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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 colour changes and UV-visible absorption spectra. The supernatant 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 colour, antibacterial and UV protection characteristics of AgNPs@silk were also evaluated. AgNPs@silk produced a beautiful colour 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.

Keywords: Silver nanoparticles; Ferulic acid; Silk; Antibacterial activity; UV protection

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.[1] 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.[2-5] In recent years, the development of colored and functional textiles by using metal nanoparticles, especially silver nanoparticles (AgNPs), has become a major focus of researchers.[6, 7] The textiles functionalized with AgNPs exhibit diverse applications and are used in various textile products.[8] 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.[9] 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.[10, 11] 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 anchoring of nanoparticles on textile substrate.[12-14]

Silk derived 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.[9, 15] However, it is highly prone to microbial attack and photo-induced aging and yellowing due to its protein nature.[16] Microbial attack of silk fabrics may lead to quality deterioration, discolouration, surface deformations and loss of mechanical strength over time.[17] Therefore, market demands for the silk fabrics with added functional features such as antibacterial and UV protective properties is increasing.[18] 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 colouring effect, antibacterial, antifungal, UV protective and hydrophobic properties.[6, 19-21] 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 colour 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.[22, 23] 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.[12, 24, 25] 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.[26-28] 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* reduction of silver ions onto silk fabric, to produce colourful, 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, colour 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 coloured and functional silk fabrics for protective and medical textile applications.

Experimental

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.

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 conical flask was then partially sealed 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.

Characterisation of residual AgNPs solutions

The formation of AgNPs was confirmed by colour 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).

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 energy disperse spectroscopy (EDS) which was used to perform the qualitative analysis of the silver on silk fabric. For XRD, XPS and FTIR measurements AgNP@silk fabrics were cut into small pieces and then the pieces were ground to obtain powdered sample. The X-ray diffraction (XRD) measurements of fabric powders were carried out on an X'Pert-Pro MPD X-ray diffractometer (PANalytical B.V., Netherlands) equipped using CuKα radiation of wavelength 0.15418 nm. X-ray photoelectron spectroscopy (XPS) was obtained by a Kratos Axis-Ultra HAS X-ray photoelectron spectroscopy (XPS) using an Al Ka X-ray source. The FTIR spectra of the silk powder samples were obtained using a Nicolet 5700 FT-IR spectrometer (Thermo Fisher Scientific Inc., USA). The silver content of the AgNPs treated

silk fabrics was measured as follows: the dried fabric (0.1g) were digested in 30 mL of 15 wt % nitric acid for 2 h at 80° C. ICP-OES was conducted on the ICAP 6300 DUO inductively coupled plasma optical emission spectrometry (Thermo Fisher Scientific Inc., USA). The Ag content was calculated by the following equation:

$$\text{Ag content (mg/g)} = \frac{C_s}{W} \cdot V \quad (1)$$

where C_s is the Ag content in the digestion solution analyzed by ICP-OES (mg/L); V is the volume of the digestion solution (0.03L); W is the weight of the dried sample (0.1g).

The L^*(lightness), a^* (redness-greenness value), b^* (yellowness-blueness value), C^* (chroma) and h (hue angle) colour coordinates as well as the apparent colour strength (K/S value) of AgNPs@silk were evaluated by a HunterLab UltraScan PRO reflectance spectrophotometer (HunterLab, USA) using illuminant D65 and 10^o standard observer. Each sample was folded twice so as to give a thickness of four layers.

Functional properties of AgNPs@silk

The functionalities of AgNPs treated silk samples were evaluated in terms of antibacterial activity and UV protection factor (UPF). The ultraviolet protection factor (UPF) and UV transmittance of silk fabrics were determined in a Labsphere UV-1000F ultraviolet transmittance analyzer (Labsphere Inc., USA). Each sample was tested four times at different positions, and the average of the data was used. The antibacterial activity of colored fabrics was first tested by a disc diffusion assay method against *Escherichia coli* (*E. coli*), as gram negative bacteria. The quantitative measurement of the antibacterial activity was done according to test method GB/T 20944.3-2008.[29] The tested fabric fragments (0.75 g) were immersed for 24 h in the conical flasks with bacteria housed in a shaker. The immersing temperature was 30 ^{o}C. Then the bacteria solutions were diluted to 1000 times with sterilizing phosphoric buffer solution so as to obtain a test bacteria solution. The diluted *E. coli* bacteria solutions were inoculated onto agar plates, and incubated at 37 ^{o}C for 24 h. Finally, the

quantity of the visually bacterial colonies on agar plates was counted, and the antibacterial activity was calculated by the following equation:

$$\text{Antibacterial activity}\,(\%) = 100 \cdot \frac{N_{\text{ctrl}} - N_{\text{spl}}}{N_{\text{ctrl}}} \qquad (2)$$

where N_{ctrl} and N_{spl} are the quantities of the visually bacterial colonies of standard cotton fabric and tested fabric, respectively. The durability of the antibacterial activity of treated silk was also assessed after repeated laundering. The washing process of treated silk in brief: the fabrics were immersed in washing solution, which contained 4 g/L commercial detergent using a liquor ratio of 1:50. Then, the samples were stirred and left for 10 min at 40±2 °C in a WashTec-P fastness tester (Roaches International, England). Finally, the fabrics were gently squeezed and rinsed with tap water. This process was repeated 5 and 10 times to get 5 and 10 washings.

Results and discussion

The AgNPs@silk was prepared by FA assisted reduction of silver ions to AgNPs directly onto the fabric surface. The silver ions were first diffused into the silk fabrics dipped in a solution of $AgNO_3$ to induce their binding with the silk matrix. On adding FA solution, the presence of precursor Ag^+ ions on the fabric led to the direct formation of AgNPs@silk and the fabric color gradually turned from white to golden brown due to the surface plasmon resonance property of synthesized AgNPs.

Characterisation of residual AgNPs solutions

The silk fabrics were removed from the AgNPs solution and the absorbance of residual solutions was immediately recorded by UV–visible spectroscopy. The position and shape of the absorption peak in UV–visible spectra are strongly dependent on nanoparticle shape and size. The broad plasma resonance peak around 420–430 nm in the absorption spectra of

residual AgNPs solution (Fig. 2) appeared due to the formation of spherical AgNPs. The absorbance increased with an increase in the concentration of both silver salt (Fig. 2a) and FA (Fig. 2b), indicating the enhanced formation of AgNPs. The residual AgNPs solution obtained from 1.0 mmol/L $AgNO_3$ + 1.0 g/L FA was used for TEM and DLS analyses. The representative TEM image (Fig. 3) indicated the formation of the well-dispersed particles that were more or less spherical. The average diameter was 15.5±2.5 nm, with a highly uniform and narrow distribution of diameters. The size distribution of AgNPs obtained DLS analysis is depicted in Fig. 4. The Z-average value represents the intensity weighted mean hydrodynamic size of the particles measured by DLS. The hydrodynamic diameter of synthesized AgNPs was 89.31 nm, and the polydispersity index (PDI) value was 0.35. A small peak in 4000-6000 nm region could be due to agglomeration of AgNPs in solution. In the DLS analysis, the hydrodynamic diameter of the particles is strongly augmented by water molecules, and the resulting particles size is somewhat higher than that obtained from TEM analysis.

Characterization of AgNPs@silk

Fig. 5 shows the low magnification SEM images of the AgNPs treated silk fabric prepared by 2.0 mmol/L $AgNO_3$ + 2.0 g/L FA. The FA-induced production of AgNPs@silk did not adversely affect the woven structure of the fabric, and thus could preserve its air-breathing properties that are so vital for clothing comfort. The high magnification SEM images showed many nanoparticles attached to the surface of silk fibre (Fig. 6a–d). The size, number and aggregation of AgNPs varied with the concentration of silver salt and FA. Due to the increase in the amount of silver reduced onto the fabric, the change in colour and the darkening of shades were observed with an increase in the concentration of both $AgNO_3$ and FA. The particle size distribution obtained through SEM image analysis ranged from 10 to 80 nm (Fig. 6e).

The presence of silver within the AgNPs@silk was confirmed by EDS, XRD and XPS analyses. The well-defined peak for silver element was seen in the EDS spectrum of AgNPs@silk, which confirms the presence of silver on the treated silk (Fig. 6f). The formation of AgNPs was also confirmed by the XRD pattern shown in Fig. 7a. Two characteristic broad peaks located at $2\theta = 20.62°$ and 28.75° were found for both untreated silk and AgNPs@silk, which are the characteristic crystalline diffraction of silk fibre. Since there is no significant change on the peaks after the treatment, it suggests that the AgNPs treatment does not alter the structure of silk fibroin. For AgNPs@silk sample a new diffraction peak appeared at $2\theta = 38.42°$, which is due to the (1 1 1) plane of the face-centered cubic structure of AgNPs.[9, 13] The results strongly confirm that AgNPs with excellent crystalline structure are successfully synthesized in-situ to prepare AgNPs-treated silk fabric. AgNPs@silk was also characterized through XPS analysis for the surface elemental composition. The successful introduction of AgNPs on the surface of silk fabric was further confirmed by the XPS spectra, where the new peak of Ag(0) at 368 eV in the spectrum of AgNPs@silk (Fig. 7b).[30] In contrast, there is no peaks attributed to Ag on the surface of the untreated silk fabric.

The FTIR spectra of original silk and AgNPs@silk are shown in Fig. 7c. The different regions of the IR spectra of silk are: 2800–3650 cm^{-1} (OH, NH and CH stretching region), 1200–1800 cm^{-1} (amide region and CH bending), 700–1200 cm^{-1} (skeletal stretches), and 400–1300 cm^{-1} (deformation modes).[31] The characteristic amide I, amide II, and amide III bands of silk relate to the peptide bonds (–CONH–). The most prominent band occurs in the range of 1700–1600 cm^{-1} (amide I band) which is associated with the C=O stretching.[32] The amide II (1540–1520 cm^{-1}) band is attributable to the N–H bending and C–N stretching vibration.[33] The spectra of both original silk and AgNPs@silk showed all the characteristic

peaks and displayed the same profile, indicating that the binding of AgNPs does not influence the chemical structures of silk even though there is change in the fabric colour.

The Ag content of AgNPs@silk was determined by nitric acid digestion followed by ICP-OES. Consistent with the previous UV–visible spectroscopic measurements, the Ag content of treated silk fabrics showed an increasing trend with an increase in concentration of both silver ion and FA (Table 1).

After the functionalization, AgNPs@silk exhibited a beautiful colour pallete (Fig. 8) ranging from light creamish brown to dark golden brown depending on the concentration of silver salt and FA used. The colour arises from the characteristic SPR optical properties of AgNPs attached to the silk. Table 1 shows the colour characteristics of AgNPs@silk. At low levels of $AgNO_3$, the colour of treated fabrics was creamish to light yellow (Fig. 8), which was also evident from the lower positive a^*, b^* and h values (Table 1). It was observed that the color saturation (C^*) could be controlled by varying the amount of silver salt and FA. Generally, the colour became darker, and more saturated (decrease in L^* and increase in C^*) with the increasing concentration of silver salt, whereas the color saturation showed a decreasing trend (decrease in C^*), resulting in relatively duller shades with an increase in FA concentration when a fixed concentration of silver salt was used. With an increase in concentration of silver salt, redness (a^* value) progressively increased giving reddish tone to the treated fabrics. The positive $b*$ value for 2 mmol/L $AgNO_3$ treated samples decreased from 49.67 to 33.79 as the concentration of FA increased from 1.0 to 3.0 g/L. As expected, the colour strength (K/S) values showed an increasing trend (Fig. 9) and the L^* values decreased (Table 1) with an increase in the amount silver salt and FA used. The progressive change in colour appearance and K/S values support the argument that the amount of silver deposited on silk surface increased with an increase in concentration of both FA and silver salt.

Functional properties of treated silk fabrics

The AgNPs application imparts significant improvements on the antibacterial activity and UV-protection of silk. The antibacterial activity of the untreated silk and AgNPs@silk was tested against *E. coli*. The photographs of agar plates containing the untreated and AgNPs@silk fabrics are shown in Fig. 10, where the cloudy areas indicate bacterial growth, where transparent areas surrounding the AgNPs@silk show bacteria-free regions (zone of inhibition). The absence of zone of inhibition (ZOI) around untreated silk (Fig. 10a) clearly showed lack of any significant antibacterial activity. However, the antibacterial activity of AgNPs@silk (Fig. 10b) was obvious from the clear ZOI around the sample, indicating that no bacterial growth was observed in this region. The formation of inhibition zone clearly implies that the antibacterial activity of the fabric is due to the leaching of silver from the fabric.[34] The quantitative evaluation of antibacterial activity also showed the excellent antibacterial properties of AgNPs@silk (>99% reduction in bacterial colonies). The presence of AgNPs on silk fabric acts as a barrier and controls the rate of bacterial proliferation. Low durability of AgNPs functionalized textiles towards washing is a big concern for textile industry. Washing durability is an important and necessary factor for reuse of nano-finished textiles. High release of nanoparticles during washing of AgNPs treated fabrics reduces their antibacterial activity and can have impact on the environment.[8, 35] Thus, antibacterial textile finishes which can withstand repeated laundering are urgently required. The quantitative results of antibacterial activity of AgNPs@silk after 1, 5 and 10 washing cycles. Interestingly, the washed AgNPs@silk exhibited very little reduction in antibacterial activity after repeated laundering cycles, which is an indication of lower release of nanoparticles during washing. The AgNPs@silk exhibited reduction efficiency of 98.03% bacterial growth after first washing cycle. Very high antibacterial activity was maintained even after five (96.78%) and ten (94.99%) washing cycles. These results further establish that the *in-situ* reduction of the

silver ions to AgNPs directly on the fabric is an efficient method for obtaining durable antimicrobial finishes. AgNPs interaction with the amino acids on the surface of silk fibers via an electrostatic and coordination interaction could contribute to the excellent durability of antimicrobial finishing.[35]

The UPF rating, which indicates the effectiveness of a fabric in blocking solar ultraviolet radiation, is defined as the ratio of average effective irradiance calculated for skin to average UV irradiance calculated for skin protected by the fabric. The UPF value of a fabric is calculated using mean percentage transmission in the UVA (315–400 nm) and UVB (280–315 nm) regions.[34] The fabric with the UPF value of more than 15 is considered as providing good protection, and the fabric with the UPF value above 40 is considered as providing excellent protection against UV radiation.[36] The UV protective property of the AgNPs@silk fabrics is expressed in terms of UPF in Table 2. The UV-protection offered by original silk fabric is very poor as indicated by a UPF value of 7.04. When a 0.5 mmol/L concentration of $AgNO_3$ was used, UPF increased in comparison to untreated silk but it was still below 15. As the concentration of silver salt increased to 1.0 mmol/L, the UPF values ranged from 20 to 35 depending on the concentration of FA used. On further increasing $AgNO_3$ concentration, the UV protective action of treated fabrics reached to excellent levels. The UVA and UVB transmittance values of the AgNPs@silk were found to be much lower than that of the untreated silk (Fig. 11), which indicates that the treated fabrics show improved blocking of UV radiation in both UVA and UVB regions. Excellent UV protection offered by AgNPs@silk can effectively decrease the aging and reduce human skin damage caused by solar UV radiation.

Conclusion

We have reported for the first time use of ferulic acid for preparing AgNPs functionalized silk fabrics. The direct *in-situ* generation of AgNPs inside silk fabric was rapid and convenient. The synthesized nanoparticles were spherical and well-dispersed on fibre surface. The AgNPs@silk produced a beautiful colour pallete ranging from light creamish brown to dark golden brown with additional functionalities. The AgNPs@silk exhibited outstanding antibacterial activity and also excellent durability towards washing, where it was able to inhibit 94.99% of *E. coli* growth even after 10 laundering cycles. Moreover, the resultant fabrics effectively blocked the UV radiation in both UVA and UVB regions providing excellent UV-protection. In conclusion, this green and simple approach for producing of vividly coloured AgNPs@silk with excellent antibacterial and UV protection performance can be used in preparing nano-enabled consumer products in a variety of usage scenarios, especially protective and medical textiles.

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TOC graphic

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

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AgNPs@silk are *in-situ* synthesized as colorant and functional finishing agent for silk by using ferulic acid as an eco-friendly reductant.

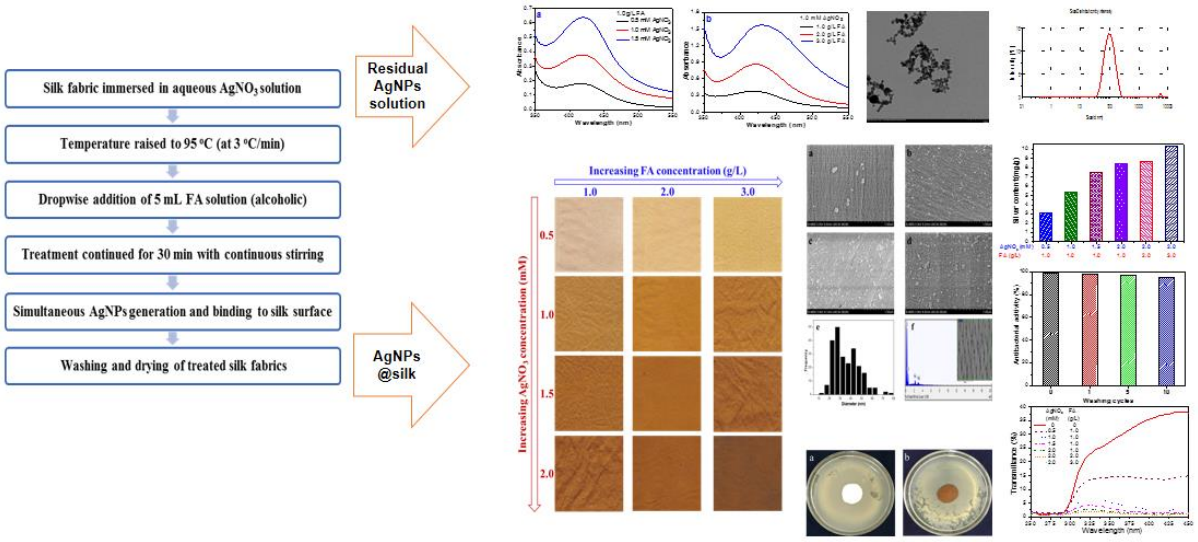

Fig. 1: A general flowchart for *in-situ* generation of AgNPs@Silk

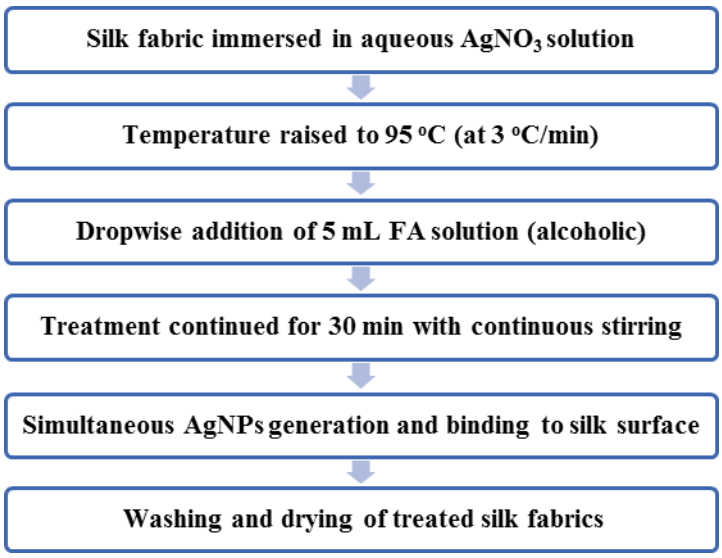

Fig. 2: UV-visible spectra (a) Effect of $AgNO_3$ concentration on absorbance of residual AgNPs solution obtained with 1.0 g/L FA, (b) effect of FA concentration absorbance of residual AgNPs solution obtained with 1.0 mmol/L FA

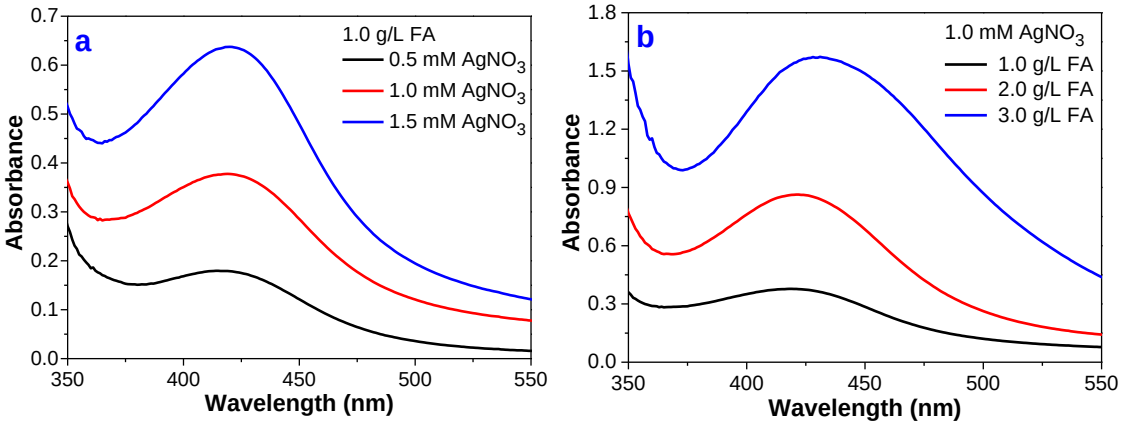

Fig. 3: TEM images of residual AgNPs solution prepared with 1.0 mmol/L $AgNO_3$ + 1.0 g/L FA (a) 100 nm and (b) 50 nm

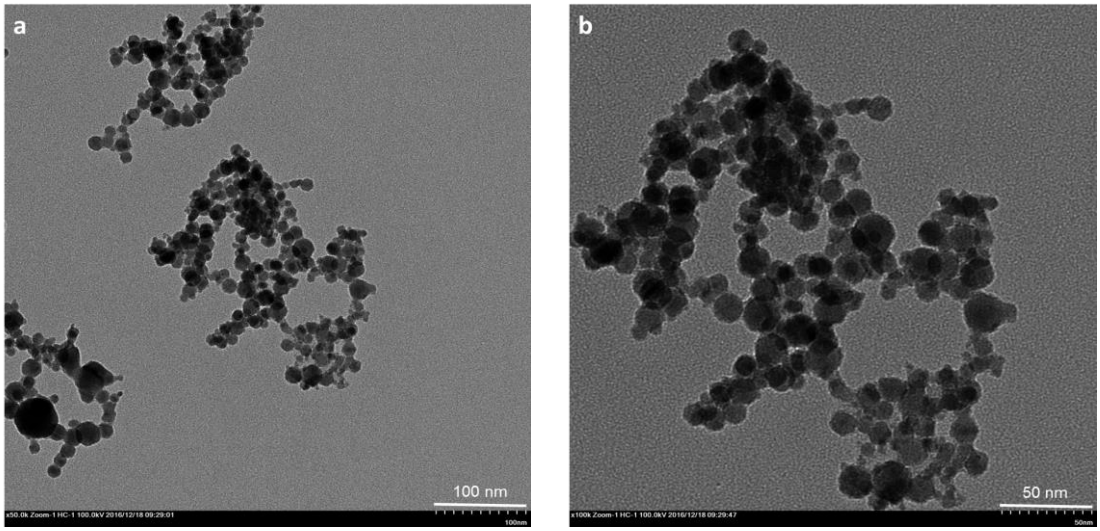

Fig 4: Size distribution obtained from DLS measurement of AgNPs prepared with 1.0 mmol/L $AgNO_3$ + 1.0 g/L FA

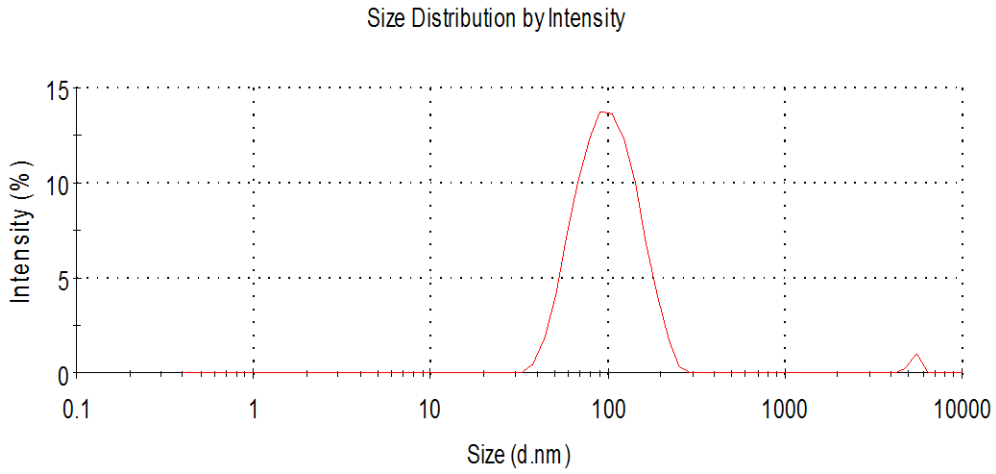

Fig. 5: Low magnification SEM images of AgNPs@silk prepared with 2.0 mmol/L $AgNO_3$ + 2.0 g/L FA

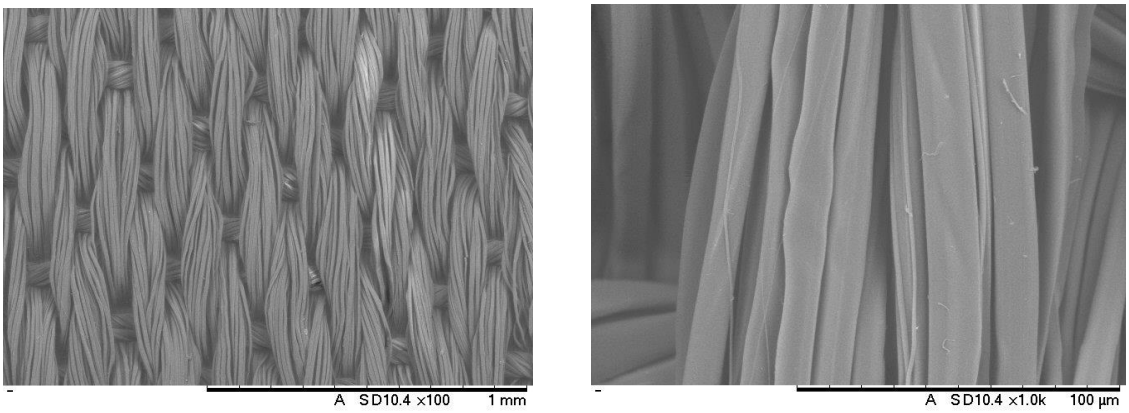

Fig. 6: High magnification SEM images of AgNPs@silk prepared with (a) 1.0 mmol/L $AgNO_3$ + 1.0 g/L FA, (b) 2.0 mmol/L $AgNO_3$ + 1.0 g/L FA, (c) 2.0 mmol/L $AgNO_3$ + 2.0 g/L FA, (d) 2.0 mmol/L $AgNO_3$ + 3.0 g/L FA, (e) Particle size distribution of AgNPs@silk prepared with 2.0 mmol/L $AgNO_3$ + 1.0 g/L, (f) EDS of AgNPs@silk prepared with 0.5 mmol/L $AgNO_3$ + 1.0 g/L FA.

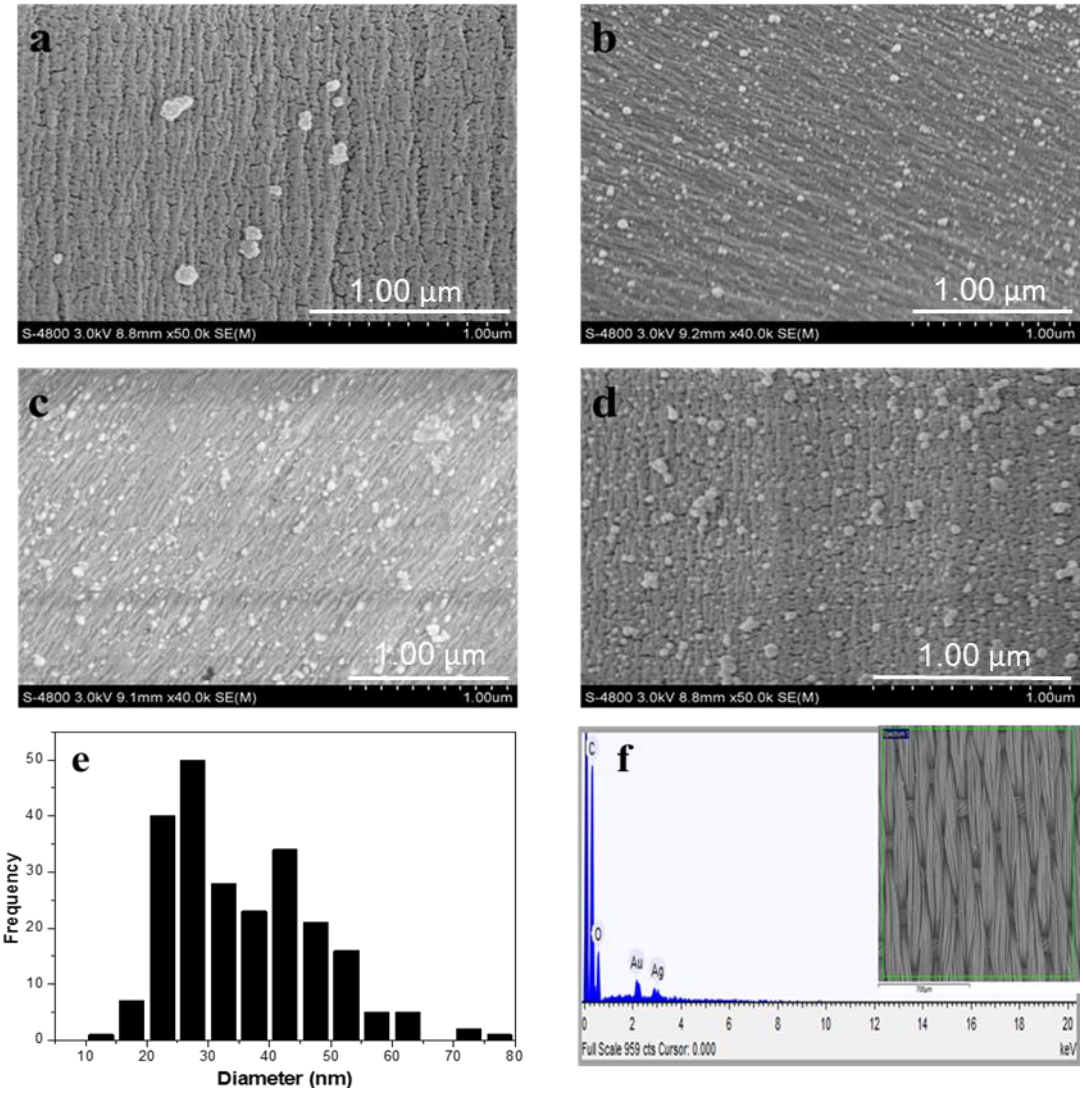

Fig. 7: (a) X-ray diffraction patterns, (b) XPS and (c) FTIR spectra of AgNPs@silk

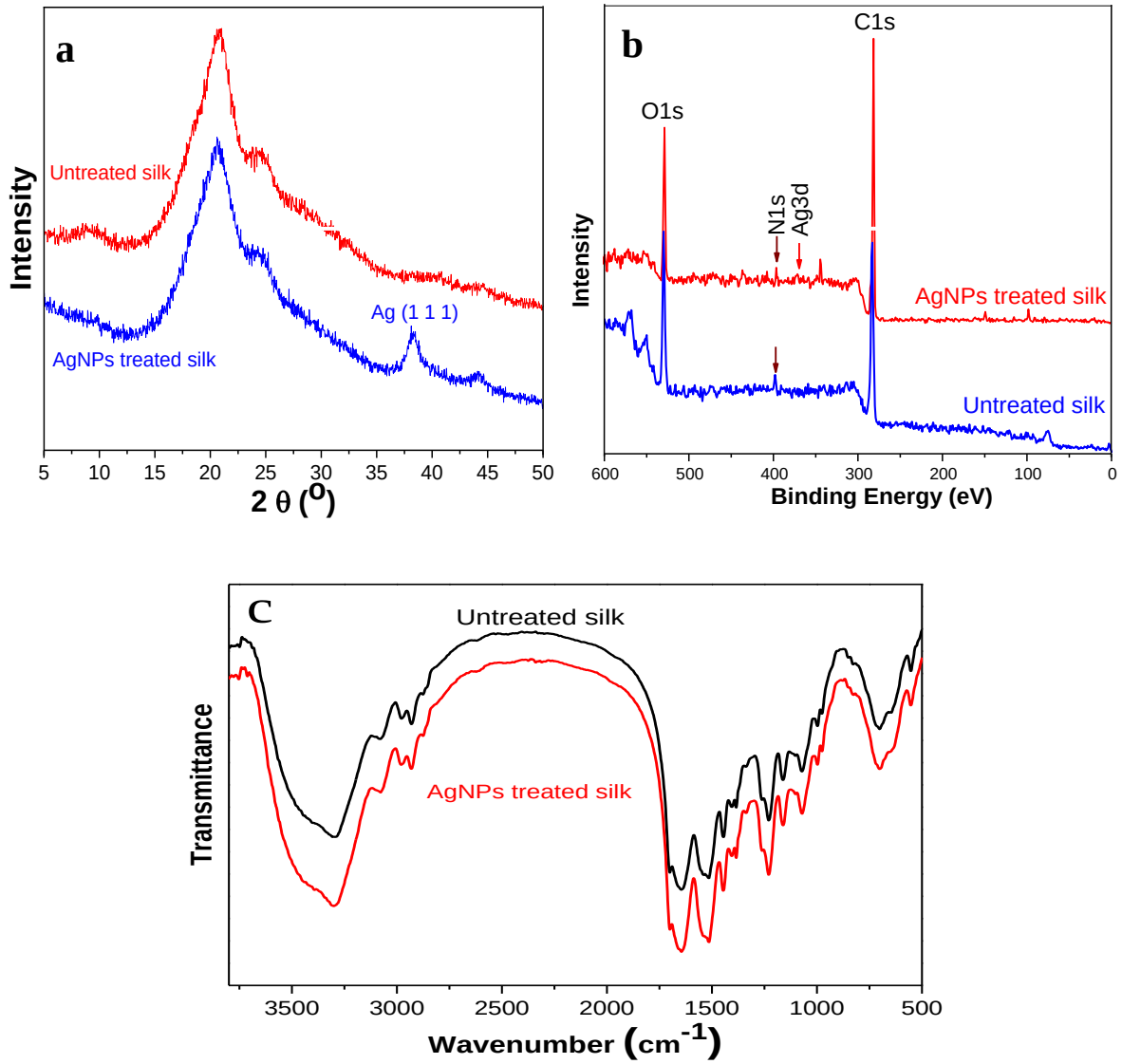

Fig. 8: Colour pallete of AgNPs@silk

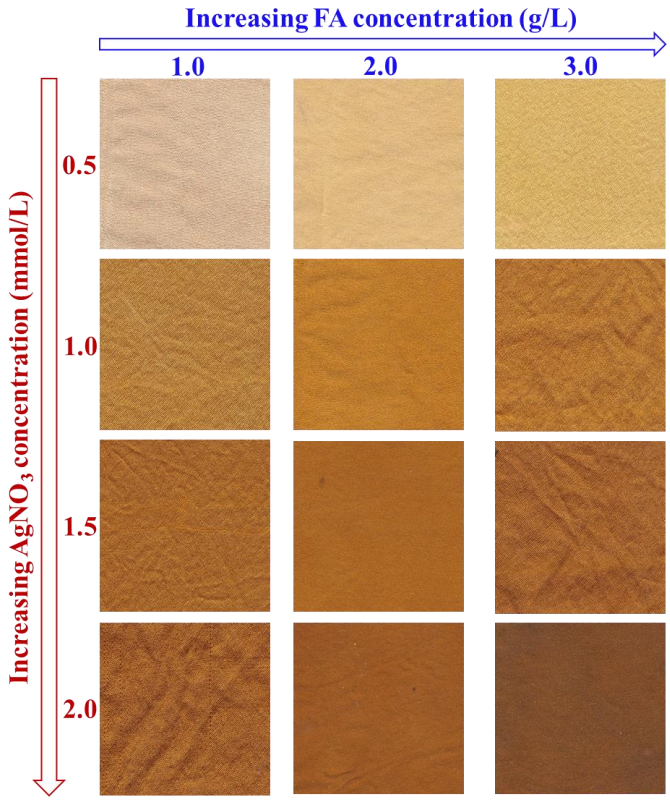

Fig. 9: Colour strength (K/S) graphs of AgNPs@silk (a) effect of FA concentration (b) effect of $AgNO_3$ concentration

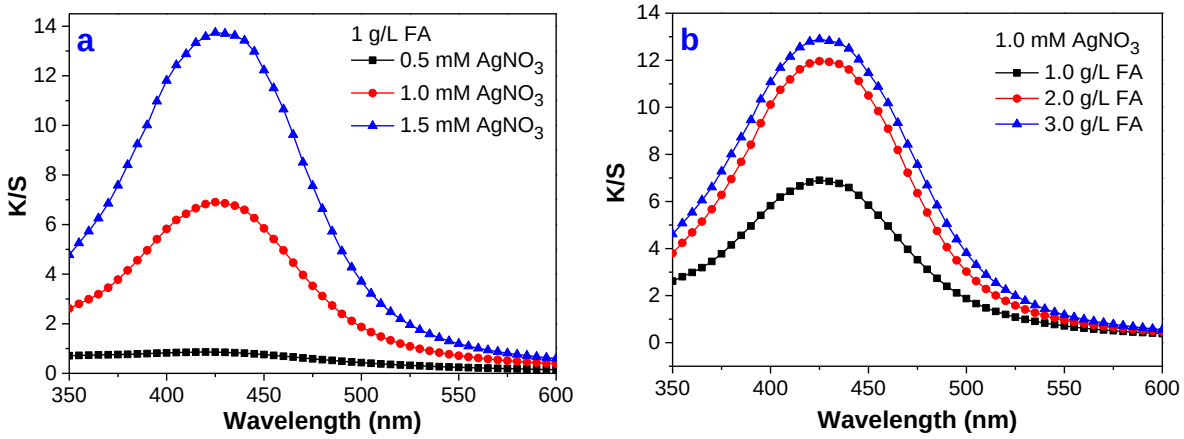

Fig. 10: Antibacterial activity against *E. coli*. (a) Untreated silk fabric and (b) AgNPs@silk

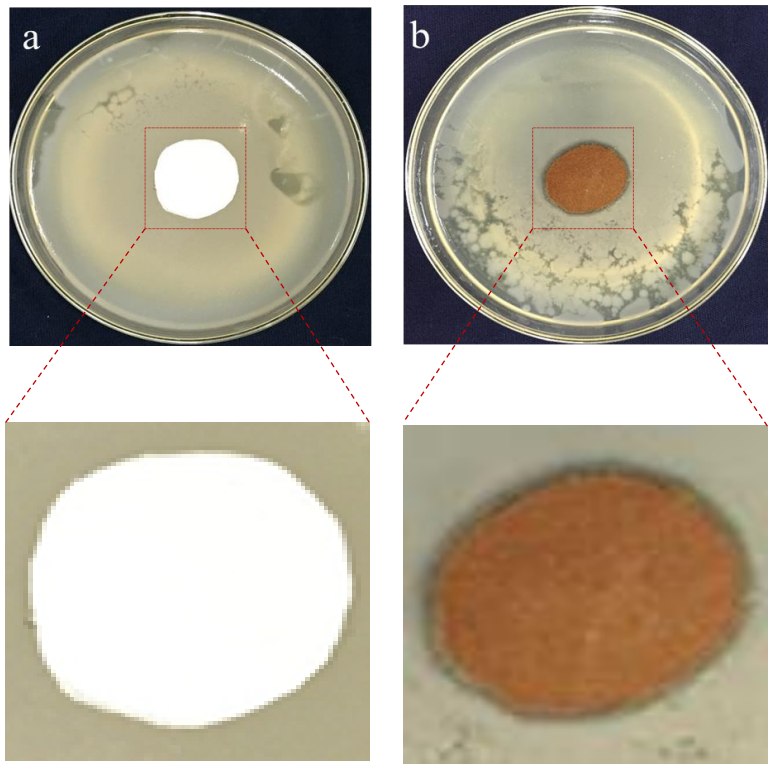

Fig. 11: UV transmittance of AgNPs@silk

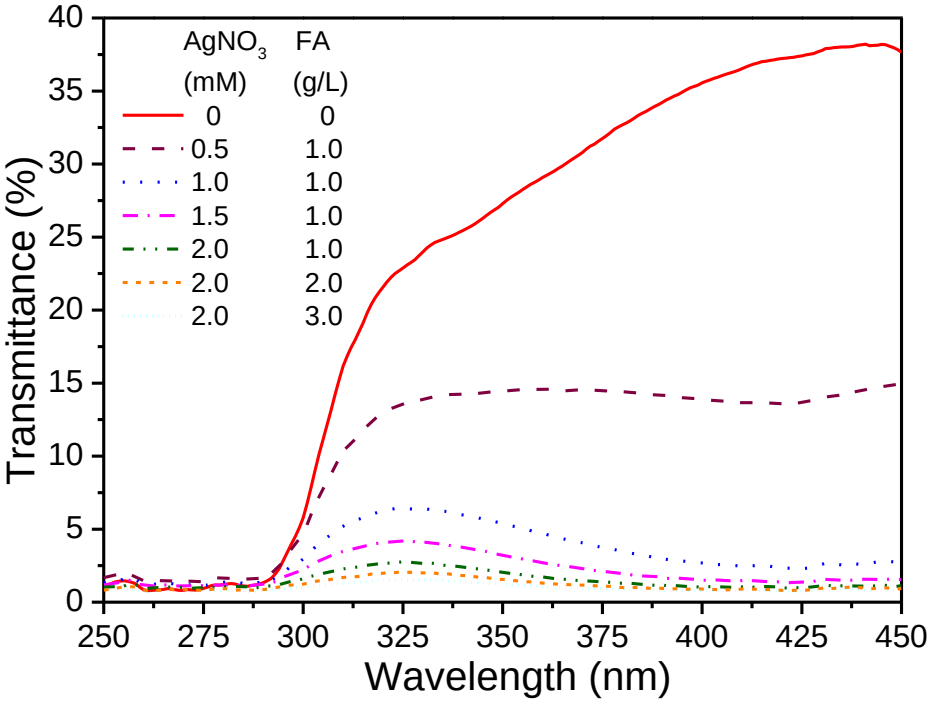

Table 1: Colour characteristics of AgNPs@silk

AgNPs@silk						
$AgNO_3$ (mmol/L)	**FA (g/L)**	***L****	***a****	***b****	**C***	**h***
0.5	1.0	76.08	4.63	21.54	22.03	77.87
1.0	1.0	62.91	9.62	47.42	48.38	78.53
1.5	1.0	56.00	14.18	52.45	54.32	74.88
2.0	1.0	50.98	16.88	49.67	52.46	71.23
2.0	2.0	48.43	18.12	45.60	49.07	68.31
2.0	3.0	42.76	14.69	33.79	36.85	66.45

Notes: *L**, lightness; *a**, redness-green value; *b**, yellowness-blueness value.

Table 2: UV-protective properties of AgNPs@silk

AgNPs@silk		UPF	T(UVA)	T(UVB)	UPF Rating
$AgNO_3$ (mmol/L)	FA (g/L)		%	%	(EN 13758-1:2001)
0	0	7.04	28.51	9.23	5
0.5	1	11.04	14.11	6.46	10
	2	13.1	11.12	5.45	10
	3	14.65	9.03	4.97	10
1.0	1	21.86	4.76	3.60	20
	2	29.35	3.27	2.78	25
	3	43.21	2.31	1.90	35
1.5	1	32.12	2.89	2.57	30
	2	40.85	2.27	2.09	35
	3	61.56	1.53	1.40	50+
2.0	1	48.5	1.88	1.78	40
	2	73.44	1.27	1.19	50+
	3	82.79	1.15	1.10	50+

Notes: UPF, UV protection factor; T(UVA), UVA transmittance; T(UVB), UVB transmittance