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Antimicrobial cellulose acetate nanofibers containing silver nanoparticles

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Abstract

It was found for the first time that polymer nanofibers containing Ag nanoparticles *on their surface* could be produced by UV irradiation of polymer nanofibers electrospun with small amounts of silver nitrate ($AgNO_3$). When the cellulose acetate (CA) nanofibers electrospun from CA solutions with 0.5 wt% of $AgNO_3$ were irradiated with UV light at 245 nm, Ag nanoparticles were predominantly generated on the surface of the CA nanofibers. The number and size of the Ag nanoparticles were continuously increased up to 240 min. The Ag^+ ions and Ag clusters diffused and aggregated on the surface of the CA nanofibers during the UV irradiation. The Ag nanoparticles with an average size of 21 nm exhibited strong antimicrobial activity.

Keywords: Cellulose acetate; Ag nanoparticles; Electrospinning; UV irradiation; Antimicrobial activity

1. Introduction

Polymer nanocomposites containing metal nanoparticles have attracted a great deal of attention, due to their unique optical, electrical, and catalytic properties (Ottaviani, Valluzzi, & Balogh, 2002; Sarma, Chowdhury, Paul, & Chattopadhyay, 2002; Shiraishi & Toshima, 2000). They can be prepared by the mechanical mixing of a polymer with metal nanoparticles, the in situ polymerization of a monomer in the presence of metal nanoparticles, or the in situ reduction of metal salts or complexes in a polymer. The properties of these polymer nanocomposites are strongly dependent on the size, content, dispersivity, and structure of the metal nanoparticles that are incorporated within them.

Recently, considerable attention has been paid to polymer nanofibers, as they exhibit outstanding properties such as a high specific surface area and high porosity. These polymer nanofibers can be used for a wide variety of applications such as separation filters, wound dressing materials, tissue scaffolds, sensors, etc. (Huang, Nagapudi, & Chaikof, 2001; Huang, Zhang, Kotaki, & Ramakrishna, 2003; Li, Laurencin, Caterson, Tuan, & Ko, 2002; Matthews, Wnek, Simpson, & Bowlin, 2002; Park & Park, 2005; Wang et al., 2002). It is possible to produce functional nanofibers having optical, electrical, or catalytic properties by incorporating metal nanoparticles into them and subsequently extend their field of application. Li, McCann, Gratt, and Xia (2004) developed Au nanostructures on electrospun titania nanofibers by photocatalytically reducing $HAuCl_4$. It is known that the attachment of Au or other metal nanoparticles onto titania nanofibers leads to a significant improvement in their photocatalytic activity and photoelectrochemical response (Subramanian, Wolf, & Kamat, 2004). These titania nanofibers can serve as catalysts and/or catalyst supports. Rutledge and his

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co-workers (Wang, Singh, Hatton, & Rutledge, 2004) produced superparamagnetic polymer nanofibers by electrospinning magnetic nanoparticle suspensions in poly(ethylene oxide) and poly(vinyl alcohol) solutions. These magnetite nanofibers exhibited superparamagnetic behavior at room temperature. Yang et al. (2003) electrospun poly(acrylonitrile) (PAN) nanofibers containing Ag nanoparticles. The average diameters of the PAN nanofibers and the Ag nanoparticles were 400 and 100 nm, respectively.

In our previous study (Son, Youk, Lee, & Park, 2004), cellulose acetate (CA) nanofibers containing Ag nanoparticles were prepared by slow photoreduction of Ag^+ ions within CA nanofibers for 20 days in a general laboratory environment, which can be used for antimicrobial separation filters for submicron particles. In this study, for the commercial production of antimicrobial separation filters, rapid photoreduction of Ag^+ ions within CA nanofibers were carried out by UV irradiation, and the photoreduction rate, distribution, and location of the resulting Ag nanoparticles were investigated. It is believed that the average size and location of the Ag nanoparticles have a great effect on the antimicrobial activity of the CA nanofibers.

2. Experimental

2.1. Materials

CA (acetyl content 39.8%, $M_w = 30{,}000$), silver nitrate ($AgNO_3$), and acetone were purchased from Aldrich Co. and used as received.

2.2. Electrospinning

In order to prepare the CA nanofibers containing Ag^+ ions, CA and $AgNO_3$ were dissolved in a mixed solvent of acetone/water (80/20, w/w). The concentrations of CA and $AgNO_3$ were 10 and 0.5 wt%, respectively. The weight percentage of $AgNO_3$ was calculated on the basis of the weight of CA. The electrospinning setup used in this study consisted of a syringe and needle (ID = 0.84 mm), an aluminum collecting plate, and a high voltage supply (Chungpa EMT). A syringe pump connected to the syringe controlled the flow rate. The CA solutions were electrospun at a positive voltage of 17 kV, a working distance of 10 cm (the distance between the needle tip and the collecting plate), and a solution flow rate of 3 ml/h. All electrospinning procedures were carried out at room temperature.

2.3. UV irradiation of the CA nanofibers

The CA nanofibers were electrospun with 0.5 wt% of $AgNO_3$ on a glass slide and then irradiated with UV light having maximum wavelengths of 254 and 365 nm using a 500 W high-pressure Hg lamp system (StabiLight, NT-LS-HG50-SR), in order to investigate the photoreduction of the Ag^+ ions incorporated within them. The glass slide was washed with deionized water in an ultrasonicator for 30 min and completely dried.

2.4. Measurement and characterization

UV–visible spectra were recorded on a Perkin Elmer Lambda 35 spectrometer. TEM images were obtained using a Philips CM 200 transmission electron microscope for samples deposited on carbon coated copper grids. In order to investigate the distribution of the Ag nanoparticles within the CA nanofibers, the latter were molded in an epoxy resin and microtomed to a thin section. The antimicrobial activity of the CA nanofibers with Ag nanoparticles was tested against Gram-positive *Staphylococcus aureus* (*S. aureus*, ATCC6538) and Gram-negative *Escherichia coli* (*E. coli*, ATCC 25922), *Klebsiella pneumoniae* (*K. pneumoniae*, ATCC 4352), and *Pseudomonas aeruginosa* (*P. aeruginosa*, ATCC 27853) by the nonwoven fabric attachment method (Antibacterial of polymeric materials (FC-TM-20), FITI Testing & Research Institute, 2001). The agar plates containing the test samples and control (blank) were incubated at 37 °C for 18 h. The reduction in the number of bacteria was calculated using the following equation, Reduction (%) $= (B-A)/B \times 100$, where A and B are the surviving cells (colony forming unit/ml) for the plates containing the test samples and the control, respectively, after 1 h of contact time.

3. Results and discussion

3.1. Rapid photoreduction of Ag^+ ions in the CA nanofibers

The incorporation of metal nanoparticles into polymer nanofibers can be achieved by either electrospinning polymer solutions containing metal nanoparticles or reducing metal salts or complexes in electrospun polymer nanofibers. In this study, CA nanofibers containing Ag nanoparticles were prepared using the latter method. Ag^+ ions can be reduced to produce Ag nanoparticles by UV or γ-ray irradiation, ultrasound, prolonged reflux, or chemicals (Lu et al., 2003; Pastoriza-Santos & Liz-Marzan, 1999; Wang & Asher, 2001; Zhang, Zhang, Wang, Chen, & Lei, 2001). When the CA nanofibers in this study were irradiated with UV light at 254 nm, a gradual change in color from colorless through yellow to brown was observed with increasing irradiation time, confirming the reduction of the Ag^+ ions and the subsequent formation of Ag nanoparticles. Fig. 1 shows the changes in the UV–visible absorption spectra of the CA nanofibers according to the UV-irradiation time. The narrow size distribution and good dispersion of the Ag nanoparticles within the CA nanofibers led to the spectra having relatively narrow and symmetrical absorption peaks. The intensity of the surface plasmon resonance absorption gradually increased and the maximum absorption peak shifted slightly to longer wavelengths, increasing from 438 to 445 nm over the initial 240 min period of irradiation (summarized in Fig. 2). This indicates that the

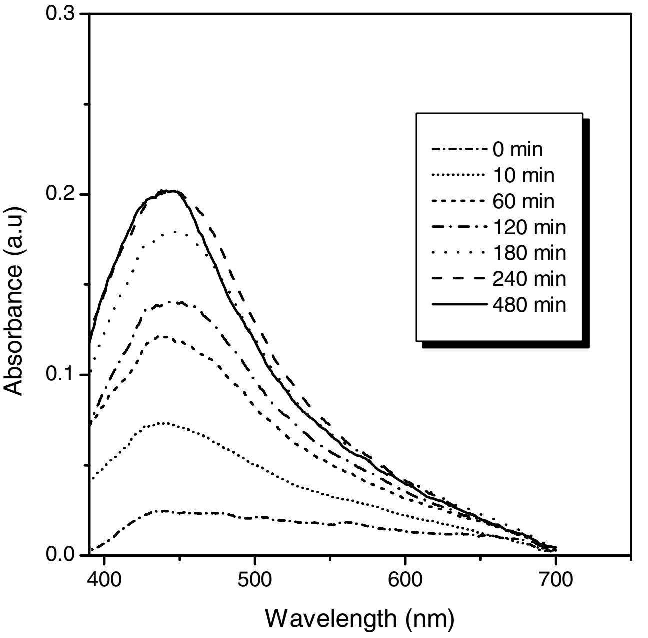

Fig. 1. The changes in the UV–visible absorption spectra of the CA nanofibers containing 0.5 wt% $AgNO_3$ according to the UV irradiation time.

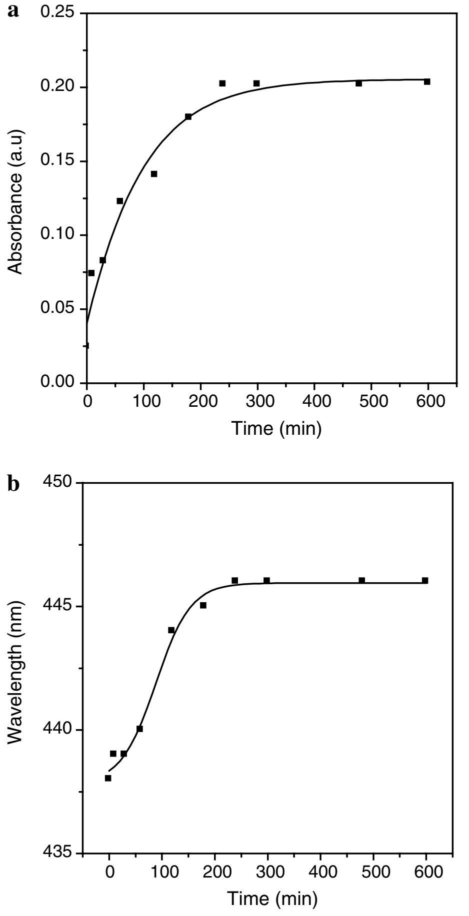

Fig. 2. (a) The increase and (b) shift of the maximum UV–visible absorption peaks of the CA nanofibers containing 0.5 wt% $AgNO_3$ according to the UV irradiation time.

number and size of the Ag nanoparticles continuously increased up to this time. However, the absorption peaks did not broaden with increasing UV irradiation time, implying that the distribution of the Ag nanoparticles was not changed, although their size was increased. After 240 min, the increase in the number and size of the Ag nanoparticles came to an end, probably due to the depletion of the Ag^+ ions in the CA nanofibers which were available to be reduced. Fig. 3 shows the changes in the TEM images of the CA nanofibers according to the UV irradiation time. A large number of Ag nanoparticles were generated and evenly distributed in the CA nanofibers. The number and size of the Ag nanoparticles increased, as the UV irradiation time increased. Fig. 4 shows the increase in the average size of the Ag nanoparticles according to the UV irradiation time. The distributions of the Ag nanoparticles did not broaden with increasing UV irradiation time, which is consistent with the UV–visible absorption analysis. The average size of the Ag nanoparticles was 21 nm after UV irradiation for 240 min. When the CA nanofibers were irradiated with UV light at 365 nm, the intensity of the maximum absorption increased much more slowly. After UV irradiation at 365 nm for 240 min, the maximum absorption intensity was less than half of that obtained by irradiation with UV light at 245 nm, and the position of the maximum absorption was located at 427 nm. In this case, the average size of the Ag nanoparticles was 12 nm (Fig. 5). These results indicate that the number and size of the Ag nanoparticles were dependent on the photoreduction rate. Numerous larger Ag nanoparticles were generated by the rapid photoreduction of the Ag^+ ions.

Fig. 6 shows the cross-sectional TEM images of the CA nanofibers after irradiation with UV light at 254 nm for 240 min. Ag nanoparticles were observed only on the surface of the CA nanofibers. Korchev, Bozack, Salten, and Mills (2004) prepared Ag^+-doped sulfonated poly(ether–ether)ketone–poly(vinyl alcohol) (SPEEK-PVA) films and irradiated them with UV light at 350 nm using a mask. Forty micrometer wide lines of Ag nanoparticles were imaged on the film surface. Initially, the Ag nanoparticles so formed were randomly distributed across the film upon irradiation with UV light at 350 nm, but Ag particle-rich layers with thicknesses of ~50 nm developed on the film surfaces along with "depletion zones" with thicknesses of ~1 μm as the photoreduction proceeded. This was explained in terms of the diffusion of the Ag^+ ions and Ag clusters generated within the film into the surface, where they aggregated to form Ag nanoparticles. By taking into consideration the depletion zones with thicknesses of ~1 μm in the SPEEK-PVA film irradiated with UV light at 350 nm, it is reasonable to suppose that the formation of Ag nanoparticles on the surface of the CA nanofibers was caused by the diffusion and subsequent aggregation of Ag^+ ions and Ag clusters during the UV irradiation. The average diameter of the CA nanofibers electrospun with 0.5 wt% $AgNO_3$ was 610 nm (Son et al., 2004).

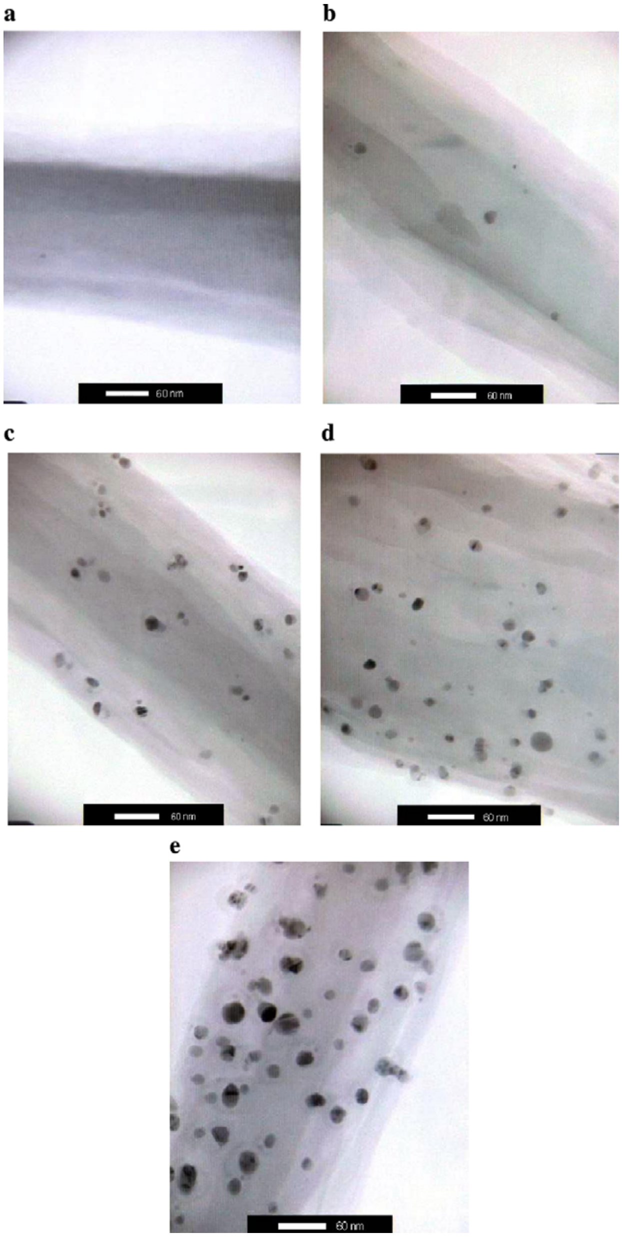

Fig. 3. TEM images of the CA nanofibers containing 0.5 wt% $AgNO_3$: UV irradiation time (a) 0 min, (b) 10 min, (c) 60 min, (d) 120 min, and (e) 240 min. The scale bars correspond to 60 nm.

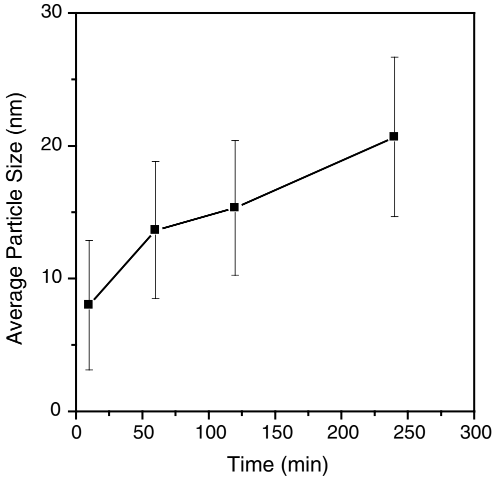

Fig. 4. Increase in the average size of the Ag nanoparticles according to the UV irradiation time.

Fig. 5. TEM images of the CA nanofibers containing 0.5 wt% $AgNO_3$ after irradiation with UV light at 365 nm for 240 min. The scale bar corresponds to 60 nm.

3.2. Antimicrobial test of the CA nanofibers after photoreduction

It is believed that the antimicrobial activity of Ag nanoparticles is dependent on their average size. Sondi and Salopek-Sondi (2004) reported the preparation of Ag nanoparticles with an average size of 12 nm, which had strong antimicrobial activity. In this study, the antimicrobial activity of the CA nanofibers containing Ag nanoparticles with an average size of 21 nm was tested against Gram-positive *S. aureus* and Gram-negative *E. coli, K. pneumoniae* and *P. aeruginosa* by the nonwoven fabric attachment method. Gram-negative bacteria are responsible for more than 80% of all infections. When these bacteria were incubated on the CA nanofibers, no bacterial colonies were observed. The number of bacteria was reduced by 99.9% after 18 h incubation, indicating that the Ag nanoparticles with an average size of 21 nm successfully inhibited the growth of these bacteria.

Practically, the antimicrobial activity of the Ag nanoparticles is exerted mainly by those nanoparticles located on the surface of the CA nanofibers. It was found in this study that Ag nanoparticles were predominantly generated on the surface of the CA nanofibers when the Ag^+ ions in the CA nanofibers were photoreduced. It is therefore suggested that the generation of Ag nanoparticles on the surface of polymer nanofibers by UV irradiation constitutes a practical method of producing antimicrobial polymer nanofiber mats.

Fig. 6. Cross-sectional TEM images of the CA nanofibers containing 0.5 wt% $AgNO_3$ after UV irradiation for 240 min. The scale bar corresponds to 200 nm.

4. Conclusions

When the CA nanofibers electrospun from CA solutions with 0.5 wt% of $AgNO_3$ were irradiated with UV light at 245 nm, the number and size of the Ag nanoparticles generated increased continuously up to 240 min, but their size distribution did not broaden. The Ag nanoparticles were generated only on the surface of the CA nanofibers and their average size was 21 nm after UV irradiation for 240 min. It is considered that Ag^+ ions and Ag clusters diffused and aggregated on the surface of the CA nanofibers during the UV irradiation. When the CA nanofibers were irradiated with UV light at 365 nm, the photoreduction of the Ag^+ ions was delayed and the average size of the Ag nanoparticles was 12 nm. The CA nanofibers incorporating Ag nanoparticles with an average size of 21 nm exhibited strong antimicrobial activity.

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