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Production of antibacterial colored viscose fibers using in situ prepared spherical Ag nanoparticles

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ABSTRACT

In situ incorporation technique was used for coloration and acquiring excellent antibacterial properties for viscose fibers by silver nanoparticles (AgNPs). AgNPs were prepared in situ and incorporated in viscose matrix directly without using any other reducing and stabilizing agents. The main objective of this research was to successfully employ the reducing and stabilizing features of cellulose to produce nanosilver–viscose composites. Coloration of fibers after in situ AgNPs incorporation is related to surface plasmon resonance of silver. Colorimetric data were recorded as a function of washings to characterize the final colored fibers. Fastness properties and silver release were all measured to study the washable and wear off properties. Depending on the silver concentration, yellowish colored fibers with different shades were produced. Good fastness properties were obtained after 20 washings without using any crosslinker or binder. The colored fibers had excellent antibacterial activities against *Escherichia coli*, even after 20 washings.

1. Introduction

Nanoparticles of noble metals showed specific colors according to their surface plasmon resonance (SPR) absorption. Hence the examination of surface Plasmon resonance is taking a part of a huge research area, to investigate the properties on the nanometer scale (El-Sayed, 2001; Eustis, 2006; Eustis & El-Sayed, 2006). Numerous characteristics of nanometals, including their optical, electronic, catalytic, chemical and physical properties had shown to be related to size and shape of the precursor nanoparticles. The shape and crystallographic structure are the two major factors affecting on the SPR bands, the catalytic properties and surface activities of nanoparticles (Dick, McFarland, Haynes, & Van, 2002). On the other hand, the size of metal nanoparticles influences their optical properties (Qiaoling & Yahong, 2012).

The reducing and stabilizing agents used in the preparation process of nanomaterials play an important role in controlling both of size and shape of the resultant nanomaterials, and in turn, affects on the color of the net produced nanosilver colloidal solution. Kotelnikova et al. reported that, using of different reducing agents affects on the color of AgNPs incorporated cellulose. Using cellulose itself or sodium borohydride as reductant gave metallic silver with yellow color. By using ammonia or glycerol as reducers the red–brown color of Ag^0 was produced, while the grey color appeared when hydrogen potassium phosphate or hydroquinone were used (Kotelnikova, Demidov, Wegener, Windeisen, & Kotelnikov, 2003; Kotelnikova, Stoll, et al., 2003).

Silver nanoparticles (AgNPs) colloidal solution was prepared with different colors including yellow, red, green, blue and grey (Abdel-Mohsen, Abdel-Rahman et al., 2014; Bois et al., 2009; Gopinath et al., 2012; Harekrishna et al., 2009; Hebeish et al., 2010 Emam et al., 2013; Salprima et al., 2013) depending on their shape. In acidic medium, the preparation of silver nanoparticles by utilizing cellulose as reducing agent produced grey color (Emam et al., 2013). The yellowish color is corresponding to the spherical AgNPs which was easily produced by using carbohydrate materials as reducing agents (Abdel-Mohsen, Abdel-Rahman et al., 2014; Harekrishna et al., 2009; Hebeish et al., 2010). The triangular silver nanoplates and silver nanoprism have been obtained by several researchers with blue color, showing three absorbance beaks at 350, 450–500 and at 700–800 nm (Bin et al., 2011; Deivaraj, Lala, & Lee, 2005; Guoli, Wentao, Kai, & Zhanfang, 2011; Huiying et al., 2008; Jia et al., 2013; Sadhan, Priyanka, Santanu, Gobinda, & Ajay, 2012). Also, the silver nanodisc colloidal solution exhibited three absorbance beaks at 350, 400 nm and the maximum beak at 500–650 nm. These three beaks are contributing to the red color (Deivaraj et al., 2005; Sadhan et al., 2012). However, silver nanorods or nanoplates colloids had a greenish color (Deivaraj et al., 2005; Sadhan et al., 2012).

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Antimicrobial activity of AgNPs was shown extensively in the literature, where many publications have studied the antibacterial activity of AgNPs coated fibers and/or fabrics (Abdel-Mohsen, Radim et al., 2012; Gorenšek et al., 2010; Ilić et al., 2009; Lee, Yeo, & Jeong, 2003; Maneerung, Tokura, & Rujiravanit, 2008; Maria et al., 2010; Matyjas-Zgondek, Bacciarelli, Rybicki, Szynkowska, & Kołodziejczyk, 2008; Ravindra, Murali, Narayana, & Mohana, 2010). Besides, anisotropic AgNPs colloidal solutions had also been used as a dye or a colorant for natural fibers and fabrics according to their color. The natural fibers and fabrics including wool, silk and cotton had been colored by different anisotropic AgNPs using wet chemistry process (Bin et al., 2011; Bin et al., 2013; Big et al., 2012; Watson, 2009). Different polymers were been used to achieve good washing fastness. Poly (diallyl dimethyl ammonium chloride) (PDDA) was used as crosslinker for cotton (Big et al., 2012), while poly-dimethyl siloxane was used for silk fibers (Bin et al., 2013).

Finally, based on literature, there are three different procedures for coloration of fibers or fabrics by using nanoparticles; firstly, metal nanoparticles colloidal solutions followed by impregnating the fabrics in the prepared colloidal solution process (Bin et al., 2011; Bin et al., 2013; Big et al., 2012; Watson, 2009). Secondly, the metal nanoparticles are prepared in situ the fabrics (Fern & James, 2011; Watson, 2009). In the third method, a polymer–nanoparticles composite is synthesized followed by spinning process to form colored fibers (Sreekumar, Arunashish, Lal, Anurage, & Bhasker, 2009).

Recently our group is started to use AgNPs as multifunctional agent for different fibers/fabric materials by in situ incorporation of AgNPs into fibers/fabric matrix. In the current work, we presented a simple procedure to produce the colored cellulose fibers based on viscose with excellent antibacterial action in one step using AgNPs. AgNPs were prepared and incorporated in cellulosic fibers matrix in situ by using cellulose itself as reducer and stabilizing agent. UV–vis spectra and transmission electron microscopy (TEM) images were both measured for the supernatant solutions. The colorimetric analyses (color strength, color difference and color space) of the colored cellulose fibers were all monitored up to 20 washings. Different fastness properties and silver release from fibers were studied after washing process. The antibacterial activity of the colored fibers was detected using the plate agar count method against gram negative bacteria *Escherichia coli*.

2. Experimental

2.1. Materials and chemicals

The regenerated cellulose fibers based on viscose 'CV' (Lenzing Viscose®) with linear density 1.3 dtex and length 38 mm, was kindly supported by Lenzing AG (Lenzing, Austria). The fibers did not contain any spin finishing and were used without further treatment.

Silver nitrate (99.5%, from Panreac, Barcelona, Spain), Sodium hydroxide (99%), Sodium carbonate monohydrate (>99%, from Merck, Darmstadt, Germany) Nitric acid (55%, from the Egyptian company for chemicals and pharmaceuticals, 10th of Ramadan-Egypt) were all used without any further purification.

2.2. Procedure

Colored/antibacterial viscose fibers were prepared in one step by using simple technique. The process was performed as follows: a 5 g of viscose fibers were stepwise immersed in 250 ml of 0.1N NaOH, the stirring was carried out for 10 min at room temperature. The silver nitrate solution with different concentration (0.4–8 mmol/l) was added dropwise to the container with stirring, then the temperature was raised to 70 ± 3 °C. After 45 min, the fibers were taken out, squeezed and rinsed by tap water for neutralization and then squeezed again. The fibers were dried at 75 ± 5 °C prior to analysis and characterization. The Absorbance of all supernatants was measured after the immersion time.

3. Measurements

3.1. UV–vis spectra

AgNPs solutions exhibit an intense absorption peak due to the surface plasmon resonance (SPR). Thus the UV–vis absorption spectra were used to measure the extinction of the residual solutions after the treatment step using a multi channel spectrophotometer (T80 UV/VIS, d = 10 mm, PG Instruments Ltd, Japan) at 250–600 nm.

3.2. Transmission electron microscope (TEM)

For more characterization of the prepared AgNPs, two drops of the supernatant colloidal solutions was placed on a 400 mesh copper grid coated by an amorphous carbon film. Then the solvent was evaporated in air at room temperature and then the grid was conducted to microscope equipment. The morphology was characterized by means of a JEOL-JEM-1200 transmission electron microscope. The diameter and size distribution of AgNPs were calculated by 4 pi analysis software using TEM photos.

3.3. Color measurements

The colorimetric analysis of the colored fibers was recorded using a spectrophotometer with pulsed xenon lamps as light source (UltraScan Pro, Hunter Lab, USA) 10° observer with D65 illuminant, $d/2$ viewing geometry and measurement area of 2 mm. All measurements were occurred at λ_{425}. The corresponding color strength value (K/S) was assessed by applying the Kubelka Munk (Menter & Hatch, 2003) (Eq. (1)).

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (1)$$

where R is the decimal fraction of the reflection of the colored fabric, K the absorption coefficient and S is the scattering coefficient.

Now, in a lot of dye houses, there is a data match system which helps colorists to obtain different shades and to judge about the acceptance of these shades against a particular standard. The most widely used is the total color difference (ΔE) (Rupp, Bohringer, Yonenaga, & Hilden, 2001), which can be calculated from the CIE LAB color space data. The color space (L, a^*, b^*) of colored samples was measured by the same spectrophotometer used for measuring of color strength at the same set up, and then the color difference was calculated using.

$$\Delta E = L^2 + (a^2 + b^2)^{1/2} \quad (2)$$

where ΔE is the total difference between the sample and the standard, L the lightness from black (0) to white (100), a^* is a red (+)/green (−) ratio and b^* is yellow (+)/blue (−) ratio.

3.4. Fastness properties (Methods, 1990)

3.4.1. Color fastness to washing

The color fastness to washing was determined according to the method ISO 105-C02 (1989). The composite specimens were sewed between two pieces of bleached cotton and wool fabrics, and then immersed into an aqueous solution containing 5 g/l nonionic detergents at liquor ratio 1:50. The bath was thermostatically adjusted to 60 °C for 30 min. After the desired time, samples were removed, rinsed twice with occasional hand squeezing, and then