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In situ synthesis of silver nanoparticles uniformly distributed on polydopamine-coated silk fibers for antibacterial application

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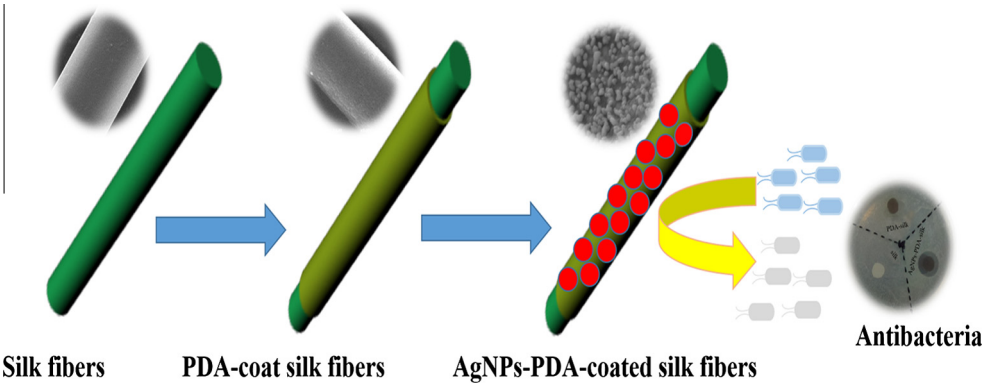
GRAPHICAL ABSTRACT



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ABSTRACT

Fabrication of silver nanoparticles (AgNPs)-modified silk for antibacterial application is one of the hottest topics in the textile material research. However, the utilization of a polymer as both 3-dimensional matrix and reductant for the *in-situ* synthesis of AgNPs on silk fibers has not been realized. In this work, a facile, efficient and green approach was developed to *in-situ* grow AgNPs on the polydopamine (PDA)-functionalized silk. AgNPs with the size of 30–90 nm were uniformly deposited on the silk fiber surface with the PDA coating layer as a reduction reagent. The AgNPs exhibit excellent face-centered cubic crystalline structures. The bacterial growth curve and inhibition zone assays clearly demonstrate the antibacterial properties of the functionalized silk. Both high Ag^+ release level and long-time release profile were observed for the as-prepared AgNPs–PDA-coated silk, indicating the high-density loading of AgNPs and the possible long-term antibacterial effects. This work may provide a new method for the preparation of AgNPs-functionalized silk with antibacterial activity for the clothing and textile industry.

1. Introduction

Silk from *Bombyx mori* cocoons is a natural fiber consisting of two main proteins: fibroin and sericin. Because of its luxury sheen and excellent skin affinity, silk has been regarded as "the queen of textiles" and used in textile productions for thousands of years. Over the past decade the application of silk has been extended to

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the biomedical field as degradable surgical sutures [1] and scaffolds for tissue engineering [2,3] due to its remarkably mechanical property, biocompatibility and controllable degradability [4]. Although silk could provide a lot of unique properties, the protein nature makes it a matrix for bacterial adhesion and thriving, further resulting in its deformation and even degradation [5]. Further applications of silk textiles and silk-based materials are greatly hindered by the easy adherence and growth of bacteria. In recent years tremendous efforts have been dedicated to the development of unique silk fabrics with antibacterial activity. Surface modification with antimicrobial substances is one of the most acceptable methods. Antimicrobial peptides [6], metal ions [7], polymers [8] and nanomaterials [9–11] have been employed to functionalize silk surface. Among them, silver nanoparticle (AgNP) is the most attractive one because it has a broad spectrum of antibacterial effects on both Gram-negative and Gram-positive bacteria [12,13].

In the early stage of research, AgNPs are pre-synthesized firstly and then immobilized on silk surface via physical or chemical adsorption. Since the procedures are quite complicated and tedious, the strategy has been gradually abandoned. The *in situ* growth of AgNPs on silk surface has been developed as an effective alternative strategy, during which silver ions (Ag^+) adsorbed on the silk surface are reduced to form AgNPs. The simple process and the strong binding of AgNPs on silk render the *in situ* synthesis a better approach for the preparation of AgNPs-coated silk.

Reduction of Ag^+ is an essential step for the *in situ* growth of AgNPs on silk. Chemical reagents such as hydrazine, glucose, sodium borohydride and citrate as well as ultrasound microwave [14] and γ-radiation [15] have been utilized to induce the Ag^+ reduction reaction. However, either environment-unfriendly chemicals or expensive instruments are needed in those works. In our previous study, we developed a method to directly immobilize AgNPs on silk via UV-assisted reduction of Ag^+ [9]. The approach is green and facile, but UV-caused aging of silk may occur after a long-term exposure. Aggregation of AgNPs on silk is also a main defect for the UV-assisted approach and most of the existing methods. Besides the reductants, high capacity loading of AgNPs is another critical issue that needs to be considered during the preparation of AgNPs-functionalized silk. Various polymers such as polyamide network polymer, poly(vinyl pyrrolidone) and polyacrylic acid have been employed as a 3-dimensional matrix for the high-density growth of AgNPs recently [16–18]. However, the utilization of a polymer as both 3-dimensional matrix and reductant for the *in-situ* synthesis of AgNPs on silk fibers has not been realized.

Polydopamine (PDA) is a biocompatible synthetic mimic of mussel adhesive proteins, which forms via polymerization of dopamine, a hormone and neurotransmitter in human body. Since it possesses metal ion chelating capability and redox activities [19], PDA could induce the reduction of Ag^+ into AgNPs. More importantly, it has been reported that PDA can adhere on almost all material surfaces [20]. Therefore, PDA could serve as a very promising material to coat the silk surface for *in situ* growth of AgNPs. The use of PDA for silk surface coating may provide three benefits: firstly, PDA may serve as a 3-dimensional matrix for high-density loading of AgNPs; secondly, PDA could adsorb silver ions and further reduce them into AgNPs without the introduction of other reductants; thirdly, the presence of PDA could avoid direct exposure of AgNPs to oxygen and slow down the release of silver ions. So far, there is no report on PDA-coated silk and its application for the preparation of AgNPs-functionalized silk.

In the present study, PDA was coated on silk and further used to adsorb and reduce silver ions for the fabrication of AgNPs-functionalized silk. The as-prepared silk fibers were characterized with scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffractometry (XRD), Fourier transfer infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) to verify the PDA coating and the growth of AgNPs on the silk surface. Antimicrobial tests including zone of inhibition and growth curve assays were conducted to investigate the antibacterial properties of the AgNPs–PDA-coated silk with *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) as model microbes. The release of Ag^+ from silk surface-immobilized AgNPs was also explored.

2. Experimental

2.1. Chemicals

Silver nitrate ($AgNO_3$) (AR, ⩾99.8%) and dopamine hydrochloride were bought from Aladdin (Shanghai, China). Tris (hydroxymethyl) aminomethane (Tris) and hydrochloric acid (HCl) were purchased from Sigma–aldrich (St. Louis, MO, USA). Deionized water (resistance over 18 MΩ cm) was generated by a Millipore Q water purification system.

2.2. Preparation of AgNPs–PDA-coated silk fibers

Raw silk fibers obtained from *B. mori* silkworm cocoons were degummed in a sodium carbonate (0.05% (w/v)) solution at the boiling temperature for 0.5 h, followed by a thorough rinse with DI water for several times. The degumming step was repeated twice to completely remove sericin from raw silk. Dopamine solutions with different concentrations (0.2, 0.5, 1.0, 2.0 and 5.0 mg/mL) were prepared by dissolving dopamine powder in Tris buffer, subsequently adjusting solution pH to 8.5. The degummed silk fibers or silk fabrics were soaked directly into the freshly prepared dopamine solutions under stirring for 12 h at room temperature. The products were taken out and washed with DI water until the rinse-water became clear. After drying at room temperature for 12 h, the PDA-coated silk fibers or fabrics were obtained. The PDA-coated silk samples were immersed into a $AgNO_3$ aqueous solution (50 mM) at room temperature for 8 h. After several times of washing, the samples were dried at 30 °C in a vacuum oven for 12 h. The final products are AgNPs–PDA-coated silk fibers/fabrics.

2.3. Materials characterization

Morphologies of the silk fibers were imaged using SEM (JSM-6510LV, JEOL, Tokyo, Japan) and field emission-SEM (FESEM, JSM-7800F, JEOL, Tokyo, Japan). EDS (INCA X-Max 250) spectra were measured during SEM tests for the analysis of chemical elements. XRD spectra of the treated and untreated silk fibers were examined with a 2θ range of 10–70° (XRD-7000, Shimadzu, Japan). Compact silk pellets were prepared for FTIR measurements (a wavelength interval of 2 cm^{-1}, Nicolet 6700, Thermo Electronic Corporation, USA). TGA was conducted under an air flow at a heating rate of 10 °C/min from 30 °C to 800 °C (TGA-Q50, TA instruments, USA).

2.4. Bacterial growth curve assay

The assay was conducted according to Pal's route with minor modifications [21]. Bacteria at lag phase were inoculated into 8 mL LB medium, culturing with constant shaking (180 rpm) at 37 °C in the presence of the silk fibers with/without PDA or AgNPs–PDA coatings. 0.5 mL bacterial suspensions were collected at different intervals for optical density measurements at the wavelength of 600 nm.