Preparation and Characterization of Cellulose-Silver Nanocomposites by *in situ* Reduction with Alkalis as Activation Reagent

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A simple, environmentally friendly, and efficient synthesis method for cellulose/silver (Ag) nanocomposites was developed by microwave heating an alkaline aqueous solution of cellulose fiber and silver nitrate ($AgNO_3$), which resulted in good utilization of silver ions and a product with high silver content. The effect of the alkaline compounds and reducing agents on the silver content and utilization rate of silver ions was investigated using atom absorption spectroscopy (AAS). The morphology, size, thermal stability, and surface components of cellulose/Ag nanocomposites were investigated using scanning electron microscopy (SEM), thermogravimetric analysis (TG), differential scanning calorimetry (DSC), and Raman spectroscopy. The alkaline compound and reducing agent influenced the size and shape of the silver nanoparticles. Reduced silver ions had the greatest influence on the surface components of cellulose; however, nano-silver particles exhibited no obvious influence on cellulose's thermal stability. Furthermore, cellulose/Ag nanocomposites exhibited excellent antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*.

Keywords: Cellulose; Silver; Nanocomposites; Alkali; Antibacterial activity

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INTRODUCTION

As the most abundant natural polymer material, cellulose has the advantages of easy access, low price, and renewability. Recently, cellulose composites containing metal nanoparticles have been formed. Such cellulose composites have the characteristics of both inorganic and organic materials, and they have potential applications in magnetic materials, biosensors, and antibacterial materials (Burke *et al*. 2002; Pothukuchi *et al*. 2004; Bakumov *et al*. 2007; Njagi and Andreescu 2007; Li *et al*. 2009; Singh *et al*. 2010).

Compared with other metals, silver has many excellent properties, including high conductivity (Johnsen *et al*. 2012; Park et al. 2012), good catalyst performance (Henglein and Tausch-Treml 1981; Jiang *et al*. 2005), and broad-spectrum antimicrobial activity (Henglein and Tausch-Treml 1981; Jiang *et al*. 2005). Because of its excellent antibacterial properties, silver has been used for accelerating the healing of skin wounds (Tian *et al*. 2007; Maneerung *et al*. 2008) and for the treatment of a variety of diseases (Ahmed *et al*. 2015). Cellulose itself does not have antimicrobial properties; however, it can be used as a support matrix for antimicrobial materials. Because silver adds antibacterial properties to cellulose, cellulose/Ag nanocomposites have potential use in healthcare (de Santa Maria *et al*. 2009; Klemenčič *et al*. 2010; Li *et al*. 2011).

When bacterial cellulose is immersed in a silver nitrate solution, $NaBH_4$ reduces silver ions on the cellulose surface; the resulting cellulose/Ag nanocomposite has strong antibacterial activity in wound dressings (Maneerung *et al.* 2008). Cellulose/Ag nanocomposites obtained by different methodologies and different cellulose sources have antibacterial activity against *Bacillus subtilis*, *Staphylococcus aureus*, and *Klebsiella pneumonia* (Pinto *et al.* 2009).

Compared with traditional bath heating, microwave heating has many advantages including rapid volumetric heating, high reaction rate, short reaction time, enhanced reaction selectivity, and energy efficiency. Microwave heating has been employed in the synthesis of cellulose nanocomposites containing silver (Silva and Unali 2011), hydroxyapatite (Ma *et al.* 2010), and carbonated hydroxyapatite (Jia *et al.* 2010). Li *et al*. (2011) successfully generated cellulose/Ag nanocomposites by microwave-heating microcrystalline cellulose in an ethylene glycol solution of silver nitrate.

Cellulose is a polysaccharide consisting of a linear chain of β(1,4)-linked D-glucose units; each glucose unit contains three hydroxyl groups. In addition, each chain contains an aldehyde group that can reduce silver ions. Therefore, cellulose/Ag nanocomposites can be prepared by microwave-heating of a mixture of cellulose and a reducing agent. However, the silver content and utilization of silver ions are generally low when cellulose is used without a reducing agent. Cellulose/Ag composites can be synthesized using Tollen’s reagent (Montazer *et al.* 2012). To extend this research, this paper reports on the use of other types of alkaline compounds to prepare cellulose/Ag nanocomposites; the silver content of nanocomposites was increased greatly under alkaline conditions.

The silver content and morphology of the silver nanoparticles were studied by atom absorption spectroscopy (AAS) and scanning electron microscopy (SEM). The effect of reducing agents was also investigated. The potential antibacterial activity of cellulose/Ag nanocomposites against *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive) bacteria was investigated by inhibition zone and sterilization assays.

EXPERIMENTAL

Materials

Cellulose fiber from fully bleached chemical pulp, derived from softwood, was provided by the Xiangtai Cellulose Corp. (Xiangtai, China). Silver nitrate (AgNO3) was obtained from the Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). Ammonia solution (NH3•H2O), sodium hydroxide (NaOH), sodium carbonate (Na2CO3), and nitric acid (HNO3) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Glucose, ascorbic acid, and trisodium citrate dihydrate were purchased from the Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). *Escherichia coli* (ATCC 8099) and *Staphylococcus aureus* (ATCC 25923) were purchased from South Nanjing Clinical Biological Technology Co., Ltd. (Nanjing, China).

Methods

Preparation of cellulose/Ag nanocomposites

To obtain cellulose/Ag nanocomposites, 1.0 g of cellulose fiber and 10 mL of 0.01 M $AgNO_3$ solution were added to a beaker containing 90 mL of distilled water. The solution was dispersed into a uniform suspension under vigorous magnetic stirring. After 8 min, different volumes of 0.05 M $NH_3{\bullet}H_2O$, NaOH, and Na_2CO_3 aqueous solution were added drop by drop. After 2 min, the beaker was heated in a microwave at 560 W for 10 min, and the solution was cooled to room temperature. Finally, the product was washed three times with distilled water and dried at 105 °C.

Characterization

The morphology of cellulose/Ag nanocomposites was observed using a TM-1000 scanning electron microscope (HITACHI, Tokyo, Japan). Raman spectra were collected using a DXRxi Raman imaging microscope (Thermo Scientific, Waltham, MA, USA). Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) were performed on an SDT Q600 apparatus (TA Instruments, New Castle, DE, USA) at a heating rate of 10 °C/min from 35 °C to 800 °C, under a nitrogen atmosphere. Silver content was measured using atomic absorption spectroscopy (model, HITACHI, Tokyo, Japan), and the sample was dissolved in concentrated nitric acid with heating before measuring.

Antibacterial properties

The antibacterial activity of cellulose/Ag nanocomposites was evaluated using an agar diffusion method. To prepare the medium, 5.0 g of beef extract, 5.0 g of sodium chloride, 10 g of peptone, and 15 g of agar were added to 1000 mL of distilled water and autoclaved at 121 °C for 15 min. Afterwards, 20 mL of agar medium was poured into each culture dish in a sterile room. When the medium solidified, 50 μL of the bacterial suspensions were uniformly smeared over each dish. The composite materials were added to the medium surface, and the diameter of the inhibition zone was measured after 24 h incubation at 37 °C.

To measure the sterilization rate, 0.1 g of the composite was added to 100 mL of fresh *E. coli* or *S. aureus* culture at a concentration of 10^6 colonies forming units per mL (CFU/mL). After 5, 10, 30, and 60 min of incubation with shaking at 37 °C, 50 μL of the bacterial suspension was drawn from each of Petri dishes. The same procedure was performed with pure cellulose. After 24 h incubation at 37 °C, the number of bacteria was counted. The sterilization rate was calculated by Eq. 1,

$$\eta\,(\%) = (N_0 - N) / N_0 \times 100 \tag{1}$$

where η is the sterilization rate, and N_0 and N are the viable bacteria count for the control (pure cellulose fiber) and experimental specimens (cellulose/Ag nanocomposites).

RESULTS AND DISCUSSION

Alkali Effects on Silver Incorporation in Cellulose/Ag Nanocomposites

Different alkaline compounds—$NH_3{\bullet}H_2O$, Na_2CO_3, and NaOH—were used for nanocomposite synthesis. The silver content of cellulose/Ag nanocomposites (Fig. 1a) and the utilization of silver ions (Fig. 1b) were measured by AAS. From 0 to 4 mL of

$NH_3{\bullet}H_2O$, the silver content (0.1%) and silver ion utilization rate (10%) remained low. The silver content was about 0.5% when 1.0 mL of 0.05 M Na_2CO_3 solution was added, but there was no obvious change at higher Na_2CO_3 concentration. The silver content reached approximately 0.7% when 2.0 mL of 0.05 M NaOH solution was added but slightly decreased when more NaOH solution was added. Thus, the incorporation of $NH_3{\bullet}H_2O$ had no obvious influence on silver content or silver ion utilization rate. Na_2CO_3 and especially NaOH solution increased the silver content noticeably.

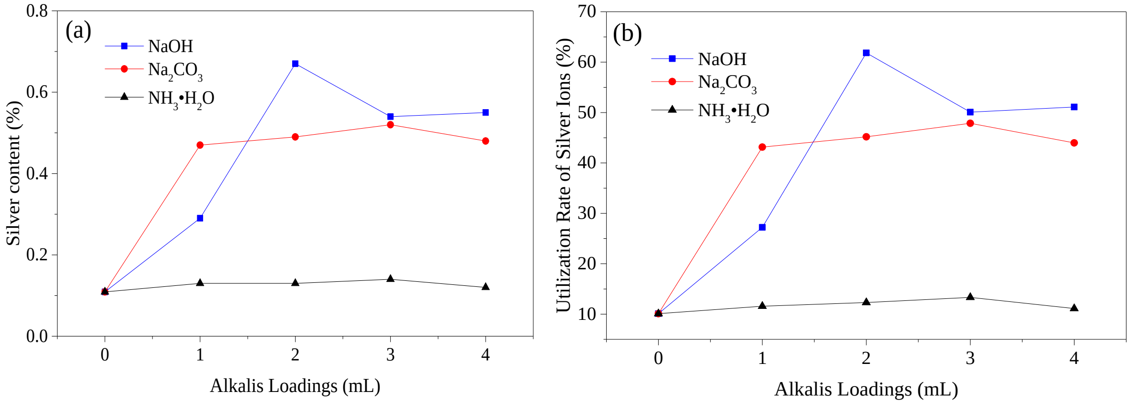

Fig. 1. Effects of the alkalis on the (a) silver content and (b) utilization rate of silver ions

Effects of Reducing Agents and Alkaline Condition on Silver Content

Reducing agents are usually added during the preparation of cellulose/Ag nanocomposites to aid in silver deposition. The effect of the reducing agents glucose, ascorbic acid, and trisodium citrate on the silver content and silver ion utilization rate were investigated (Fig. 2).

Compared with the control, the silver content exhibited no obvious increase after glucose and ascorbic acid were added. Therefore, most of the silver nanoparticles were retained in the aqueous solution. However, the silver content increased greatly in the presence of trisodium citrate.

Trisodium citrate selectively binds to (111) facets of silver nanoparticles (Sun *et al*. 2003; Xue *et al*. 2008; Zhang *et al*. 2011). The carboxyl group of trisodium citrate reacts with cellulose to form cellulose ester (Schramm *et al*. 1997). In the initial reaction, cellulose reacted with silver ions and generated a large number of hydrogen ions. As a result, in the presence of hydrogen ions, trisodium citrate reacted with cellulose to form cellulose citrate. Due to the enhanced reducibility of cellulose, more silver ions were deposited on the fiber surface.

The cellulose/Ag nanocomposites were also prepared in the presence of Na_2CO_3 (alkaline conditions) with different reducing agents. In composites formed without reducing agents, the silver content increased greatly and was higher than in the other composites.

With glucose, the alkaline condition positively affected the silver content. In contrast, when either ascorbic acid or trisodium citrate was added, there was an adverse affect on the silver content. The silver content of the latter condition decreased more than in the former. Therefore, cellulose reduced silver ions, and the alkaline conditions were more conducive to silver ion reduction than was the presence of reducing agents.

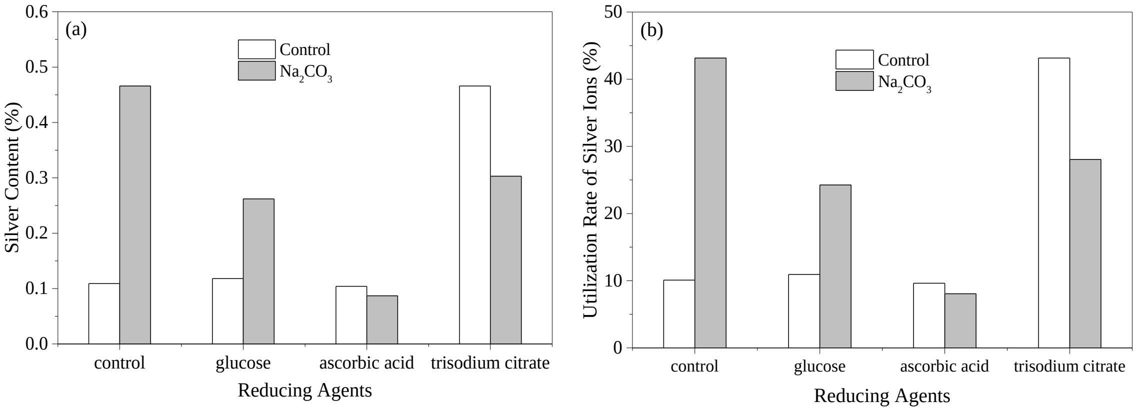

Fig. 2. Effects of reducing agents and alkaline conditions on the (a) silver content and (b) utilization rate of silver ions. The ratio of $AgNO_3$: reducing agent: Na_2CO_3 was 1:10:0.5.

SEM Characterization of the Nanocomposites

In SEM micrographs of cellulose/Ag nanocomposites prepared by microwave heating cellulose fiber under alkaline conditions with different reducing agents, silver nanoparticles of less than 100 nm and polyhedral morphology were homogeneously dispersed on the cellulose fiber surface (Fig. 3a). No agglomerates were observed.

Cellulose-based nanocomposites obtained in alkaline conditions exhibited smaller average nanoparticle size and a narrower particle size distribution than those formed in the absence of alkaline compounds. The silver nanoparticles decreased in size with the incorporation of different alkaline compounds from NH_3•H_2O to NaOH and Na_2CO_3 (Fig. 3b, c, d). Taking the change of silver content into consideration (Fig. 1a), higher silver content was associated with a smaller nanoparticle size. One possible explanation is that cellulose promotes more silver reduction, which generates more nano-silver crystal nuclei in the cellulose matrix. Therefore, silver nanoparticles would have a smaller size.

The effect of the reducing agents on cellulose/Ag nanocomposites was also studied (Fig. 3e-g and h-j). When glucose and ascorbic acid were added as the reducing agents, a portion of the unabsorbed silver ions were reduced into silver nanoparticles in aqueous solution. Without the limitation of the cellulose matrix, a portion of the silver nanoparticles agglomerated on the cellulose matrix. The latter resulted in considerable more agglomeration of silver nanoparticles because of its stronger reducibility, which reduced more unabsorbed silver ions into silver nanoparticles. No agglomeration of silver nanoparticles was observed when trisodium citrate dihydrate was the reducing agent (Fig. 3g and j); citrate acts as a capping agent that selectively binds to the 111 facets (Sun *et al*. 2003; Zhang *et al*. 2011). The role of citrate is similar to polyvinyl pyrrolidone, which selectively absorbs on the 100 plane of silver nanoparticles and inhibits their agglomeration (Wang *et al*. 2005; Wiley *et al*. 2005). Therefore, reducing agents inhibit the dispersion of silver nanoparticles on the cellulose fiber surface.

Chemical Structure Analysis

Cellulose has weak reducibility because of its content of hydroxyl groups and a reducing end group. Cellulose chains can be oxidized to oxycellulose during the reduction of silver ions into silver nanoparticles (Montazer *et al*. 2012; Maryan *et al*. 2015). The oxidation of cellulose was confirmed by Raman spectroscopy (Fig. 4). A characteristic band around 1086 cm^{-1} was attributed to the symmetric and asymmetric stretching of the COC bond in glycosidic linkages (Schenzel and Fischer 2001).

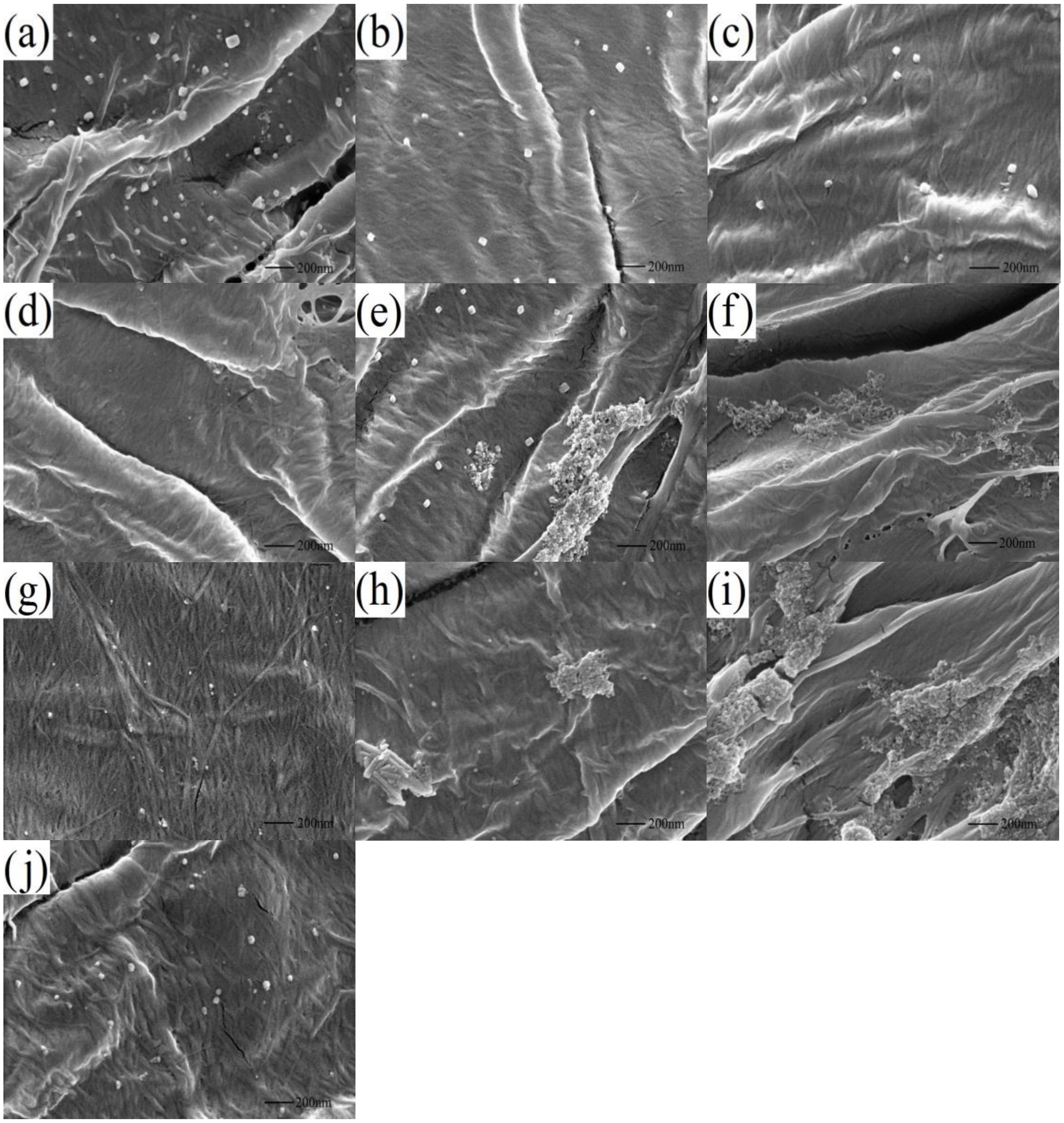

Fig. 3. SEM of cellulose/Ag nanocomposites prepared by microwave heating a cellulose fiber suspension containing 10 mL of 0.01 M $AgNO_3$ solution: a) control; b) 1.0 ml of 0.05 M $NH_3 \bullet H_2O$ solution; c) 1.0 mL of 0.05 M NaOH solution; d) 1.0 mL of 0.05 M Na_2CO_3 solution; e) 0.180 g of glucose; f) 0.176 g of ascorbic acid; g) 0.294 g of trisodium citrate dehydrate; h): 1 mL of 0.05 M Na_2CO_3 solution and 0.180 g of glucose; i) 1 mL of 0.05 M Na_2CO_3 solution and 0.176 g of ascorbic acid; j) 1 mL of 0.05 M Na_2CO_3 solution and 0.294 g of trisodium citrate dehydrate.

A band at 2900 cm^{-1} was assigned to O-H stretching vibrations (Kavkler and Demšar 2011). For cellulose/Ag nanocomposites, the peaks corresponded to COC and weakened O-H bonds. Two strong peaks appeared at 1351 cm^{-1} and 1585 cm^{-1}, representing COO^- and C=O, respectively (Jenkins *et al*. 2005; Maryan *et al*. 2015). These peaks were stronger when trisodium citrate dehydrate was added. This effect may be due to trisodium citrate on the surface of silver nanoparticles, which increased the carboxyl content of the fiber surface. These results showed that cellulose was oxidized during the reduction of silver ions.

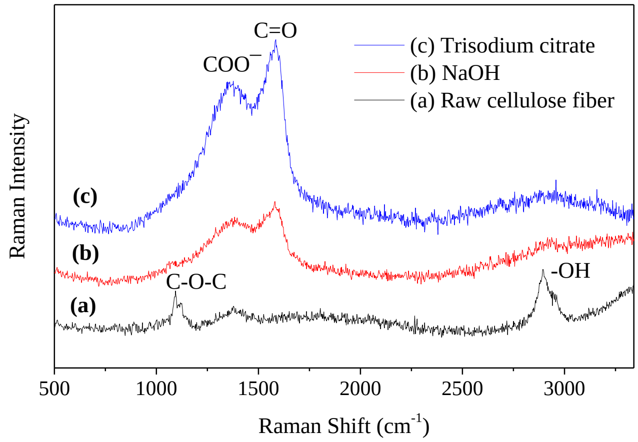

Fig. 4. Raman spectra of raw cellulose fiber and cellulose/Ag nanocomposites

TG/DSC Analysis

The effect of the temperature on the thermal behavior of cellulose/Ag nanocomposites was investigated by TG/DSC analysis (Fig. 5). The raw cellulose fiber and cellulose/Ag nanocomposites exhibited similar TG curves. When the temperature was increased from room temperature to about 300 °C, both samples exhibited a slight loss in weight, which was attributed to the loss of water molecules. From 300 to 370 °C, a rapid weight loss occurred because of thermal degradation and cellulose decomposition. As the temperature increased, the rate of weight loss began to slow down. As a result, the raw cellulose fiber and cellulose/Ag nanocomposites were reduced by 8.84% and 10.66% in mass, respectively. The latter exhibited a higher residue mass than the former, which was related to the silver particles.

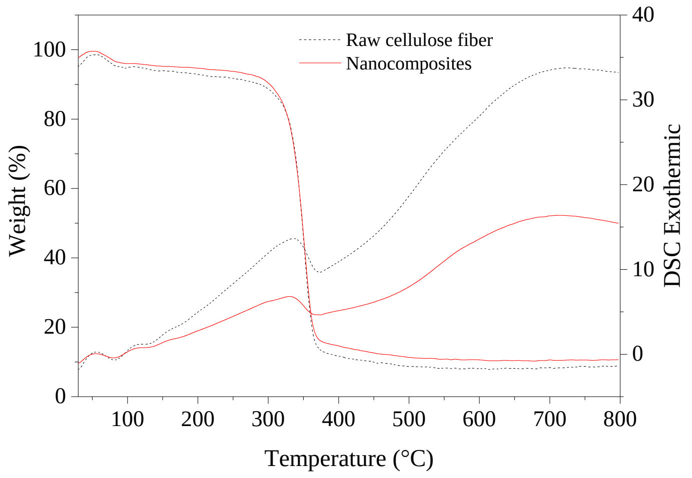

Fig. 5. TG and DSC curves of raw cellulose fiber and cellulose/Ag nanocomposites

DSC analysis showed that in the primary stage of heating, the materials were similar, but raw cellulose fiber exhibited a higher exothermic value than nanocomposites at higher temperatures (≥370 °C). Gases are produced during the charring process when cellulose is degraded (Yang *et al*. 2007). While the former has relatively high activation energy, as an endothermal process, volatilization has relatively low activation energy, as an exothermal process (Ball *et al*. 2004). The DSC value of the nanocomposites was lower than that of raw cellulose fiber, which suggests that the silver nanoparticles contributed to gas release during cellulose charring. These results indicate that the silver nanoparticles exhibited no obvious influence on the thermal stability of cellulose; however, they may promote the release of gases during the charring process.

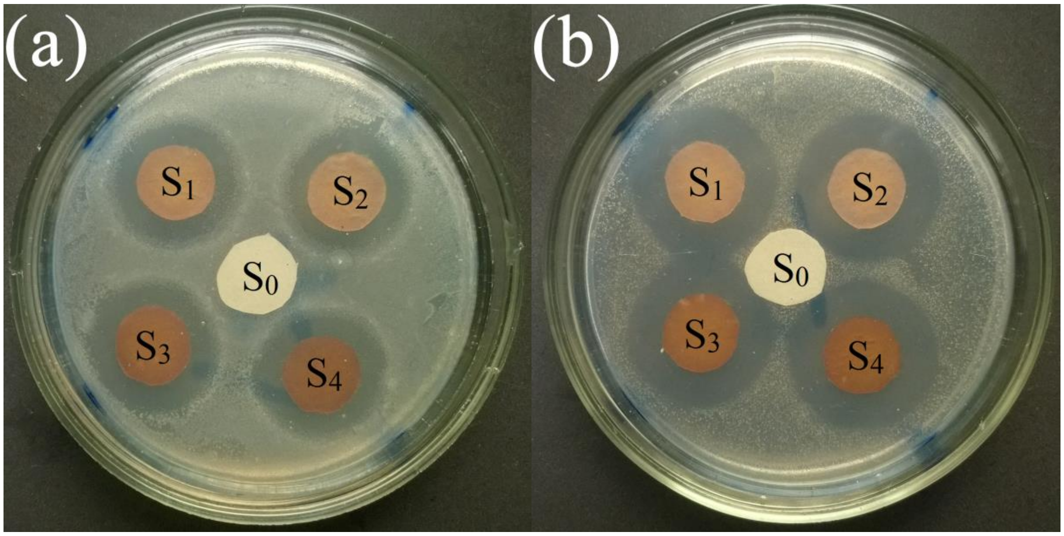

Fig. 6. Antibacterial activity of cellulose/Ag nanocomposites against (a) *E. coli* and (b) *S. aureus*. (S_0) raw cellulose fiber; (S_1) control; (S_2) $NH_3•H_2O$; (S_3) NaOH; (S_4) Na_2CO_3

Antibacterial Activity

Silver nanoparticles inherently possess bactericidal properties. The antibacterial activity of cellulose/Ag nanocomposites prepared in different alkaline solutions was measured against *E. coli* and *S. aureus* (Fig. 6 and Table 1). Raw cellulose fiber and cellulose/Ag composites obtained without the incorporation of basic compounds were used as controls. No inhibition zones were found for the raw cellulose fiber, as pure cellulose has no antibacterial activity. However, there were obvious bacterial inhibition zones for the cellulose/Ag nanocomposites prepared in different solutions. The antibacterial mechanism of nano-silver particles is still not fully understood, but it may be due to free radical and silver ions or direct interactions with bacteria (Dibrov *et al*. 2002; Cho *et al*. 2005; Danilczuk *et al*. 2006). Because the inhibition zones were similar in size, this may mean that only free radical and silver ions killed the bacteria directly, and the size of inhibition is mainly determined by their diffusion. In the suspension containing composite, nano-silver particles can interact with bacteria fully and play the role as an antibacterial agent more efficient. Therefore, the sterilization rate of cellulose/Ag nanocomposites increases with increasing silver content.

Table 1. Cellulose/Ag Nanocomposite Sterilization of *E. coli* and *S. aureus*

	E. coli (% reduction)				*S. aureus* (% reduction)			
Time/min	5	10	30	60	5	10	30	60
Control	1.3	78.4	92.3	99.8	68.4	83.5	97.7	99.99
$NH_3•H_2O$	64.5	81.6	96.1	99.9	70.3	85.6	98.8	99.99
NaOH	91.6	98.2	99.9	99.9	93.4	98.9	99.9	99.99
Na_2CO_3	94.3	99.2	99.9	99.9	95.4	99.4	99.9	99.99

CONCLUSIONS

1. Compared with $NH_3•H_2O$, NaOH or Na_2CO_3 increased the silver content of cellulose/Ag nanoparticles. NaOH resulted in a greater increase. The silver content reached a nearly invariant value when the Na_2CO_3 content was greater than 2.0 mL.
2. Glucose and ascorbic acid did not increase silver content, but trisodium citrate had a somewhat positive effect on silver content.
3. The size of silver nanoparticles decreased when more silver ions were reduced. The incorporation of reducing agents caused the agglomeration of silver nanoparticles.
4. The reduction of silver ions generated a large number of carboxyl groups on the cellulose fiber surface. Silver nanoparticles did not influence the thermal stability of cellulose.
5. Cellulose/Ag nanocomposites exhibited excellent antibacterial activity against *E. coli* and *S. aureus*.

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