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In-situ synthesis of gold nanoparticles for multifunctionalization of silk fabrics

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ABSTRACT

A simple in-situ synthesis route for gold nanoparticles (NPs) was developed to realize multifunctions for silk fabrics. The gold NPs were prepared in a heated solution containing white silk fabric samples. The silk fabrics were colored red and brown by the gold NPs because of their localized surface plasmon resonance (LSPR) property. Gold nanospheres on silk were obtained at a low gold content, and gold nanoplates were synthesized as the gold content increased. The silk fabrics treated with gold NPs showed good light fastness. Moreover, the gold NPs endowed silk fabrics with strong antibacterial activity, excellent UV protection property and enhanced thermal conductivity.

1. Introduction

Noble metal nanoparticles (NPs) present brilliant and fascinating colors due to their localized surface plasmon resonance (LSPR) properties. LSPR is derived from the interaction of light and the metal NPs, when conductive electrons oscillate locally around the metal NPs at a certain frequency. The phenomenon of excitation of surface plasmons generated by light is termed as LSPR [1]. The LSPR property of noble metal NPs is important for applications in surface enhanced spectroscopy [2,3], sensing [4], and nanophotonic devices [5]. Noble metal NPs with bright colors have been used as decorative pigments for glass [6] and ceramics [7] since ancient times. More recently, these particles have been used for textiles including cotton [8–10] and wool [11–14]. The noble metal NPs are different from conventional dyes, in that it is the LSPR property not the chromophore that gives rise to captivating colors. This optical feature of noble metal NPs is related to particle shape, size, composition, environment, and interspaces [15–20]. The shape and size of the NPs govern their LSPR optical features, which have been illustrated already [21,22]. Therefore, the color of the noble metal NPs can be adjusted by controlling their shape and size.

Textile products with multiple functionalities have generated great interest in recent years. Many attempts have been made to enhance functionalities of textiles, such as antibacterial [23], self-cleaning [24], and UV protection [25]. Silk as a natural protein fiber is widely used in the textile industry due to its inherently elegant sheen, excellent flexibility, environmental friendliness and good comfort. Recently, some strategies based on modification with NPs have been developed to enhanced functions of silk fabrics. For examples, Zheng et al. colored silk fabrics using gold nanorods with different aspect ratios [9]. The gold nanorod coated silk fabrics showed significant improvements on both UV protection and antibacterial functions. But the washing fastness of silk fabrics colored with gold nanorods was unsatisfactory. Li et al. modified silk fibers with TiO_2 and TiO_2@Ag NPs through chemical assembly technique [26]. The treated silk fabric exhibited multifunctions including UV protection, antibacterial activity, and photocatalytic capability. Besides, the anisotropic silver NPs were assembled onto the silk fibers to impart different colors and antibacterial feature to silk fabrics [27].

In the present study, an in-situ synthesis method for gold NPs was described to functionalize silk fabrics. Color and optical properties were investigated at different levels of gold concentration. Moreover, the relation between morphologies and optical features of synthesized gold NPs on silk fibers were studied. The functions of silk fabrics treated with gold NPs, including UV blocking, antibacterial activity and thermal conductivity, were investigated.

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The colorfastness properties to washing and light of gold nanoparticle (NP) modified silk were evaluated as well.

2. Experimental

2.1. Materials

Tetrachloroauric(III) acid ($HAuCl_4 \cdot 3H_2O$, >99%) was purchased from Sigma–Aldrich. The chemicals were analytic grade reagents, and used without further purification. Crepe satin silk fabrics, with a weight of 123.4 g/m^2 and a density of 51 threads/cm in the warp direction and 41 threads/cm in the weft direction, were purchased from the local Beautiful Silks store.

2.2. Instruments

The UV–vis absorption spectra of $HAuCl_4$ solutions were obtained using a Varian Cary 3E UV/vis spectrophotometer. The UV–vis diffuse reflectance absorption spectra of silk fabrics were recorded by a Varian Cary 5000 UV–VIS–NIR spectrophotometer with a diffuse reflectance accessory (DRA-2500). Scanning electron microscopy (SEM) measurements were performed with a Supra 55 VP field emission SEM. The color strength (K/S) and color difference (ΔE) of silk fabrics with gold NPs were obtained using a Datacolor Spectraflash SF600 Plus-CT spectrophotometer. Fourier transform infrared (FTIR) spectra were measured with a PerkinElmer Fourier transform infrared spectrometer (FTIR-1730) in attenuated total reflection (ATR) mode. Infrared thermal images were recorded by an infrared thermography video camera (H2640, NEC). Heating reaction was performed in a Stuart SBS40 shaking water bath.

2.3. In-situ synthesis of gold NPs in silk

Pristine silk fabrics were immersed in aqueous solutions with different concentrations of $HAuCl_4$ (1.79×10^{-4} M, 2.38×10^{-4} M, 2.99×10^{-4} M, 4.48×10^{-4} M, 5.97×10^{-4} M and 7.46×10^{-4} M). The weight ratio of $HAuCl_4$ solution to silk is 60. The $HAuCl_4$ solutions with silk were placed for 30 min at room temperature. The silk changed to light yellow due to absorption of chloroaurate ions ($AuCl_4^-$). After that, the solutions were heated at 85 °C for 60 min in an oscillating water bath. The color of silk in the solutions became red or brown. The silk fabrics were taken out and rinsed with running deionized water. And then the silk fabrics with different gold content (0.21 wt%, 0.28 wt%, 35 wt%, 0.53 wt%, 0.71 wt% and 0.88 wt%) were dried at room temperature.

2.4. Colorfastness test to washing

Washing fastness tests were performed in accordance with Australian Standard AS 2001.4.15—2006. The silk fabrics with gold NPs were washed for 45 min at 50 °C in the presence of ECE reference detergent by using a lab dyeing machine (Ahiba, Top Speed Nuance). The CIE Lab color coordinate values (L^*, a^*, and b^*) for each specimen were measured before and after washing. L^* represents the lightness/darkness, a^* value represents the red or green chroma, and b^* represents the chromaticity coordinate for yellow/blue. The color difference (ΔE) was obtained based on the changes in color coordinates (ΔL^*, Δa^*, and Δb^*) with the formula: $\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$. The color difference ($\Delta E$) of silk fabrics before and after washing was measured by spectrophotometer to assess washing fastness of silk fabrics according to Australian Standard AS 2001.4.A05—2004.

2.5. Measurement of fastness to light

The gold NP treated silk fabrics (8 × 4 cm) with different colors were stapled on to white cardboard, and a portion (4 × 4 cm) of each fabric specimen was covered with cardboard and aluminum foil. The specimens were then exposed to simulated sunlight for 60, 120 and 180 h inside the Suntest instrument (SUNTEST XLS+ from Atlas Material Testing Technology LLC). Color changes were determined with the Delta E value (DE CIELAB) by a Datacolor instrument. This parameter was used to quantify the difference between two colors of the samples with and without irradiation at each exposure period.

2.6. Antibacterial test

Gram negative bacteria, *Escherichia coli* (*E. coli*) (ATCC 11229), were used as test organisms. Antibacterial test was performed on untreated and treated silk fabrics. The antibacterial test was carried out according to the AATCC 100-2004 (Clause 10.2) test standard with slight modifications. 50 μL of bacteria were added on treated samples in separate flasks. After 1.0 min, 50 mL of sterile deionized water was poured into each flask, followed by vigorous shaking. Then the flasks were incubated for 18 h in a shaker oven at 120 rpm at 37 °C. After that, the fabric samples were collected and the solution left in the flask was further diluted to get countable number of bacterial colonies. 10^3 dilution was suitable for obtaining colonies between 30 and 300. 100 μL of the 10^3 dilution obtained were placed on the nutrient agar plates. These plates were then incubated for 18 h in an oven at 37 °C. The bacterial activity was

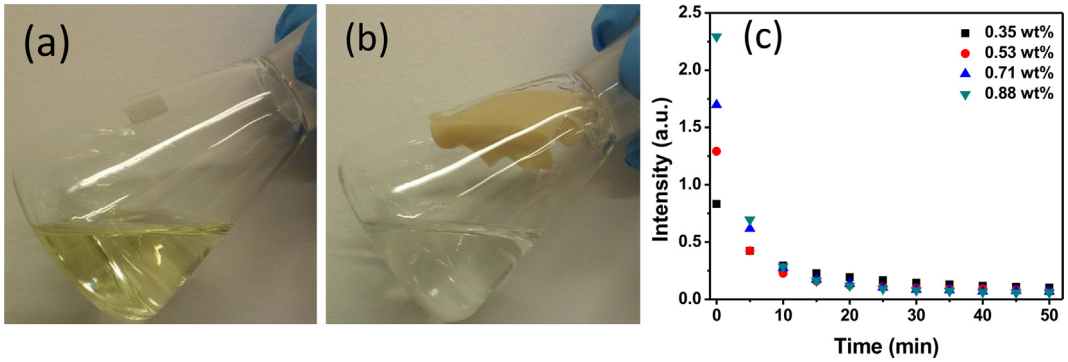

Fig. 1. Photographs of $HAuCl_4$ solutions (corresponding to 0.53 wt% gold content) (a) before and (b) after silk fabric was soaked in solution for 30 min, and (c) plots of absorbance intensity of $HAuCl_4$ solution around 290 nm as a function of soaking time corresponding to different gold content after the silk fabrics were immersed in $HAuCl_4$ solution.