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Short communication

Electrospun chitosan/gelatin nanofibers containing silver nanoparticles

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ABSTRACT

This paper addresses a new method for making silver nanoparticles (AgNPs) containing chitosan/gelatin nanofibers via electrospinning. In the current paper, the AgNPs sizes ranging from 1 nm to 5 nm were synthesized at room temperature using microcrystalline chitosan as the reducing agent and stabilizer followed by dissolving the AgNPs-chitosan composites in gelatin containing acetic acid solution and then electrospinning the prepared solution into AgNPs containing chitosan/gelatin nanofibers. The structure of the resultant nanofibers was examined with the aid of scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The measurement results indicated that the nanofibers having the diameter range of 220–400 nm were apparently smooth and the silver nanoparticles with the size distribution from 2 nm to 10 nm were successfully incorporated into the electrospun nanofibers.

1. Introduction

Silver nanoparticles (AgNPs) are well known for strong antibacterial properties and no harm on human cells (Reneker & Yarin, 2008). Recently, Considerable attention has been paid to incorporation of AgNPs into ultrathin fibers for many important applications, such as using wound dressing materials in medical field (Son, Youk, & Park, 2006; Tofoleanu et al., 2008; Xu et al., 2006). Some researchers electrospun AgNPs containing nanofibers by adding metallic salts (mainly silver nitrate) into polymer solutions and further treating the nanofibers by heating, UV or γ irradiation (Hong, 2007; Jin, Lee, Jeong, Park, & Youk, 2005; Yoksan & Chirachanchai, 2009; Xu et al., 2006).

Some polymers have been successfully used for the synthesis of metal nanoparticles (Raveendran, Fu, & Wallen, 2003). The binding interaction between polymer and the metal nanoparticles, polymer stabilises the metal nanoparticle–polymer composite, and hence, the nanoparticles attached to the polymer chains will disperse in the solution when the composite dissolve. Therefore, it is possible to prepare the metal nanoparticles containing nanofibers via electrospinning the solution of the metal nanoparticle–polymer composite, if the size of nanoparticles is small enough.

Chitosan, a copolymer of glucosamine and N-acetylglucosamine units linked by 1,4-glucosidic bonds, is the second most abundant natural polymer. It has been used as both a reducing agent and stabilizer to form AgNPs through heating, γ or UV irradiation (Chen, Song, Liu, & Fang, 2007; Murugadoss & Chattopadhyay, 2008; Yoksan & Chirachanchai, 2009). In the present study, microcrystalline chitosan (MCCh) was used as the initiating material to synthesize AgNPs at room temperature without any special treatment, and then the solution of AgNPs-chitosan composite was dissolved in gelatin containing acetic acid solution and electrospun to produce nanofibers. The morphology and structure of the electrospun fiber mats were examined and discussed.

2. Experimental

2.1. Materials

Chitosan, with viscosity-average molecular weight of 5.1×10^4 and deacetylation degree of 0.87, was provided by Zhejiang Ao-Xing Biotechnology Co. Ltd. (Zhejiang, P.R. China). Gelatin (from porcine skin, Sigma Aldrich), silver nitrate ($AgNO_3$, 99.5%; Merck), acetic acid (glacial, 99–100%; Merck), sodium hydroxide (NaOH, 98%; Merck) were used as received. Milli-Q grade water was used in all experiments.

2.2. Synthesis of AgNPs-chitosan composite

Microcrystalline chitosan (MCCh) in the form of a gelatinous water dispersion was prepared according to a previously reported method by which chitosan was regenerated via adding NaOH solution into chitosan solution at constant stirring (Struszczyk, 1987). The final pH of the dipsersion was 10.0 and the total polymer content amounted to 1% (w/w), including chitosan and gelatin.

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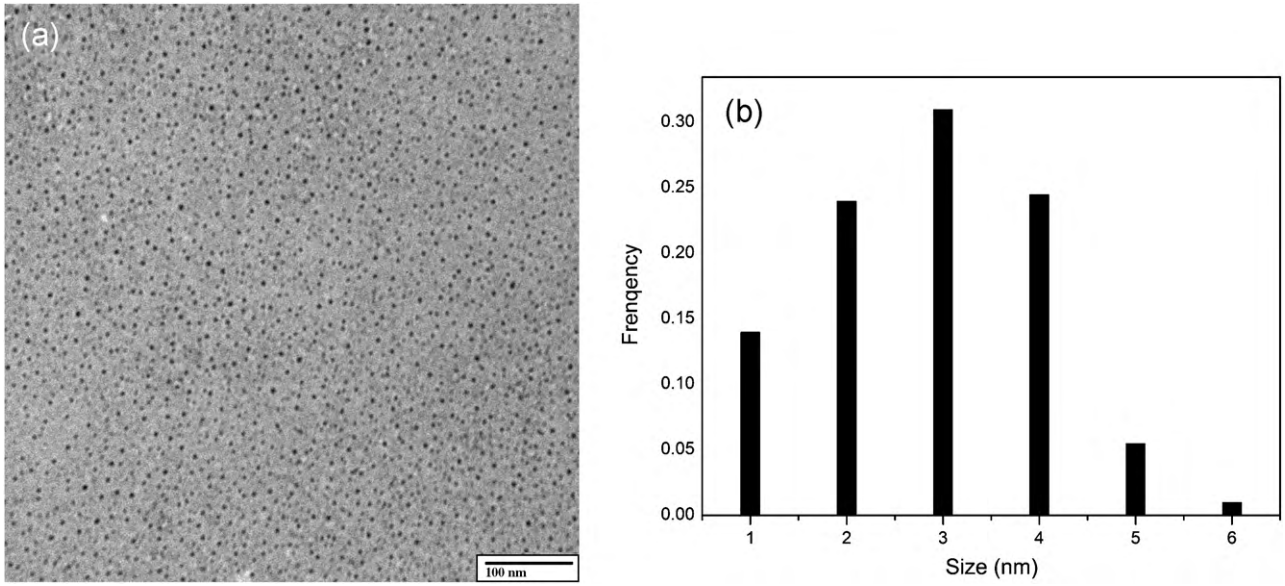

Fig. 1. TEM image (a) and histograms size distributions (b) of silver nanoparticles.

AgNPs-chitosan composite was synthesized by adding 2 ml of freshly prepared 1.0×10^{-2} mol/l $AgNO_3$ solution to 50 ml of MCCh gelatinous water dispersion, at constant stirring and room temperature. The reaction was kept for 60 min and the precipitate was filtered, washed and air-dried.

2.3. Electrospinning AgNPs containing chitosan/gelatin nanofibers

The AgNPs-chitosan composite was dissolved in 0.1% (v/v) acetic acid solution and a transparent solution was obtained with the concentration of 0.2% (w/w). Gelatin was dissolved in the foresaid solution to obtain a polymer solution for electrospinning at a 10% (w/w) concentration. The resulting polymer solution was electrospun using the following conditions in which the electrical potential was 25 kV, the distance between the nozzle tip and collector was 20 cm; the diameter of nozzle was 0.1 mm, and the feed rate of the solution was 3 ml/h, using 10% (w/w) gelatin solution as the control. The collected nanofibers were dried in a vacuum oven overnight at room temperature.

2.4. Measurement and characterization

Zeta (ζ) potential value of the silver nanoparticle solutions was determined using a Delsa^{TM} Nano Submicron Particle Size and Zeta Potential Particle Analyzer; a drop of aqueous solution was dropped onto a carbon-coated copper grids, air-dried and observed with a HITACHI H-7650 transmission electron microscope (TEM).

The fiber morphology was observed using a JEOL JSM-5800LV scanning electronic microscopy (SEM). Fiber diameters were obtained using Java Image Processing Software Image J 1.29. The X-ray photoelectron spectra were recorded on a Bruker AXS D8 discover XPS (X-ray Photoelectron Spectroscopy) using a monochromated Al Kα X-ray source. The distribution and morphology of AgNPs in the fibers were observed using TEM.

3. Results and discussion

3.1. Synthesis of silver nanoparticles

Chitosan is an oxygen-rich natural polysaccharide consisting of anhydroglucose units joined by an oxygen linkage. When $AgNO_3$ was mixed with chitosan solution, Ag^+ ions could be bound to chi-

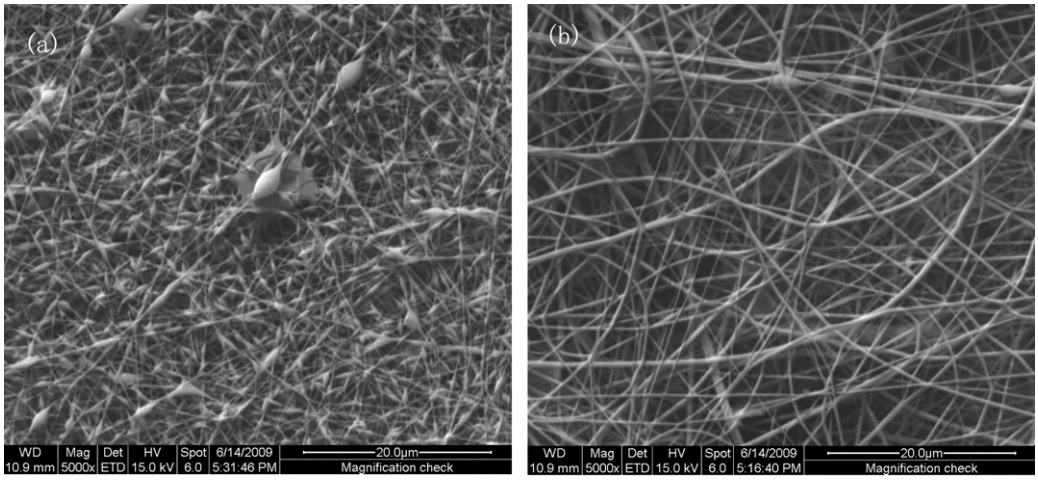

Fig. 2. SEM images of the pure gelatin nanofibers mat (a) and silver nanoparaticles containing mats (b).

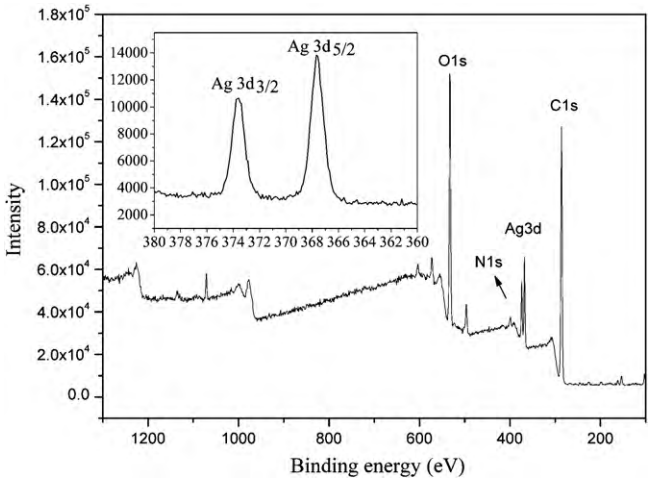

Fig. 3. XPS spectra of gelatin nanofibers mats containing silver nanoparticles.

tosan chains via electrostatic (i.e., ion–dipole) interactions, because the electron-rich oxygen atoms of polar hydroxyls and ether groups from chitosan were expected to interact with electropositive transition metal cations, forming chitosan-Ag^+ complex (Huang, Yuan, & Yang, 2004). Under certain conditions, further reducing Ag^+ to Ag would result in the aggregation of silver clusters into nanoparticles. In the reactions occurred in this study, the formed silvers clusters and nanoparticles were bound by chitosan chains, while the previously reported reactions were performed with the aid of heating treatment, γ or UV irradiations.

Microcrystalline chitosan (MCCh) is a specific physical form of chitosan and is superior over standard chitosan in terms of its ability to chelate metals form hydrogen bonds and retain water. It was observed in the present study that MCCh dispersion turned yellow with the addition of $AgNO_3$ solution even at room temperature without any other special treatments in about 10 min, suggesting the formation of AgNPs.

The TEM image of the silver nanoparticles was shown in Fig. 1(a). The diameters of nanoparticles were calculated with DigitalMicrograph™ software (Gatan, Inc.) and the histogram of the size distribution was showed in Fig. 1(b). It is observed that the AgNPs were highly monodispersed and the sizes of most particles fell in the range of 1 nm and 5 nm. The Zeta potential (ζ) of the AgNPs solution was determined as −45.27 mV which indicated a high stability.

3.2. Morphology and structure of the chitosan/gelatin nanofibers

As a natural polymer, gelatin has been used for several biomedical applications due to its biodegradability and biocompatibility, and many attempts have been reported to form gelatin nanofibers by electrospinning using polar organic solvents such as 2,2,2-trifluorothanol (TFE), hexafluoro isopropanol (HFIP) and water in which organic acid such as formic acid, acetic acid were usually added to improve the spinnability of the solutions (Chang et al., 2005; Huang et al., 2004; Xu, Yu, Wu, & Zhou, 2007; Yin et al., 2009; Zhang, Venugopal, Huang, Lim, & Ramakrishna, 2006). In this study, gelatin was selected as the polymer component for its specific application in medical field and acetic acid solution was selected as the solvent. Fig. 2(a) showed the SEM image in which many polymer beads were observed, which were probably attributed to the relatively high surface tension of the polymer solution. However, the gelatin solution mixed with AgNPs was successfully electrospun into nanofibers and the SEM image (ca. Fig. 2(b)) showed cross-sectionally round fibers without beads, the diameters of which were between 220 nm and 400 nm.

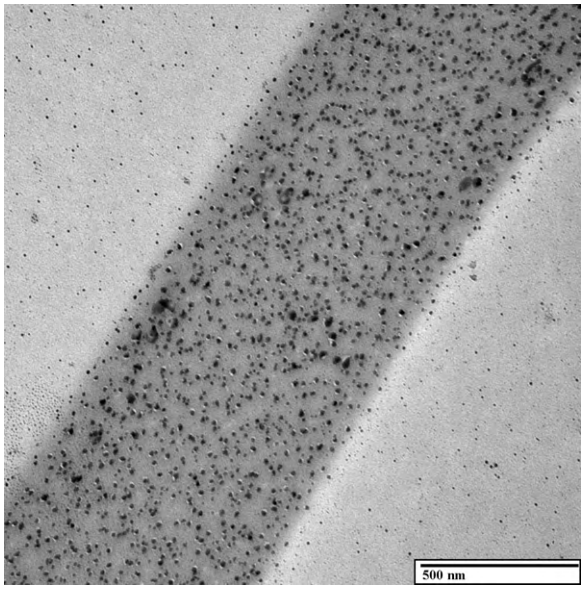

Fig. 4. Section TEM image of an electrospun fiber containing silver nanoparticles.

The XPS spectrum of the gelatin/chitosan nanofiber mat was shown in Fig. 3. The Ag $3d_{5/2}$ spectra of AgNPs in the gelatin matrix appeared as a single peak at the binding energy (BE) of 367.4 eV, indicating that the AgNPs were successfully combined into the electrospun mat. Also, the N 1s peak was found at 397.5 eV which suggests the presence of chitosan. The observation to TEM image in Fig. 4 confirmed the structure described above. Apparently, AgNPs were successfully combined into the fibers. A few particles seem to aggregate to some extent and the size range was between 2 nm and 10 nm which is lager than that in the solution.

4. Conclusion

Silver nanoparticles with size of 1–5 nm were prepared using microcrystalline chitosan as a reducing agent and stabilizing agent at room temperature. The AgNPs-chitosan composite was dissolved in acetic acid with gelatin and the solutions were successfully electrospun into chitosan/gelatin nanofibers which contained AgNPs. The results of XPS and TEM confirmed the structure of AgNPs containing nanofibers, and the resultant composite nanofibers could find important application in biomedical field, e.g., as wound dressings, due to the advantages of chitosan, gelatin and silver nanoparticles.

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