Synthesis of Antimicrobial Silver Nanoparticles on Silk Fibers Via γ-Radiation

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Received 26 January 2008; accepted 11 November 2008
DOI 10.1002/app.29716
Published online 18 February 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Antimicrobial silver nanoparticles (NPs) were successfully synthesized on the surface of silk fibers via γ-ray irradiation. The products were characterized with scanning electron microscope (SEM), energy dispersion spectrum, and X-ray diffraction. The results revealed that the silver particles with a diameter of less than 20 nm were immobilized and well dispersed on the surface of silk fibers. The antimicrobial capability against the gram positive bacterium *Staphylococcus aureus* and the washing stability of the silk fibers produced with different conditions were tested and found to be excellent. The silk fibers treated with 1 m*M* solution and 10 kGy γ-radiation showed 96% antimicrobial activity and still kept above 85% antibacterial activity after 10 washing cycles. Moreover, a mechanism for the formation of silver NPs on silk fibers under γ-radiation was generally discussed. The resulting silk fibers coated with silver NPs can be useful as functional fabrics in a range of applications. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2511–2515, 2009

Key words: fibers; nanotechnology; radiation; silver; antimicrobial

INTRODUCTION

As the rapid development of the nanotechnology, a wide range of nanoparticles (NPs) and nano-structures have been used to modify the textile fibers to bring new properties and special function to the final clothing products.[1–4] In recent years, much interest has been given to the development of clean textiles by means of surface modification of the cloth fibers with antistain, self-cleaning or antimicrobial coatings. For example, antistain coating can be prepared by the deposition of a fluorinated layer[5] or through the use of coatings which roughness mimics the well-known lotus flower effect.[6,7] Self-cleaning surfaces can be designed trough the use of titanium dioxide NPs which can act as photocatalyst under UV light.[8] Antimicrobial fibers can be made by grafting antimicrobial metal NPs or antimicrobial organic substances on their surfaces.[9–11] Various methods can be used for the surface modification of fibers with NPs, including blending of the NPs in the polymer matrix before spinning, depositing the desired functional NPs onto fibers, or directly chemical synthesizing nano-structures on the surface of textiles.[12–15]

Silver ions have been used as antimicrobial agents throughout history.[16,17] The application of silver NPs for imparting antimicrobial capabilities properly to textile has recently received a growing interest from both the academic and commercial fields. Lee et al., achieved antibacterial cotton and polyester fabrics by padding them with nano-sized silver colloidal solution.[18] Tarimala et al., reported a new approach to produce antimicrobial cotton fabric with silver nanoparticle-doped silica using sol-gel process.[19] Arai et al., made antimicrobial silk fabrics by tow steps: first, they modified the silk fabrics with TA or EDTA dianhydride; next, they let the modified fabrics absorb silver ions to realize antibacterial activity.[20,21] Dubas et al., reported the preparation of antimicrobial silk fibers modified with silver NPs by the layer-by-layer deposition method.[22]

In this study, we developed a simple method to synthesize silver NPs on the surface of silk fibers via γ-ray irradiation. Scanning electron microscope (SEM), X-ray diffraction (XRD) and energy dispersion spectrum (EDS) were used to identify the products and we found that well-dispersed silver NPs with diameter of less than 20 nm were bound on the surface of silk fibers. The antimicrobial capability against the gram positive bacterium *Staphylococcus aureus* and the washing stability of the silk fibers produced with different conditions were tested and found to be excellent. A mechanism for the formation of silver NPs on silk fibers under γ-irradiation was generally discussed. The resulting fibers might be useful as functional fabrics in a range of applications in the future.

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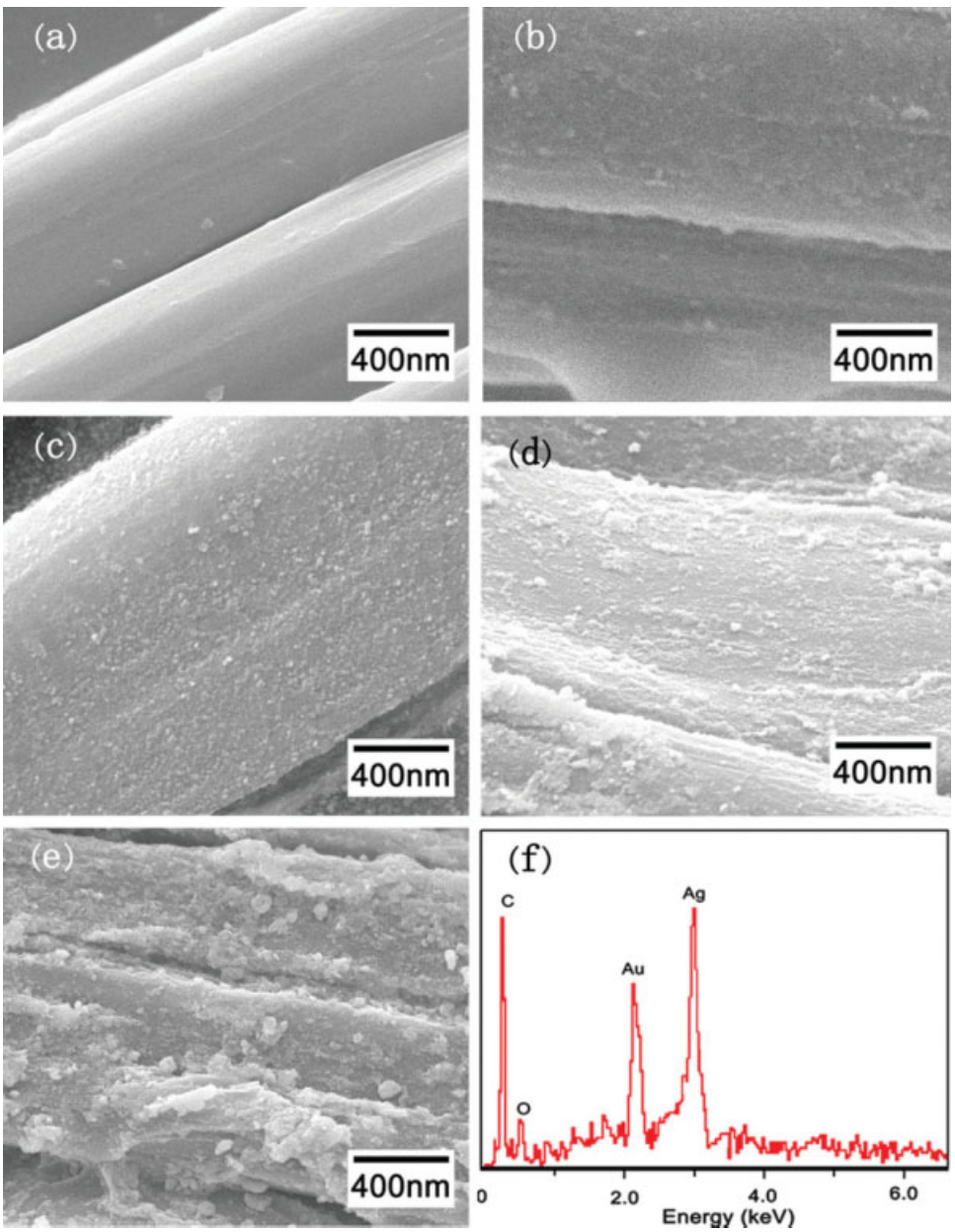

Figure 1 SEM images of silk fiber treated with different reaction conditions: (a) the raw silk fiber; (b) 0.2 m*M* $AgNO_3$, 10 kGy; (c) 1 m*M* $AgNO_3$, 10 kGy; (d) 1 m*M* $AgNO_3$, 20 kGy; (e) 5 m*M* $AgNO_3$, 30 kGy. (f) the EDS spectrum of the silk fibers with silver NPs in (c). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

EXPERIMENTAL

Materials

Silk fibers (no twist) were provided by Huajia Company (Suzhou, China). Silver nitrate ($AgNO_3$), isopropyl alcohol ($(CH_3)_2CHOH$) were purchased from Shanghai Reagent Company and used without further purification. All other chemicals used in experiments were of analytical grade.

Preparation of silver NPs on the surface of silk

We directly synthesized silver NPs on the surface of silk fibers via γ-ray irradiation in $AgNO_3$ solution at room temperature under ambient pressure. A typical synthesis route: 10 mL $AgNO_3$ (10 m*M*) and 5 mL $(CH_3)_2CHOH$ were added into 85 mL distilled water; then the silk fibers were put into the solution and the pure N_2 was bubbled for 1 h to remove the O_2 dissolved in the solution; afterwards, the solution with silk fibers was irradiated under γ-ray for a given absorbed dose (6 kGy/h, 10 kGy) and the silver NPs were synthesized on the silk; lastly, products were obtained after washing with ethanol and water three times and dried in vacuum at 60°C. To study the effects of concentration of reaction solution and absorbed dose on the products, multiple

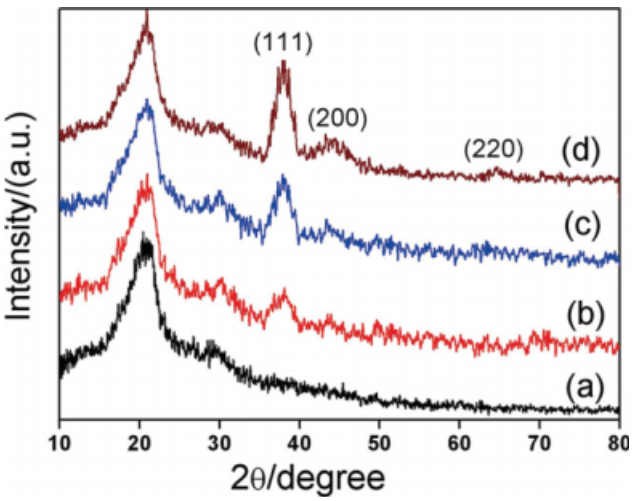

Figure 2 XRD patterns of the products obtained in different reaction conditions: (a) the raw silk fiber; (b) 0.2 m*M* $AgNO_3$, 10 kGy; (c) 1 m*M* $AgNO_3$, 10 kGy; (d) 5 m*M* $AgNO_3$, 30 kGy. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

concentrations of final reaction solution (0.2, 1, 5 m*M*) and various levels of absorbed dose (2, 5, 10, 20, 30 kGy) were used to treat silk fibers following the methods mentioned above. All treatments were done in three or more independent experiments.

Characterizations

SEM images were taken on LEO1530VP SEM, using an accelerating voltage of 21 kV. The elementary analysis was carried out at an EDS. Before SEM analysis, the prepared silk fibers were mounted on the sample holder with double sided tape and coated with a thin layer of evaporated gold.

XRD patterns were recorded on Bruker D8-ADVANCE X-ray diffractometer with graphite-monochromatized Cu -Kα radiation ($\lambda = 0.154178$ nm).

The antimicrobial activity of the products was tested by a colony count method according to AATCC 100, a standard test method for determining the antimicrobial activity of immobilized antimicrobial agents. The tests of antimicrobial activity were done in four independent experiments. To study the washing stability, the results fibers were subjected to washing cycles according to the ISO 105 C-01 procedure. After a required number of such washing cycles, the antimicrobial property was examined. The examinations of washing stability were carried out in three independent experiments.

RESULTS AND DISCUSSION

The concentration of reaction solution and the irradiation dose may be the important parameters in our experiments. The concentration of reaction solution maybe decides the ultimately quantity of the NPs on silk fibers and affect the size and diameter distribution of NPs. The irradiation dose maybe determines the extent of the reaction and also can lead to the damage of the surface structures of the silk fibers in a high value. So we studied and discussed the effect of those two critical conditions on the products.

Figure 1 is the SEM images of the samples treated with different reaction conditions. Figure 1(b) shows that very few particles are attached on the silk fiber. Figure 1(c) reveals that well-dispersed silver NPs with the mean size of less than 20 nm are synthesized on the surface of the silk fiber. The EDS spectrums [Fig. 1(f)] also identify the formation of silver NPs on the silk. The presence of silver element on the surface of silk fibers guarantees the antimicrobial activity of products, which will be detailedly discussed in the next section. From Figure 1(d,e), we can observe that the big size silver particles are aggregated on the fiber and the surface of the silk fiber is destroyed in a way and looks very rough compared with Figure 1(a). So, we conclude that 1 m*M* and 10 kGy are proper conditions to produce better silver NPs modified silk fibers.

Figure 2 shows the XRD patterns of the raw silk fibers (a) and the silk fibers with silver NPs (b, c, d). Besides the characteristic peak of the silk at 20°, three peaks at about 38, 44, and 65 degree are observed in Figure 2(b–d), which correspond to the (111), (200), (220) planes of crystalline Ag (JCPDS card. No. 4-0783). The XRD peaks are broadened due to the small nature of NPs. From Figure 2(c),

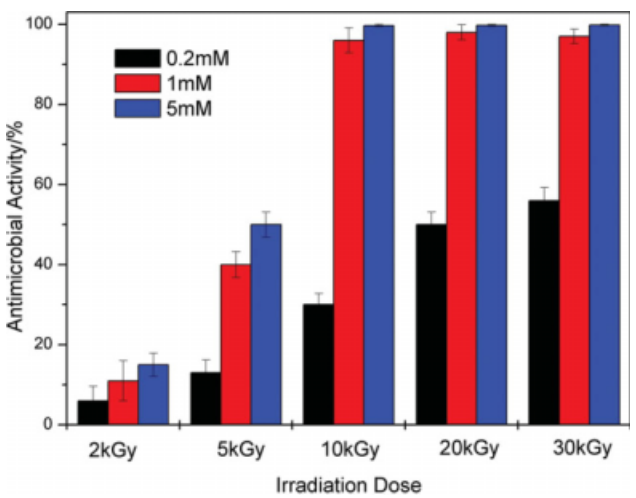

Figure 3 Antimicrobial test on silk fibers with silver NPs. Data represents mean ± SEM for four independent experiments, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

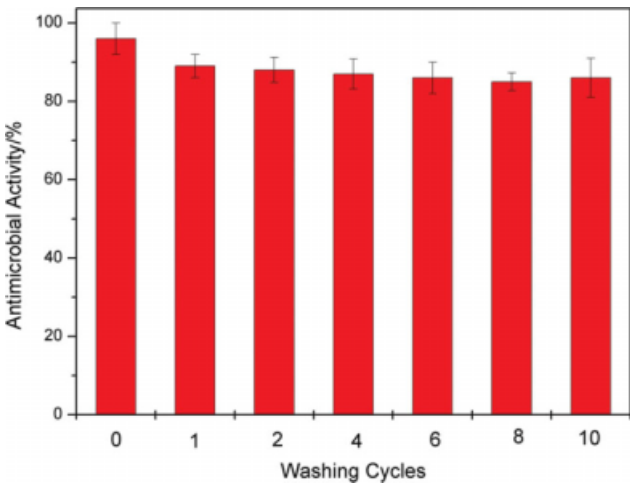

Figure 4 Washing stability of the silk fibers treated with silver NPs. Data represents mean ± SEM for three independent experiments, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the average crystallite size determined from the Debye-Scherrer formula is estimated to be about 20 nm, which is in good agreement with the SEM results.

Figure 3 reveals that the antimicrobial activity of products is enhanced as the increase of reaction concentration and the elevation of irradiation dose. But when the irradiation dose becomes very high, the antibacterial activity of fibers increases slowly (even decreases), which is probably because of the damage of the surface structure of the silk fibers in a high irradiation dose. When the reaction conditions are 1 m*M* and 10 kGy, the antimicrobial activity of resulted silk fibers can reach 96%.Therefore, we will discuss the washing stability of the product obtained in this conditions next.

Figure 4 shows the washing stability of the treated silk fibers with silver NPs, which synthesized in the condition of 1 m*M* and 10 kGy. It implies that the silk fibers with silver NPs have excellent washing stability and can keep above 85% antimicrobial activity after 10 washing cycles.

The schematic presentation of the formation of silver NPs on the surface of silk fibers via γ-radiation is shown in Figure 5. As $AgNO_3$ aqueous solution was added into the reaction mixture containing silk fibers, Ag^+ was absorbed quickly onto the surface of the silk fibers by both electrostatic and coordination interactions between Ag^+ and the amino acids on the silk fibers. Under γ-ray irradiation, Ag^+ was reduced and Ag atom immediately attached on the surface of fibers. The main reaction processes are:

$$H_2O \xrightarrow{\gamma-ray} e_{aq}^-, H_2O^+, H^\bullet, HO^\bullet, H_2, H_2O_2,$$

$$(CH_3)_2CHOH + HO^\bullet \rightarrow (CH_3)_2(HO)C^\bullet + H_2O,$$

$$Ag^+ + e_{aq}^- \rightarrow Ag^0(\downarrow).$$

As the reaction was going on, Ag underwent further aggregation to larger clusters and finally formed Ag NPs. The resulted silver NPs could interact with the amino acids on the surface of silk fibers via electrostatic and coordination interaction. So the silver NPs were firmly attached on the surface of silk fibers, which reduced the probability of their contact between each other and prevented silver NPs from undergoing a second aggregation. On the other hand, the interaction between NPs and amino acids

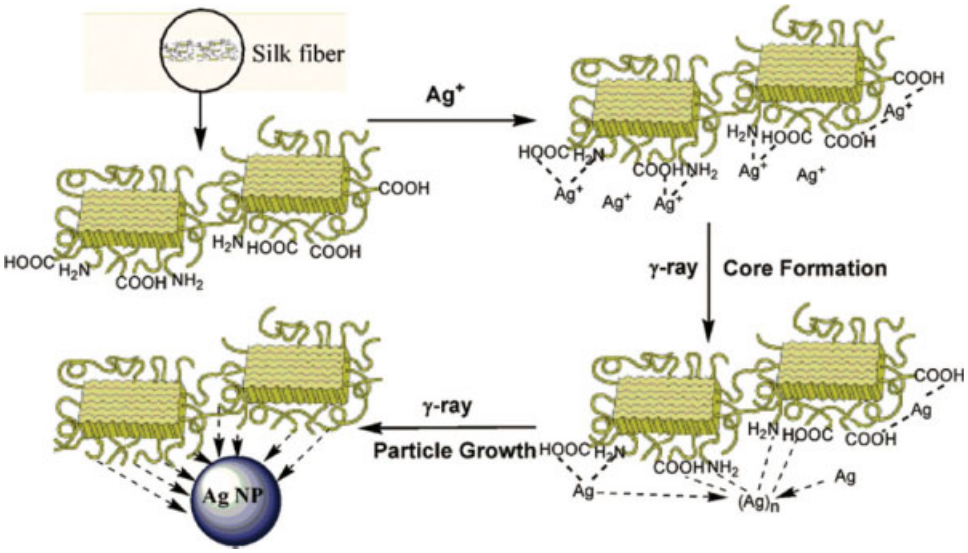

Figure 5 Schematic presentation of the formation of silver NPs on the surface of silk fibers via γ-radiation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

induced the surface of silver NPs was partially taken up by amino acids, which also lessened the contact between NPs and guaranteed the steady existence of silver NPs on silk fibers. In our experiments, isopropyl alcohol as a scavenger of oxidative radical was added to remove the OH radicals and improve the yield of NPs, which was very critical.

CONCLUSIONS

We have demonstrated that it was a possible and simple method to synthesize silver NPs on silk fibers via γ-ray irradiation at room temperature under ambient pressure. We studied the effect of the concentration of reaction solution and the irradiation dose on the products and found that 1 m*M* and 10 kGy were proper conditions to produce better silver NPs modified silk fibers. In these conditions, well-dispersed silver particles with a diameter of less than 20 nm were synthesized on the surface of silk fibers and these products showed 96% antimicrobial activity and still kept above 85% antibacterial activity after 10 washing cycles. The formation processes of silver NPs on silk fibers under irradiating were generally discussed. This method might be used to synthesize other NPs on the surface of textile fibers.

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