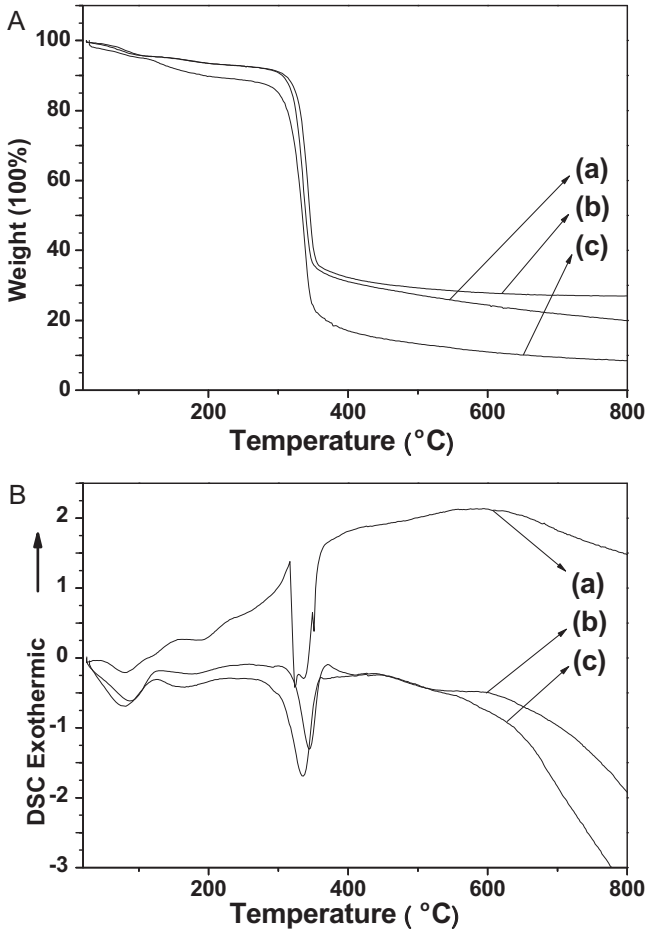

Fig. 7. (A) TG and (B) DSC curves of the typical cellulose–Ag nanocomposites obtained by testing under nitrogen atmosphere at heating rate of 10 °C/min. The samples were prepared for: (a) 10 min; (b) 30 min; (c) 60 min.

Fig. 5 shows the SEM images of the cellulose–silver nanocomposites prepared at 160 °C and 180 °C for 30 min, respectively. When the heating temperature was increased to 160 °C, no significant differences were observed on the morphology of the cellulose–silver nanocomposites (Fig. 5a and b), compared to that in Fig. 3. When the heating temperature was increased to 180 °C, the size of cellulose in nanocomposites obviously decreased (Fig. 5c and d). These results indicated that the heating temperature had an influence on the morphology of cellulose–silver nanocomposites.

3.2. Thermal stability of the cellulose–silver nanocomposites

The thermal stability of the cellulose–silver nanocomposites is measured with TG and DSC under air and nitrogen atmosphere, respectively. Fig. 6 shows the TG and DSC curves of the typical cellulose–Ag nanocomposites obtained by testing in air at heating rate of 10 °C/min. As can be seen, the samples synthesized at 140 °C for 10 min and 30 min had the similar TG curves. From TG curves, it is observed that the weight loss of ~81.0% from 290 °C to 470 °C is due to the thermal degradation of cellulose in the nanocomposites, accompanied by exothermic peak at about 368 °C in the DSC curves (Fig. 6a and b), indicating that the increasing temperature from 10 min to 30 min had slight effect on the cellulose–Ag nanocomposites. However, the weight loss of ~94.2% was obtained for the cellulose–Ag nanocomposite synthesized at 140 °C for 60 min (Fig. 6c). All of the samples had the similar weight loss range and exthermal peak position, suggesting the heating time had slight effect on the thermal stability of the cellulose–silver nanocomposites.

TG and DSC curves were also obtained by testing under nitrogen atmosphere, as shown in Fig. 7. It can be seen that the temperature range of mass loss of the nanocomposite samples in Fig. 7 is approximate to that in Fig. 6. From TG curves, it is observed that the weight loss of ~69.3%, 68.0% and 83.3% from 290 °C to 400 °C are due to the thermal degradation of cellulose in the nanocomposites (Fig. 7). The samples synthesized at 140 °C for 10 min and 30 min had the similar weight loss, which is consistent with the previous from testing in air.

3.3. Antimicrobial activity of the cellulose–silver nanocomposites

The antibacterial activity of the cellulose–silver nanocomposites with low concentration was obtained using 0.075 g of cellulose–silver nanocomposites, while by using 0.150 g of cellulose–silver nanocomposites, the antibacterial activity of the cellulose–silver nanocomposites with high concentration was obtained. Pure microcrystalline cellulose was used as control. The antibacterial activity of cellulose–silver nanocomposites against *E. coli* and *S. aureus* was measured. *E. coli* and *S. aureus* are general bacteria that are found on the contaminated wound. It was found that the cellulose–silver nanocomposites exhibited an inhibition zone. The inhibition zones of the cellulose–silver nanocomposites with low concentration for *E. coli* and *S. aureus* were 10 mm and 2.5 mm, respectively (Fig. 8a and b), while inhibition zones of the cellulose–silver nanocomposites with high

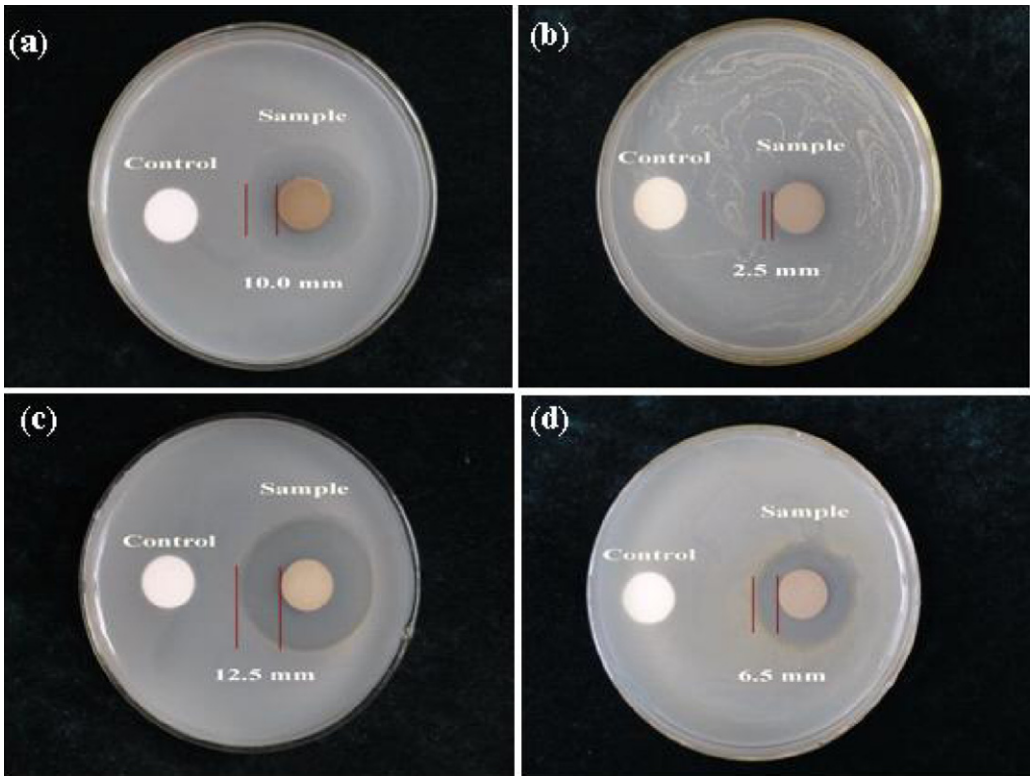

Fig. 8. Antimicrobial activities of the cellulose–Ag nanocomposites:(a and c) *Escherichia coli* and (b and d) *Staphylococcus aureus*.

concentration for *E. coli* and *S. aureus* were 12.5 mm and 6.5 mm, respectively (Fig. 8c and d). These results clearly demonstrated that the cellulose–silver nanocomposites had good antibacterial activity against both *E. coli* (Gram-negative) and *S. aureus* (Gram-positive), and the antimicrobial activity against *E. coli* is higher than that against *S. aureus*, probably due to the difference in cell walls between Gram-negative and Gram-positive bacteria. As the concentration of cellulose–silver nanocomposites increased from 0.075 g to 0.150 g, the inhibition zone against *S. aureus* was dramatically increased. From the images, no inhibition zone was observed for the microcrystalline cellulose as control (Fig. 8), implying that the microcrystalline cellulose do not have any antibacterial properties. These results clearly indicate that the antibacterial activity is only due to the silver nanoparticles which were impregnated inside cellulose and not due to the microcrystalline cellulose.

4. Conclusions

In summary, the cellulose–silver nanocomposites with excellent antimicrobial properties have been successfully synthesized through the microwave-assisted method. XRD and FT-IR results implied that the obtained samples were cellulose–silver nanocomposites. SEM images showed that the silver nanoparticles were dispersed in the cellulose matrix and the strong interaction was formed between the cellulose and silver particles. TG and DSC results of the cellulose–silver nanocomposites indicated that the heating time and temperature in the preparation had slight effect on the thermal stability of the cellulose–silver nanocomposites. The cellulose–silver nanocomposites exhibited a strong antibacterial activity against both *E. coli* (Gram-negative bacteria) and *S. aureus* (Gram-positive bacteria).

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