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Ferulic acid promoted *in-situ* generation of AgNPs@silk as functional colorants

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ABSTRACT

A rapid, green and simple procedure for the *in-situ* generation of AgNPs@silk as functional colorant is described herein. Silver (Ag^+) ions were first diffused into the silk fabric matrix by soaking into aqueous $AgNO_3$ solution, subsequently, alcoholic solution of ferulic acid, a natural polyphenol, was added as an eco-friendly reductant for the generation of AgNPs@silk. The formation of AgNPs was confirmed by visible color changes and UV–visible absorption spectra. The residual AgNPs solution was characterized via UV–visible spectroscopy, TEM and DLS. The UV–visible spectra and TEM analyses confirmed the formation of more or less spherical well-dispersed AgNPs. The AgNPs@silk was characterized by SEM, EDS, XRD, XPS and FTIR. The Ag content of AgNPs@silk was determined by nitric acid digestion followed by ICP-OES. The color, antibacterial and UV protection characteristics of AgNPs@silk were also evaluated. AgNPs@silk produced a beautiful color pallete ranging from light creamish brown to dark golden brown. The AgNPs treated silk exhibited outstanding antibacterial activity (>99% bacterial reduction) and excellent laundering durability, where it inhibited >94% of *E. coli* even after 10 washing cycles. Moreover, AgNPs@silk was highly effective blocking of UV radiation in both UVA and UVB regions, and thus offered excellent UV protection.

1. Introduction

The introduction of nano-enhanced materials to a variety of consumer products for future commercial developments is becoming increasingly popular. Among the commercialized nanomaterials, silver nanoparticles (AgNPs) attracted the attention of many industries including food, textile, construction, medicine, cosmetics, pharmaceuticals etc. and the global market for silver nanoparticles expanding rapidly (Pulit-Prociak and Banach, 2016). They find a wide range of high performance applications due to their broad spectrum of shape and size distribution, high stability, large surface area, unique optical, catalytic, biophysical, and antibacterial properties (Cheng et al., 2013; Chakraborty et al., 2016; González et al., 2014; Gan and Li, 2012). In recent years, the development of colored and functional textiles by using metal nanoparticles, especially AgNPs, has become a major focus of researchers (Islam et al., 2016; Yetisen et al., 2016). The coloration of textiles through AgNPs application is due to the localized surface plasmon resonance (LSPR) property of these nanomaterials (Tang et al., 2018). The textiles functionalized with AgNPs exhibit diverse applications and are used in various textile products (Ding et al., 2016). The incorporation of AgNPs on textiles is usually achieved by a two-step procedure (*ex situ* method): synthesis of AgNPs followed by their impregnation on textile surface by different methods (Lu et al., 2014; Zhou et al., 2018). The *ex situ* AgNPs functionalization of fabrics exhibits several shortcomings such as requirement of protecting or stabilizing agents to prevent the aggregation of AgNPs during the solution preparation; extraction and purification of the prepared nanoparticles before use; non-uniform distribution of AgNPs on fabric surface; and lack of durability which directly relates to toxicity concerns associated with the release of silver into the environment by washing, rubbing and abrasion (Perera et al., 2013; Mitrano et al., 2014). On the other hand, *in situ* method, where the pre-adsorbed silver ions on the fabrics are locally converted into AgNPs, is regarded as more suitable strategy for the preparation of AgNPs-coated textiles because of process simplicity, resource saving potential and strong

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anchoring of nanoparticles on textile substrate (Shahid et al., 2017; Lu et al., 2015; Meng et al., 2016; Montazer et al., 2016).

Silk obtained from silkworm (*Bombyx mori*), a highly popular natural fiber suitable for high-grade clothing, is used in textile industry for thousands of years due to its elegant sheen, softness, smooth texture, mechanical strength, excellent flexibility, and good biocompatibility (Lu et al., 2014; Xiao et al., 2016). However, it is highly prone to microbial attack and photo-induced aging and yellowing due to its protein nature (Li et al., 2011). Microbial attack of silk fabrics may lead to quality deterioration, discoloration, surface deformations and loss of mechanical strength over time (Park et al., 2008). Therefore, market demand for the silk fabrics with added functional features such as antibacterial and UV protective properties is increasing (Tang et al., 2014). Many different approaches have been developed in the recent past to impart these functionalities to silk. Among all, AgNPs are the most promising material for the large scale production of functional textiles due to their vibrant coloring effect, antibacterial, antifungal, UV protective and hydrophobic properties (Islam et al., 2016; Wu et al., 2016; Kelly and Johnston, 2011; Dastjerdi and Montazer, 2010). The production of AgNPs for textile finishing by various physical and chemical methods is practiced for a long time. Several reports are available on utilizing the localized surface plasmon resonance property of AgNPs for imparting color and functional properties to textiles. The recent interest in using plant based products for nanoparticle synthesis has further boasted the new "green chemistry" approach in textile industry using eco-friendly and renewable, nontoxic reductants for AgNPs fabrication (Iravani, 2011; Huang et al., 2015). Several plant derived reductants have been used for the production and application of AgNPs to different types of textile substrates by both *ex situ* and *in situ* methods (Shahid et al., 2017; Ballottin et al., 2017; Islam et al., 2014). Among plant derived reductants, natural polyphenols play a key role in these processes and are suitable for the large-scale biosynthesis of highly stable nanoparticles (Kharissova et al., 2013; Rajan et al., 2015; Makarov et al., 2014). Ferulic acid, a natural plant polyphenol, is used as reductant in this study. Here, we report a green 'one-step' ferulic acid-induced *in-situ* generation of AgNPs@silk, to produce colorful, antibacterial and UV protective textiles. The characteristics of AgNPs in solution phase were studied by UV–visible spectrophotometer, transmission electron microscope (TEM) and dynamic light scattering (DLS) technique. Scanning electron micrograph (SEM), energy dispersive spectroscopy (EDS), X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transfer infrared spectroscopy (FTIR), and inductively coupled plasma optical emission spectrometry (ICP-OES) were employed to characterize the AgNPs@silk. Moreover, color characteristics, UV-blocking, and antibacterial properties of the treated fabrics were also evaluated. The AgNPs functionalized silk fabrics showed excellent durability even after 10 laundering cycles. Overall, we have demonstrated a simple, green and feasible strategy for the production of colored and functional silk fabrics for protective and medical textile applications.

2. Experimental

2.1. Materials

The crepe satin plain silk fabric was purchased from Wujiang Zhiyuan Textile Co. Ltd., China. The specification of this fabric is as follows: warp and weft count, 23.3 dtex/2; warp density, 42 threads/cm, and weft density, 60 threads/cm; weight per unit area, 52 g/m^2. Silver nitrate ($AgNO_3$) was purchased from Sinopharm Chemical Reagent Co. Ltd., China, as an analytical reagent. Ferulic acid (FA) with a purity above 98% was obtained from Wuhan Yuancheng Group, China.

2.2. In-situ generation of AgNPs@silk

A general flowchart for *in-situ* generation of AgNPs@silk is shown in Fig. 1. A set of $AgNO_3$ solutions of pre-determined concentration (0.5, 1.0, 1.5 and 2.0 mmol/L) was prepared by adding the precisely weighed amount of $AgNO_3$ in 95 mL of water in conical flask and placed in a XW–ZDR low-noise oscillated dyeing machine (Jingjiang Xinwang Dyeing and Finishing Machinery Factory, China). The temperature was set at 30 °C. Silk fabric (1 g) was immersed in the $AgNO_3$ solution. The temperature of the solution was raised to 95 °C at a rate of 3 °C/min. Subsequently, 5 mL FA solution (alcoholic) of requisite concentration (1.0–3.0 g/L) was added dropwise. The mouth of conical flask was covered with aluminium foil and held at 95 °C for 30 min with continuous agitation. At the end of the process, the fabric was washed with deionized water several times to remove unfixed materials. The resulting silk fabric was dried at room temperature.

2.3. Characterisation of residual AgNPs solutions

The formation of AgNPs was confirmed by color changes and UV–visible spectra of residual solution recorded on a Shimadzu UV-1800 UV–visible spectrophotometer (Shimadzu Co., Japan). The TEM images of synthesized silver nanoparticles were obtained with a HT-700 transmission electron microscope (Hitachi High Technologies America Inc., USA) operating at 120 kV; the samples for TEM analysis were prepared by dripping a drop of residual silver nanoparticle solution onto the carbon coated copper grids and drying them in the air at room temperature. The hydrodynamic diameters of AgNPs were determined using Zetasizer Nano ZS 90 (Malvern Instruments Ltd., UK).

2.4. Characterization of AgNPs@silk

The surface morphology of silk fabric was observed using Hitachi TM3030 tabletop and Hitachi-S4800 field-emission scanning electron microscope (Hitachi High Technologies America Inc., USA); TM3030 scanning electron microscope was equipped with

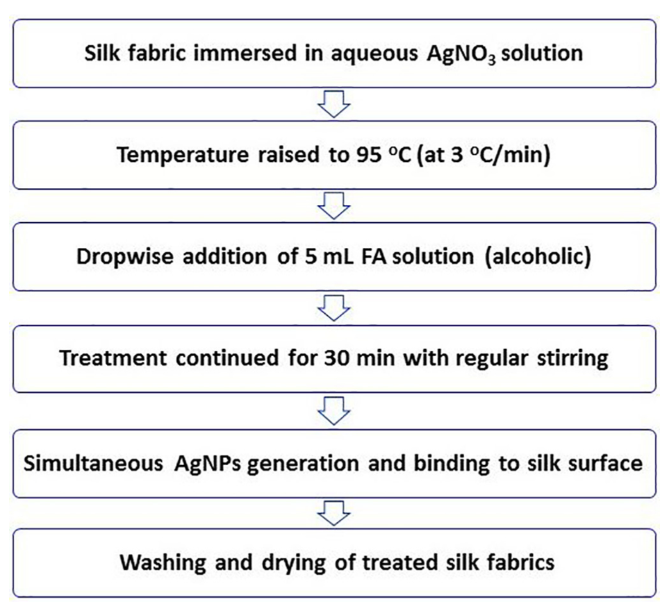

Fig. 1. A general flowchart for *in-situ* generation of AgNPs@Silk