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# Ferric ion-assisted *in situ* synthesis of silver nanoplates on polydopamine-coated silk

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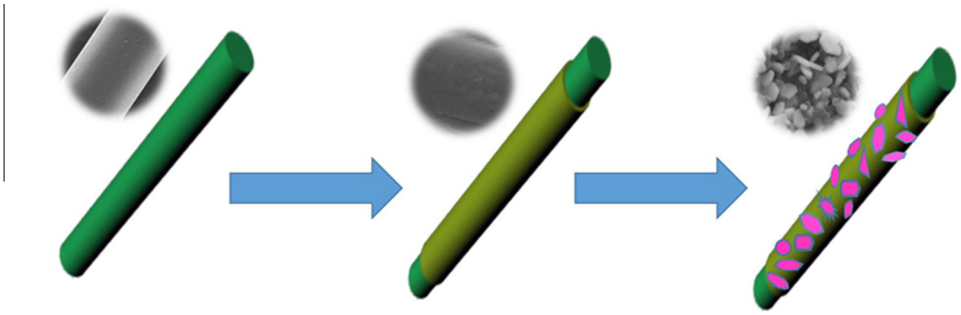
## GRAPHICAL ABSTRACT

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## ABSTRACT

In the present study, a ferric ion ($Fe^{3+}$)-assisted *in situ* synthesis approach was developed to grow silver (Ag) nanoplates on the polydopamine (PDA)-coated silk without the use of additional reductants. The essential role of $Fe^{3+}$ in the formation of Ag nanoplates is revealed by comparing the morphologies of Ag nanostructures prepared on the silk-coated PDA film with/without $Fe^{3+}$ doping. Scanning electron micrographs show that high-density Ag nanoplates could be synthesized in the reaction system containing 50 μg/mL $FeCl_3$ and 50 mM $AgNO_3$. The size of the Ag nanoplate could be tuned by adjusting the reaction duration. Based on the data, a mechanism involving the $Fe^{3+}$-selected growth of Ag atoms along the certain crystal faces was proposed to explain the fabrication process. Transmission electron microscopy and X-ray diffractometry indicate that the Ag nanoplates possess good crystalline structures. Raman spectra demonstrate that the nanoplates could strongly enhance the Raman scattering of the PDA molecules. The Ag nanoplate-coated silk could be utilized as a flexible substrate for the development of surface-enhanced Raman scattering biosensors.



## 1. Introduction

Silk from *Bombyx mori* cocoons has been widely used in textile industry for thousands of years due to its inherently elegant sheen, excellent flexibility and good biocompatibility [1]. As rapid advancement of nanotechnology, a number of research works have been carried out to modify silk fibers with functional

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nanomaterials in recent years, endowing the old material with unique properties [2,3]. ZnO and $TiO_2$ nanoparticles have been immobilized on silk surface to prevent it from ultraviolet light-caused damage [4,5]. $CeO_2$ nanoparticle has been deposited on silk fibers to enhance the thermal stability for the fabrication of the flame retardant fabric [6]. Conductive nanomaterials like gold nanoparticle and graphene have also been coated on silk for the production of electrically conductive fibers or fabrics [7,8].

Among various nanomaterials used for silk functionalization, silver (Ag) nanoparticle is the most attractive one because of its excellent antibacterial activity [9]. The efficient immobilization of Ag nanoparticles on silk could inhibit the growth of microbes [10,11], which is the main drawback of the natural protein fiber. Since the *in situ* growing technique could provide strong anchoring force between Ag nanoparticles and silk, it has been regarded as the most suitable strategy for the preparation of Ag nanoparticle-coated silk [12,13]. In our previous work, UV has been employed to reduce Ag ions adsorbed on silk for the generation of Ag nanoparticles [14]. Although the UV-assisted synthesis is a facile technique for the preparation of Ag nanoparticle-coated silk, the density of the nanoparticles is restricted by the surface chemical groups of silk that could adsorb Ag ions. To increase the surface density, various polymers possessing Ag ion adsorption groups have been modified on silk as 3-D matrices for the *in situ* growth of Ag nanoparticles [13,15,16]. As a bio-inspired material, polydopamine (PDA) has attracted tremendous interests because of its strong adherence to nearly any substrate and its capability for the reduction of metal ions [17,18]. It has been utilized to form an adhesive layer on silk for the *in situ* synthesis of Ag nanoparticles without the use of additional reductants [19]. High-density Ag nanoparticles can be prepared on PDA-coated silk. Moreover, the PDA film could prolong the release profile of Ag ions to achieve a long-term antibacterial activity [19].

Ag nanomaterials with different sizes and shapes have been prepared as ideal systems for the investigation of surface plasmon resonance [20,21]. Besides particulate-shaped nanosilver, 2-dimensional Ag nanoplate is another attractive nanomaterial due to its strong shape-dependent optical properties [22,23]. The Ag nanoplates have been deposited on a glass slide to enhance the fluorescence of organic fluorophores [24]. After entering into tumor cells, they can kill cells under infrared (IR) irradiation via photo-thermal effects [25]. Ag nanoplates have also been applied to enhance the specific Raman scattering spectrum of molecules for high-sensitive molecular identification [26]. In comparison to Ag nanoparticles, Ag nanoplates could provide stronger surface enhancement of Raman scattering due to its localized surface plasmon resonance adsorption in IR region [27]. Triangular and hexagonal Ag nanoplates have been successfully synthesized with a number of optical or chemical reduction approaches [28,29]. However, the preparation of Ag nanoplates on PDA film, in particular on PDA-coated silk, has not been reported so far. The objective of the present study is to develop a method to fabricate Ag nanoplates on PDA-coated silk for the possible application in surface enhanced Raman scattering (SERS) sensing.

Herein, Ag nanoplates are synthesized on the PDA-coated silk without the use of additional reductants for the first time. Morphologies of the modified silk prepared with different reaction durations and different concentrations of $AgNO_3$ solutions were examined to reveal the intermediate steps in the formation of Ag nanoplates. The energy dispersive spectroscopy (EDS) and X-ray diffractometry (XRD) were carried out to characterize the immobilized silk in order to verify the growth of Ag nanoplates. The Ag nanoplate-induced surface enhanced Raman scattering (SERS) was also demonstrated to show the potential applications of the Ag nanoplate-PDA-silk in molecular sensing.

## 2. Experimental

### 2.1. Chemicals

Ferric chloride ($FeCl_3$), 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 (Singapore). Poly (A) single-stranded DNA with 17 nucleotides was synthesized by Sangon Biotech (Shanghai, China). Deionized water (resistance over 18 MΩ·cm) was generated by a Millipore Q water purification system.

### 2.2. Coating of silk fibers with a PDA film

The dopamine powder was dissolved in a Tris buffer solution (pH = 8.5) at a concentration of 1 mg/mL. The raw silk fibers reeled from *B. mori* silk worm cocoons were degummed with a sodium carbonate (0.05% (w/v)) solution at 100 °C for 30 min, followed by thorough rinse with water. The above steps were repeated twice to completely remove sericin from raw silk. The degummed silk was soaked in a Tris-buffer solution containing ferric chloride and dopamine under stirring for 10 h at room temperature. Then, the modified silk was sonicated in water for ten minutes, followed by water rinse for several times until the water turns clear. The products are called as $Fe^{3+}$-doped PDA (FDPDA)-coated silk in the subsequent discussion.

### 2.3. Growth of silver nanomaterials on the FDPDA-coated silk

The FDPDA-coated silk was immersed in a 50 mM $AgNO_3$ aqueous solution at ambient conditions for 11 h. After washing with water for three times, the silk was dried at 60 °C in a vacuum oven for 12 h. The final products were obtained for the following characterizations.

### 2.4. Materials characterization

Morphologies of the samples were imaged using a JSM-7800F scanning electron microscope (SEM) (JEOL, Tokyo, Japan) operating at 10 kV and a JEM-2100 transmission electron microscope (TEM) (JEOL, Tokyo, Japan) operating at 200 kV. EDS (INCA X-Max 250) spectra were collected to analyze the chemical elements on the surface of the silk. XRD and Raman spectra were collected using an X-ray diffractometer (XRD-7000, Shimadzu, Japan) and a macroscopic confocal Raman spectrometer (inVia Raman microscope, Renishaw, UK) with an excitation wavelength of 532 nm, respectively.

## 3. Results and discussion

Since PDA has been used to coat silk for the growth of particulate-shaped Ag nanoparticles, for easy comparison the PDA-modified silk was fabricated. The pristine silk possesses a very smooth surface (Fig. S1 in supporting information), indicating the thorough removal of sericin in the pre-treatment process. After coating with a layer of PDA film, the surface becomes rough and uneven (Fig. 1A). As being shown in Fig. 1B, the doping of $Fe^{3+}$ does not obviously change the surface morphology of the PDA layer. The $Fe^{3+}$ ions may be just complexed in the film without affecting the polymeric structure. The formation of Ag nanoparticles on the PDA-coated silk is verified in Fig. 1C. Particulate-shaped nanosilver with the size ranging from 30 to 90 nm can be *in situ* synthesized without the addition of external reductants, agreeing well with our previous report [19]. Interestingly, plate-like nanostructures