Carbohydrate Polymers 92 (2013) 2088–2094

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Antibacterial cotton fabric grafted with silver nanoparticles and its excellent laundering durability

Desuo Zhang[a], Ling Chen[b], Chuanfeng Zang[a], Yuyue Chen[a], Hong Lin[a,*]

[a] College of Textile and Clothing Engineering, Soochow University, Mail Box No. 64, The North Campus of Soochow University, No. 178 of Ganjiang East Road, Suzhou 215021, People's Republic of China
[b] Patent Examination Cooperation Center of SIPO, Room C5049 Building No. 1 of Chuangye park, No. 209 of Zhuyuan Road, Suzhou 215011, People's Republic of China

ARTICLE INFO

Article history:
Received 2 August 2012
Received in revised form
17 September 2012
Accepted 30 November 2012
Available online 11 December 2012

Keywords:
Amino-terminated hyperbranched polymer
Oxidized cotton fabric
Graft
Silver nanoparticles
Antibacterial property
Laundering durability

ABSTRACT

In order to fabricate antibacterial cotton fabric with excellent antibacterial property and laundering durability, amino functional silver nanoparticles (Ag NPs) were prepared by one-step reaction with amino-terminated hyperbranched polymer (HBP-NH_2) and grafted on the oxidized cotton fabric subsequently. The synthesized amino functional Ag NPs and Ag NPs grafted oxidized cotton fabric (Ag-GOCF) were characterized which indicated that the average size of Ag NPs was 10.8 nm with narrow size distribution and the Ag NPs have been grafted on the cotton fabric. 99.43% and 99.45% bacterial reduction rates were obtained for *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) respectively in case the cotton fabric was treated with 10 mg/L Ag NPs solution to produce Ag-GOCF with 149.88 mg/kg Ag content. After 50 washing cycles, the Ag content of this Ag-GOCF was maintained at 116.08 mg/kg with its antibacterial activity at over 96% reduction level.

1. Introduction

Natural fiber products, especially cotton fabrics, are highly popular with people and widely applied in daily life because of their excellent properties, such as softness, hygroscopicity, affinity to skin, bio-degradability and regeneration property (Lu, Lin, Chen, Wang, & Hua, 2007; Saravanan, Vasanthi, & Ramachandran, 2009). However, these products could be easily damaged by microorganisms on account of its natural feature and ability to retain moisture, which not only cause discoloration, mechanical strength loss and foul odor generation of the products but also result in a series of negative health effects to human beings (Hebeish, Abdel-Mohdy et al., 2011; Hebeish, El-Naggar et al., 2011; Zhang, Chen, Ling, & Zhang, 2009). With increasing awareness of consumers toward health and hygiene, demand for antibacterial textiles is now expanding. Therefore, many antibacterial agents have been applied to fabricate antibacterial textiles, such as quaternary ammonium compounds (Sun, Li, Qiu, & Qing, 2005), chitosan (Ali, Joshi, & Rajendran, 2011), triclosan (Kalyon & Olgun, 2001), nanoparticles of noble metals and metal oxides (Jiang, Liu, & Yao, 2011; Joshi, Ali, & Rajendran, 2007; Mary, Bajpai, & Chand, 2009; Montazer & Seifollahzadeh, 2011; Vasilev et al., 2010; Xia, Cai, Jiang, & Yao, 2011), and bioactive plant-based products (Alemdar & Agaoglu, 2009), in which silver nanoparticle (Ag NP) has been widely used due to its broad spectrum of antibacterial activity and low toxicity toward mammalian cells (Hebeish, El-Naggar et al., 2011; Kim et al., 2009). However, Ag NPs are lack of chemical bonds to link with natural fibers which will bring about unsatisfied laundering durability of Ag NPs treated antibacterial textiles. Moreover, when Ag NPs release in great number into natural environment, the antibacterial ability of them could potentially compromise the health of organisms, e.g. alga in river, microorganisms especially vital bacteria that are important in the support and continuation of all forms of life, such as the degradation of organic matter, transformation of elements, and recycle of nutrients (Bradford, Handy, Readman, Atfield, & Mühling, 2009; Miao et al., 2010). Hence, some binders, such as dimethylodihydroxyethylene urea, polyacrylic esters and polyurethane resin, were applied to fix Ag NPs on the fibers to provide durability of antibacterial properties (Tomšič et al., 2008). The usage of these chemicals may lead to undesirable effects on the properties of natural fibers products or make them associated with toxicity to endanger human body and environment.

As is known, cotton fibers almost consist of cellulose which can be chemically modified to yield cellulose derivatives. Periodate oxidation of cotton fiber gave rise to an opened ring product containing

---

Abbreviations: Ag NP, silver nanoparticle; Ag-GOCF, silver nanoparticles grafted oxidized cotton fabric; Ag-TUCF, silver nanoparticles treated un-oxidized cotton fabric.

* Corresponding author. Tel.: +86 512 67487152.
E-mail address: linhong523@suda.edu.cn (H. Lin).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.11.100

two aldehyde groups formed by oxidative scission at the C-2 and C-3 of the anhydro D-glucopyranose residues in the fiber molecule (Nikolic et al., 2010). The conversion of hydroxyl groups to aldehyde groups by periodate oxidation is an efficient method widely used in derivatization of cellulose to activate cotton fibers for further reactions. It can provide a “green” approach to modify cotton fiber without undesirable chemicals (Lin, Yao, Chen, & Wang, 2008).

Over the past two decades, dendrimers and hyperbranched polymers have been widely developed due to their unique chemical and physical properties together with their potential application in additives, drug and gene delivery, nanotechnology, and supramolecular science (Gao & Yan, 2004; Menjoge, Kannan, & Tomalia, 2010). With numerous interior cavities as well as inward and outward oriented functional groups, they can be utilized as templates to control synthesis of nanoparticles with small size, good monodispersity and stability, such as Ag NP, Au NP, ZnO NP, etc. (Castonguay & Kakkar, 2010; Richter, Schüler, Thomann, Mülhaupt, & Ludwigs, 2009; Scott, Wilson, & Crooks, 2005). In our previous study, an amino-terminated hyperbranched polymer (HBP-NH_2), characterized by a three-dimensional structure with a large number of imino groups and terminal primary amino groups, was synthesized by one-step polycondensation. It has been applied to cotton fabric as an auxiliary to realize salt-free dyeing for reactive dyes (Zhang, Chen, Lin, & Lu, 2007).

In this study, in order to fabricate Ag NPs treated cotton fabric with excellent antibacterial property and laundering durability, HBP-NH_2 was employed to prepare Ag NPs by one-step reaction in aqueous medium without any other reducer and stabilizer. After generation of Ag NPs, HBP-NH_2 would tightly absorb on the surface of Ag NPs which not only could stabilize Ag NPs but also functionalize them with amino groups. This interaction between HBP-NH_2 and Ag NPs was confirmed by Energy-dispersive X-ray spectroscopy (EDS) and Fourier transform infrared spectroscopy (FT-IR). The amino functional Ag NPs were then grafted on the oxidized cotton fabric by the reaction between amino groups and aldehyde groups in mild condition to provide the cotton fabric with durable antibacterial properties. This process is a “green” approach because it does not involves toxic materials or any other undesirable impurities. The laundering durability of Ag NPs grafted oxidized cotton fabrics (Ag-GOCF) were investigated and the antibacterial activities of them were measured quantitatively against Gram positive bacteria (*Staphylococcus aureus*) and Gram negative bacteria (*Escherichia coli*).

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$, 99.8%), sodium periodate ($NaIO_4$, 99.8%) and nitric acid (65%) were purchased from Sigma–Aldrich. HBP-NH_2 ($M_n = 2684$, $M_w = 7759$) was prepared as described in our previous paper (Zhang et al., 2007). All chemicals were used as received without any further purification or treatment. Woven, bleached, and scoured cotton fabric (58×30 number of yarns per cm^2, $120\,g\,m^{-2}$) was obtained from the Huafang Group (China). *Staphylococcus aureus* (*S. aureus*, ATCC 6538) and *Escherichia coli* (*E. coli*, ATCC 8099) were obtained from College of Life Science, Soochow University (China). Nutrient broth and nutrient agar were purchased from Scas Ecoscience Technology Inc. (China). Deionized water ($18\,M\Omega\,cm$) was used in the preparation of all samples.

2.2. Preparation of amino functional Ag NPs by HBP-NH_2

$AgNO_3$ and HBP-NH_2 were dissolved in deionized water, respectively. Then $AgNO_3$ aqueous solution was added dropwise into HBP-NH_2 solution under vigorous stirring at room temperature. The initial concentrations of the reaction components were 0.28 g/L $AgNO_3$ and 5 g/L HBP-NH_2. The mixture was then heated till it turned yellow in color, and the solution was ceased heating, left to cool down. To compensate the loss of water during the heating process, deionized water was added to maintain the initial level of solution before heating.

2.3. Preparation of Ag-GOCF

Cotton fabric was immersed in an aqueous solution of $NaIO_4$ (2 g/L) with a liquor ratio of 30:1. The solution was oscillated gently at 40 °C for 30 min. Then the oxidized cotton fabric was washed with tap water to remove the oxidant. Subsequently, the oxidized cotton fabric was immersed in Ag NPs polymer hybrid aqueous solution (range from 10 mg/L to 150 mg/L of Ag NPs) for 30 min at ambient temperature with liquor ratio of 50:1, and then washed with tap water for 3 cycles with 2 min per wash. The resulting sample was air-dried at ambient temperature to produce the Ag-GOCF. In comparison, the un-oxidized cotton samples were also treated with Ag NPs according to the above process.

2.4. Characterization of amino functional Ag NPs and Ag-GOCF

A JEOL 3010 transmission electron microscope (TEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) was employed to take the TEM micrographs at an accelerating voltage of 300 kV and analyze the elemental composition of the amino functional Ag NPs. Samples were prepared by placing small drops of Ag NPs aqueous solution on carbon-coated copper grid till the solvent slowly evaporated at ambient temperature. The size distribution of Ag NPs was measured with high performance particle sizer (HPPS) (Malvern Instruments Ltd., UK) at 25 °C. UV spectrum of Ag NPs aqueous solution was determined by a Cary 50 Bio UV-visible spectrophotometer (Varian, USA) at ambient temperature in a quartz cuvette of path length 1 cm.

Infrared spectra of HBP-NH_2, Ag NPs/HBP-NH_2 hybrid, control cotton fiber, oxidized cotton fiber and Ag NPs grafted cotton fiber were recorded in a Nicolet 380 FT-IR spectrophotometer (Thermo Electron Corporation, USA). JSM-6700F scanning electron microscope (SEM) was used to observe the morphologies of control cotton fiber, oxidized cotton fiber and Ag NPs grafted cotton fiber. Breaking strength measurements of fabrics were realized at YG026B electronic fabric strength tester (Ningbo Textile Instrument Factory, China) according to ISO 13934-1. Test length was 30 cm, and speed was 200 mm/min. Whiteness of the fabrics was determined using a WSD-5 Full-automatic Whiteness Meter (Shanghai Jingshen Scientific Instrument Limited Company). Ag contents in the Ag treated cotton fabrics were measured via a Vista MPX Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) (Varian, USA). 100 mg sample was cut into small pieces and immersed in 10 ml solution of HNO_3 (65%). After dissolved, 90 ml deionized water was used to dilute it. 1 ml of the diluted solution was then drawn to measure the concentration of Ag^+. The Ag content in cotton fabric was calculated by Eq. (1):

$$C_{Ag}\,(mg/kg) = C_{Ag^+} \times 10^{-3} \tag{1}$$

where, C_{Ag^+} (mg/L) is the concentration of Ag^+ in the solution.

2.5. Laundering durability test

To evaluate the durability of the Ag-GOCF against repeated launderings, the AATCC Test Method 61-1996 was applied. An AATCC standard wash machine (Atlas Launder-Ometer) and detergent (AATCC Standard Detergent WOB) were used. Samples were cut into 5 cm × 15 cm swatches and put into a stainless steel container

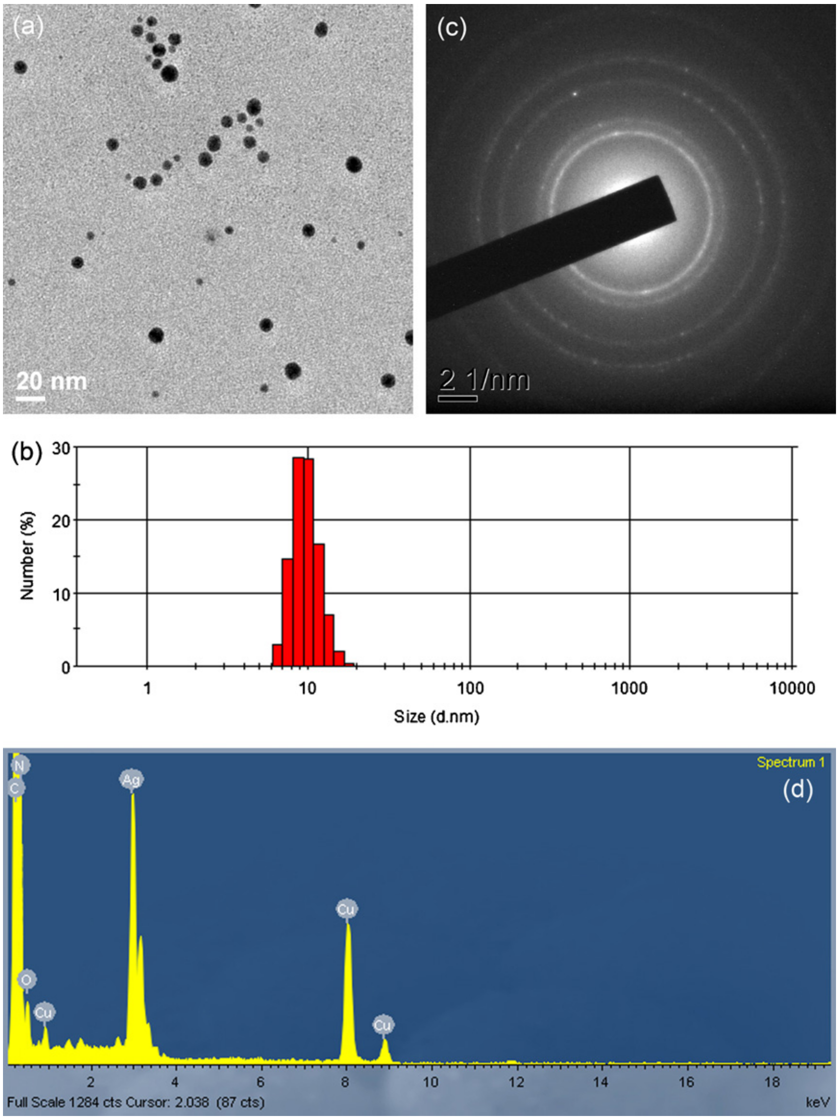


Fig. 1. (a) TEM image of Ag NPs prepared by HBP-NH_2, (b) size distribution of the Ag NPs, (c) corresponding electron diffraction pattern and (d) EDS spectrum of the Ag NPs.

with 150 ml of 0.15% (w/v) WOB detergent solution and 50 steel balls (0.25 in. in diameter) at 49 °C for various washing time to simulate 10, 30, and 50 wash cycles of home/commercial launderings. Afterwards, the samples were washed with tap water several times and air-dried at ambient temperature. The Ag content of the washed cotton fabrics was measured to determine the fastness of Ag NPs grafted on cotton fabric. In comparison, the un-oxidized cotton samples treated with Ag NPs were also tested according to the above process.

2.6. Antibacterial activity test

The antibacterial activity of Ag-GOCF was tested against *E. coli* and *S. aureus* by a shake flask method according to GB/T 20944.3-2008 (China). The test procedure is as follows: 0.75 g sample fabric was cut into small pieces of dimensions around 0.5 cm × 0.5 cm and dipped into a flask containing 70 ml PBS (pH ≈ 7.2) and 5 ml bacterial culture with a cell concentration of 3×10^5 to 4×10^5 CFU/ml. The flask was placed on a rotary shaker at 150 rpm for 18 h at 24 °C. 1 ml of solution was drawn from each sample well, diluted and distributed into an agar plate. All plates were incubated at 37 °C for 24–48 h and the colonies were counted. The percentage reduction (R, %) was determined as Eq. (2):

$$R(\%) = \frac{C - A}{C} \times 100 \qquad (2)$$

where, C and A are the bacterial colonies of the control cotton fabric and Ag-GOCF, respectively.

3. Results and discussion

3.1. Preparation of amino functional Ag NPs and its characterization

Ag NPs were easily obtained in one-step manner based on the reaction between $AgNO_3$ and HBP-NH_2. HBP-NH_2 has a three-dimensional architecture with numerous imino groups and terminal primary amino groups which can capture Ag^+ and reduce them to generate Ag NPs. The synthesized Ag NPs were characterized by TEM and their size distribution was measured by HPPS. Fig. 1(a) and (b) shows the TEM image and size distribution of Ag NPs prepared by HBP-NH_2 respectively. The size and polydispersity determined by HPPS are in accordance with the results in TEM

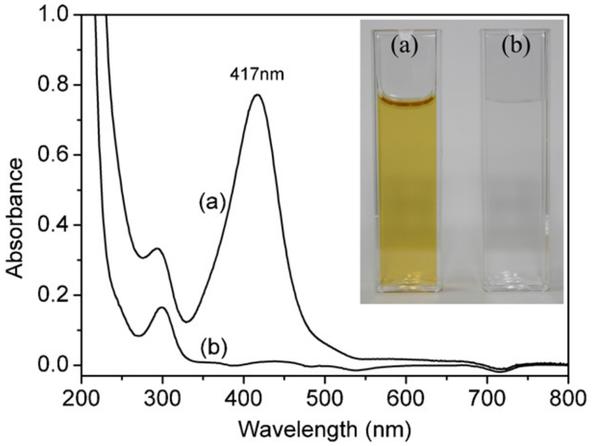


Fig. 2. UV spectra of HBP-NH_2/Ag^0 and HBP-NH_2/Ag^+ after reacted at different pH conditions: (a) pH 10.8 (original pH condition of HBP-NH_2/Ag^+ solution); (b) pH 3 (insets are their digital images under indoor light).

image. The average size of Ag NPs is about 10.8 nm with narrow size distribution, ranging from 6 nm to 20 nm. In order to support that the produced particles are Ag NPs, the corresponding electron diffraction pattern of (a) was determined (Fig. 1(c)). It exhibits concentric rings with intermittent bright dots indicating that these NPs are highly crystalline in nature. The rings can be attributed to the diffraction from face centered cubic (fcc) phase with (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of Ag crystals (Kora, Sashidhar, & Arunachalam, 2010).

During the reduction process, the fact that additional reducing agents were absent in the system suggests HBP-NH_2 themselves acted as reducers for Ag^+. With primary, secondary, and tertiary amines, they can entrap Ag^+ by complexation and potentially provide electron source for the reduction process (Kavitha, Parida, Prasad, Vijayan, & Deshmukh, 2009). The mechanism of Ag NPs formation can be explained in the following one electron transfer process (Eqs. (I)–(III)) (Kéki, Török, Deák, Daróczi, & Zsuga, 2000).

$$Ag^+ + -\ddot{N}H_2 \xrightarrow[\triangle]{} Ag^0 + -\overset{\cdot +}{N}H_2 \qquad (I)$$

$$Ag^+ + -\ddot{N}H- \xrightarrow[\triangle]{} Ag^0 + -\overset{\cdot +}{N}H- \qquad (II)$$

$$Ag^+ + -\underset{|}{\ddot{N}}- \xrightarrow[\triangle]{} Ag^0 + -\underset{|}{\overset{\cdot +}{N}}- \qquad (III)$$

This mechanism was also corroborated by the observation that Ag NPs would not generate with HBP-NH_2 at acidic condition (pH 3). Fig. 2 shows the UV spectra of HBP-NH_2/Ag^0 and HBP-NH_2/Ag^+ after reaction at different pH conditions. When HBP-NH_2 dissolved in deionized water, it displayed alkalinity (pH 10.8) because of the protonation of part amino groups in HBP-NH_2 and the other amino groups and imino groups could take part in the reaction to produce Ag NPs. Therefore the synthesized HBP-NH_2/Ag NPs hybrid solution (a) exhibits a strong absorption peak at 417 nm and presents light yellow. These phenomena are due to the surface Plasmon absorption of Ag NPs, which can confirm the formation of crystalline spherical Ag NPs (Sun & Xia, 2003). When the pH value of HBP-NH_2 solution was adjusted to 3, all the amino groups and imino groups would be protonated. Consequently, no electron source could be provided for the reduction process. As for the solution of HBP-NH_2/Ag^+ (b), there is only one absorption peak at 299 nm which is attribute to the absorption peak of HBP-NH_2 and the solution exhibits no color and transparent. This clearly suggests that protonation of amines blocked the reduction process.

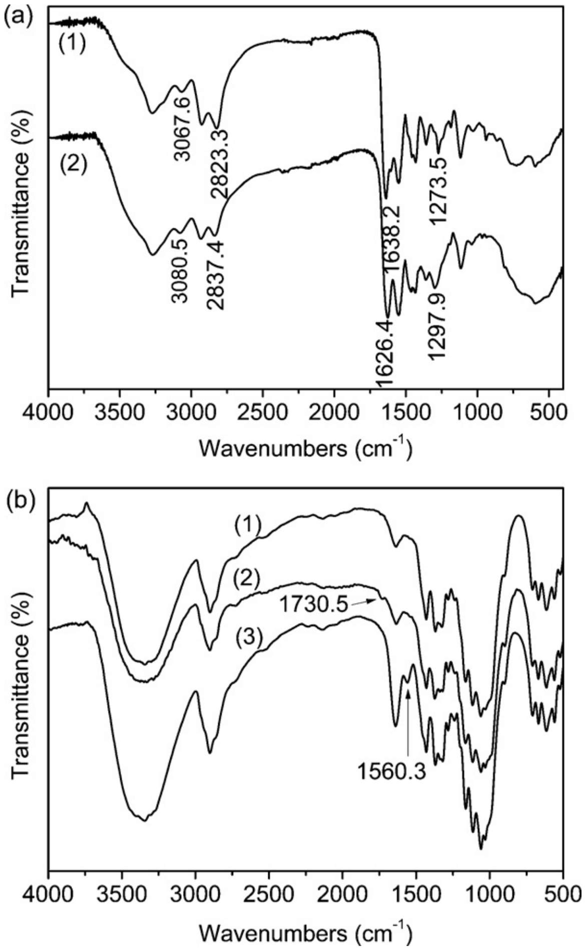


Fig. 3. (a) FT-IR spectra of (1) pure HBP-NH_2 and (2) Ag NPs/HBP-NH_2 hybrids, (b) FT-IR spectra of (1) control cotton fabric, (2) oxidized cotton fabric, and (3) Ag-GOCF.

According to the mechanism of reduction process, HBP-NH_2 performed positive charge after reaction to generate Ag^0. Meanwhile, the protonation of sectional amino groups in deionized water also made it display positive charge. Thus the HBP-NH_2 could be absorbed on the surface of Ag NPs immediately after generation of Ag NPs due to the negative zeta potential and high surface energy of NPs. As a result, the amino functional Ag NPs were produced. They were verified by EDS and FT-IR. The EDS spectrum of amino functional Ag NPs was shown in Fig. 1(d). As expected, it exhibits strong copper and carbon peaks. Copper peak arose from the supporting copper grids and carbon from the supporting carbon film in the copper grids together with the component of polymer. It stands to reason that the distinct Ag peak was resulted from the generation of Ag NPs. In the spectrum, oxygen and nitrogen peaks indicated that Ag NPs were surrounded by HBP-NH_2 on the surface. FT-IR spectrum was utilized to further confirm the interaction between Ag NPs and HBP-NH_2. Fig. 3(a) represents the comparison of FT-IR spectra from 4000 to 400 cm^{-1} between the pure HBP-NH_2 and Ag NPs/HBP-NH_2 hybrids. It clearly showed that the bands positions of HBP-NH_2 shifted apparently. The band position at 3067.6 cm^{-1}, corresponding to amide B (NH stretching vibration modes) of HBP-NH_2, transferred to higher regions (3080.5 cm^{-1}) after the formation of Ag NPs. The band position of CH_2 symmetric stretching at 2823.3 cm^{-1} shifted to 2837.4 cm^{-1}. The bands positions of amide I and III of HBP-NH_2 at 1638.2 and 1273.5 cm^{-1} respectively moved to lower point at 1626.4 cm^{-1} for amide I and higher region of 1297.9 cm^{-1} for amide III. All of these variations implied the interaction between HBP-NH_2 and Ag NPs which not only prevented Ag NPs to aggregate with each other but also functionalized the Ag NPs with amino groups (Mahapatra & Karak, 2008; Manna, Imae, Aoi, Okada, & Yogo, 2001). The polymer

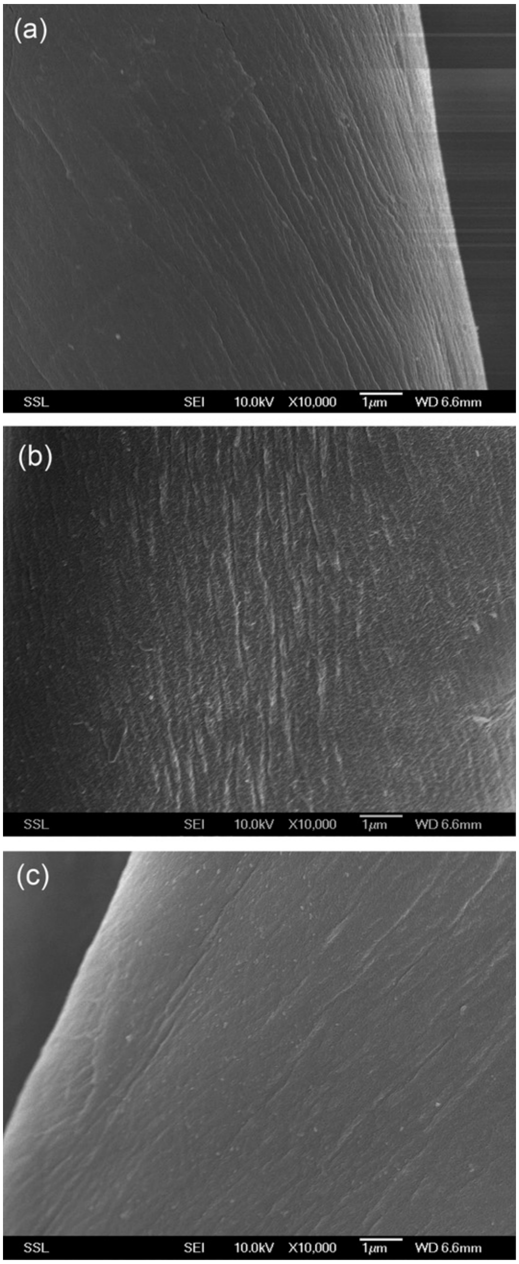


Fig. 4. SEM images of (a) control cotton fiber, (b) oxidized cotton fiber, and (c) Ag-GOCF.

functionalized Ag NPs exhibited good stability which had no color change or precipitation after a 6-month placement.

3.2. Preparation of Ag-GOCF

In our previous work, HBP-NH_2 has been grafted on cotton fabric to provide it with antibacterial properties and realized salt-free dyeing with reactive dyes (Zhang, Chen, Lin, Wang, & Zhao, 2008; Zhang, Zhang, Chen, & Lin, 2008). Thereinafter, the similar process was employed to prepare Ag-GOCF. The mechanism was described in Scheme 1. Firstly, the cotton fabric was oxidized by $NaIO_4$ to cleave 2,3-vicinal diol of the cellulose glucose units (a) and produce the oxidized cotton fabric (b). Subsequently, the resulting aldehyde groups on the oxidized cotton fabric reacted with the amino groups on the Ag NPs to generate Ag-GOCF (c).

The reaction process was monitored by infrared spectroscopy. Fig. 3(b) shows the FT-IR spectra of control cotton fabric, oxidized cotton fabric and Ag-GOCF. Compared with control cotton fabric, a new characteristic absorption band of the oxidized cotton fabric clearly appeared at 1730.5 cm^{-1} which was attributed to the stretching vibration of the C=O double bond of the aldehyde group. After amino functional Ag NPs grafting on oxidized cotton fabric, the absorption peak at 1730.5 cm^{-1} disappeared and another absorption peak at 1560.3 cm^{-1} corresponding to N—H bending of unreacted primary amino groups on Ag NPs appeared. This transformation leads to the conclusion that amino functional Ag NPs have been grafted on the oxidized cotton fabric by the reaction between aldehyde groups on it and the amino groups on Ag NPs.

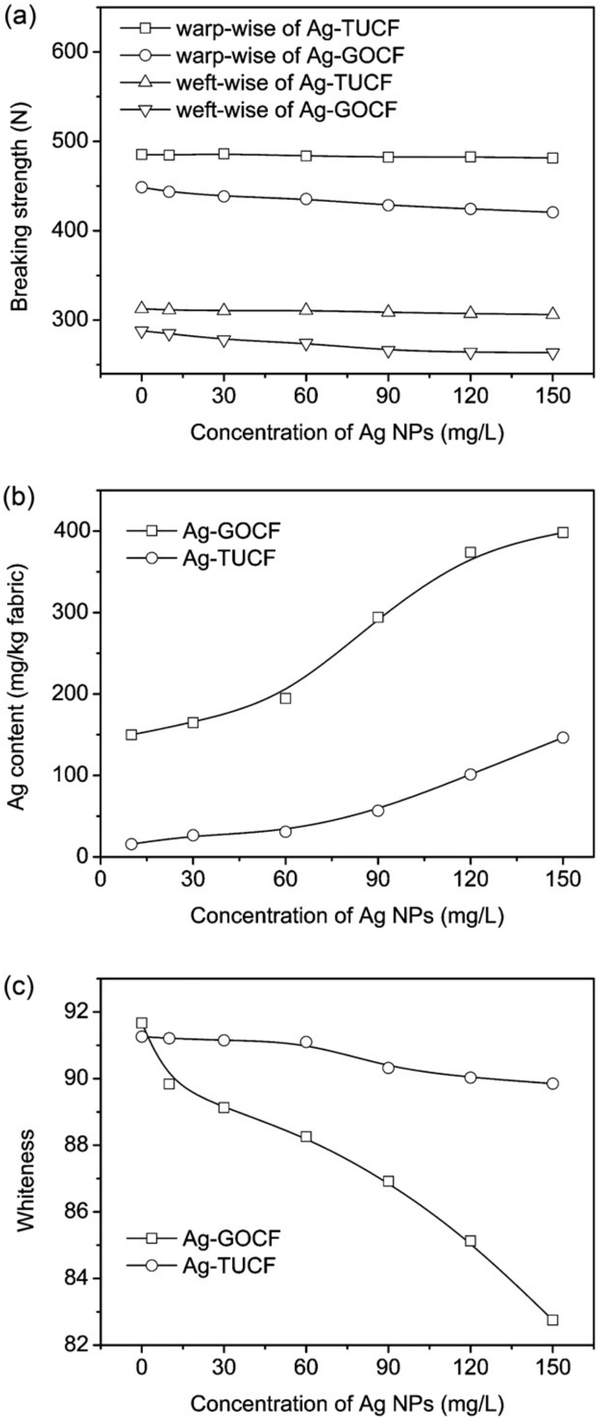
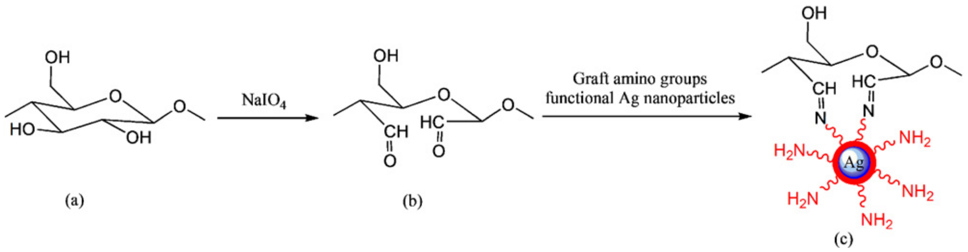


Fig. 5. (a) breaking strength, (b) Ag content, and (c) whiteness of Ag NPs treated cotton fabrics.



Scheme 1. Preparation of Ag-GOCF.

The surface morphologies of control cotton fiber, oxidized cotton fiber and Ag NPs grafted cotton fiber were all observed through SEM, shown in Fig. 4. It displayed an obvious difference between the control cotton fiber (a) and Ag NPs grafted one (c), while no apparent change between control cotton fiber and oxidized one (b). Oxidation of cellulose is a destructive treatment to cotton fibers which may cause variation in structure and crystallinity, resulting the decrease of mechanical properties of cotton fibers. In order to avoid the unfavorable effect on the mechanical properties for its application, referring to our previous studies, a mild oxidation process was chosen in this research which has been described in detail in the section of experimental. On this occasion, it affected little on the surface morphology of cotton fibers obviously. After grafting Ag NPs on the oxidized cotton fiber, many NPs could be found dispersed on the surface of cotton fiber.

During the process of grafting Ag NPs on cotton fabric, the concentration of Ag NPs aqueous solution is the most important factor to determine the amount of Ag NPs grafted on fabric which is related to the antibacterial properties of treated fabric directly. Thus the breaking strength, Ag content and whiteness of grafted fabrics with different concentrations of Ag NPs were all measured. In comparison, control cotton fabrics were also treated with Ag NPs aqueous solution. Fig. 5(a) shows the breaking strength of amino functional Ag NPs treated cotton fabrics. It indicated that Ag-GOCF presented lower breaking strength than Ag NPs treated un-oxidized cotton fabric (Ag-TUCF) due to the oxidization. The breaking strength of Ag-GOCF deceased slightly with the increase of the concentration of Ag NPs, which was possibly caused by the damage to the structure of oxidized cotton fiber when grafting reaction proceeded in the alkaline solution of Ag NPs/polymer hybrids (pH values ranged from 9.9 to 10.8 with different concentration). However this decrease of breaking strength almost made no influence on its application. Ag contents of the treated cotton fabrics were illustrated in Fig. 5(b). The Ag contents of Ag-GOCF were higher than that of Ag-TUCF. With the increasing of concentration of Ag NPs, the Ag contents in the two cotton fabrics both enhanced. When the concentration of Ag NPs was only 10 mg/L, the Ag content of Ag-GOCF reached 149.88 mg/kg, while the Ag content of Ag-TUCF was only 15.7 mg/kg. This result indicated that the reaction between aldehyde groups and amino groups enabled oxidized cotton fabric to capture Ag NPs initiatively and settle them on the fabric. However Ag-TUCF was implemented by surface absorption of Ag NPs to fabrics, which was lack of enough strength to fix Ag NPs. Oxidized cotton fabric therefore possessed higher Ag content than control fabric in same treatment. Fig. 5(c) shows the whiteness of Ag NPs treated cotton fabrics. The Ag NPs treated cotton fabric turned yellow due to the surface Plasmon absorption of Ag NPs. The color became deeper with the increase of Ag NPs content in the fabric (Kelly & Johnston, 2011). Thus the whiteness of Ag NPs treated cotton fabrics is related to the Ag content of the fabrics. Hence the whiteness of Ag-GOCF is lower than that of Ag-TUCF, and they both declined with the increase of the concentration of Ag NPs aqueous solution.

Table 1
Ag content of treated cotton fabrics after different washing times.

	Washing times			
	0	10	30	50
Ag content of Ag-GOCF (mg/kg)	149.88	140.56	127.62	116.08
Ag content of Ag-TUCF (mg/kg)	146.46	83.88	29.64	10.46

3.3. Laundering durability and antibacterial activity of Ag-GOCF

To evaluate the laundering durability of Ag-GOCF, Ag content in fabric was measured after different washing times, displayed in Table 1. Ag content of Ag-TUCF, with similar Ag content to Ag-GOCF initially, was also determined to compare the laundering durability of them. It clearly indicated that Ag content of Ag-GOCF decreased slightly, while the Ag content of Ag-TUCF decreased sharply with washing times increasing. The Ag-GOCF was able to fix amino functional Ag NPs on the fabric via chemical bond, while the Ag-TUCF could only absorb them on the surface. For this reason, the Ag-GOCF exhibits excellent laundering durability.

The antibacterial property of Ag NPs treated cotton fabrics is related to their Ag contents. Table 2 shows the antibacterial activities of Ag-GOCF against *S. aureus* and *E. coli*, corresponding to the samples in Table 1. All the samples performed splendid antibacterial activities owing to the high Ag content in the cotton fabrics. Due to the outstanding fastness between Ag NPs and oxidized cotton fibers, the antibacterial activity of Ag-GOCF decreased slightly after suffering different washing times. After 50 washing cycles, the Ag-GOCF still exhibited bacterial reduction of 96.96% and 96.50% against *S. aureus* and *E. coli*, respectively. The high antibacterial activity of Ag-GOCF is attributed to the excellent antibacterial properties of Ag NPs. The antibacterial activity of

Table 2
Antibacterial activities of Ag-GOCF after different washing times.

Samples	Washing cycles	Antibacterial activities			
		S. aureus		*E. coli*	
		Surviving cells (CFU/ml)	% Reduction	Surviving cells (CFU/ml)	% Reduction
Untreated	–	1.25×10^6	–	2.03×10^6	–
Ag-GOCF	–	7.10×10^3	99.43	1.12×10^4	99.45
	10	1.05×10^4	99.16	1.82×10^4	99.10
	30	2.72×10^4	97.82	4.20×10^4	97.93
	50	3.80×10^4	96.96	7.10×10^4	96.50

Ag NP is considered to be the result of the generation of reactive oxygen species (ROS), including superoxide ($^{\bullet}O_2^{-}$), hydrogen peroxide (H_2O_2), and hydrogen radical ($^{\bullet}OH$) from its surface. They could interact with the cell wall and membrane, damage the cell membrane, increase the cell permeability and leak the intracellular contents by cell disruption (Kora & Arunachalam, 2011; Xu et al., 2011). Therefore the "green" process of grafting amino functional Ag NPs on oxidized cotton fabric can provide it with excellent antibacterial properties and marvelous laundering durability for its commercial applications.

4. Conclusions

In this study, Ag NPs were prepared successfully by one-step reaction between $AgNO_3$ and HBP-NH_2. During the process, HBP-NH_2 not only acted as reducer and protector, but also tightly absorbed on the surface of Ag NPs to modify the synthesized Ag NPs with amino groups. The size of the amino functional Ag NPs ranged from 6 nm to 20 nm with average size at 10.8 nm. The amino functional Ag NPs were then grafted on the oxidized cotton fabrics via the reaction between aldehyde groups and amino groups at ambient temperature. Due to the existence of aldehyde groups, the oxidized cotton fabric was capable of entrapping amino functional Ag NPs initiatively and fixing them on the cotton fabric. When the concentration of Ag NPs solution is only 10 mg/L, the Ag content of Ag-GOCF has reached 149.88 mg/kg, while the Ag content of Ag-TUCF is no more than 15.7 mg/kg. The Ag-GOCF showed excellent antibacterial property and laundering durability. After exposing to 50 consecutive home washing conditions, the Ag content of Ag-GOCF only decreased from 149.88 to 116.08 mg/kg, and the bacterial reduction was maintained over 96% against both *S. aureus* and *E. coli*.

Acknowledgements

The authors are grateful for the financial support by The National High Technology Research and Development Program of China (No. 2012AA030313) and Natural Science Foundation of Jiangsu Higher Education Institutions of China (No. 11KJB540002).

References

Alemdar, S., & Agaoglu, S. (2009). Investigation of in vitro antimicrobial activity of aloe vera juice. *Journal of Animal and Veterinary Advances*, *8*(1), 99–102.

Ali, S. W., Joshi, M., & Rajendran, S. (2011). Novel, self-assembled antimicrobial textile coating containing chitosan nanoparticles. *AATCC Review*, *11*(5), 49–55.

Bradford, A., Handy, R. D., Readman, J. W., Atfield, A., & Mühling, M. (2009). Impact of silver nanoparticle contamination on the genetic diversity of natural bacterial assemblages in estuarine sediments. *Environmental Science and Technology*, *43*(12), 4530–4536.

Castonguay, A., & Kakkar, A. K. (2010). Dendrimer templated construction of silver nanoparticles. *Advances in Colloid and Interface Science*, *160*(1-2), 76–87.

Gao, C., & Yan, D. (2004). Hyperbranched polymers: From synthesis to applications. *Progress in Polymer Science*, *29*(3), 183–275.

Hebeish, A., Abdel-Mohdy, F. A., Fouda, M. M. G., Elsaid, Z., Essam, S., Tammam, G. H., et al. (2011). Green synthesis of easy care and antimicrobial cotton fabrics. *Carbohydrate Polymers*, *86*(4), 1684–1691.

Hebeish, A., El-Naggar, M. E., Fouda, M. M. G., Ramadan, M. A., Al-Deyab, S. S., & El-Rafie, M. H. (2011). Highly effective antibacterial textiles containing green synthesized silver nanoparticles. *Carbohydrate Polymers*, *86*(2), 936–940.

Jiang, T., Liu, L., & Yao, J. (2011). In situ deposition of silver nanoparticles on the cotton fabrics. *Fibers and Polymers*, *12*(5), 620–625.

Joshi, M., Ali, S. W., & Rajendran, S. (2007). Antibacterial finishing of polyester/cotton blend fabrics using neem (Azadirachta indica): A natural bioactive agent. *Journal of Applied Polymer Science*, *106*(2), 793–800.

Kalyon, B. D., & Olgun, U. (2001). Antibacterial efficacy of triclosan-incorporated polymers. *American Journal of Infection Control*, *29*(2), 124–125.

Kavitha, M., Parida, M. R., Prasad, E., Vijayan, C., & Deshmukh, P. C. (2009). Generation of Ag nanoparticles by PAMAM dendrimers and their size dependence on the aggregation behavior of dendrimers. *Macromolecular Chemistry and Physics*, *210*(16), 1310–1318.

Kéki, S., Török, J., Deák, G., Daróczi, L., & Zsuga, M. (2000). Silver nanoparticles by PAMAM-assisted photochemical reduction of Ag^{+}. *Journal of Colloid and Interface Science*, *229*(2), 550–553.

Kelly, F. M., & Johnston, J. H. (2011). Colored and functional silver nanoparticle–wool fiber composites. *ACS Applied Materials and Interfaces*, *3*(4), 1083–1092.

Kim, K. J., Sung, W. S., Suh, B. K., Moon, S. K., Choi, J. S., Kim, J., et al. (2009). Antifungal activity and mode of action of silver nano-particles on Candida albicans. *Biometals*, *22*(2), 235–242.

Kora, A. J., & Arunachalam, J. (2011). Assessment of antibacterial activity of silver nanoparticles on *Pseudomonas aeruginosa* and its mechanism of action. *World Journal of Microbiology and Biotechnology*, *27*(5), 1209–1216.

Kora, A. J., Sashidhar, R. B., & Arunachalam, J. (2010). Gum kondagogu (Cochlospermum gossypium): A template for the green synthesis and stabilization of silver nanoparticles with antibacterial application. *Carbohydrate Polymers*, *82*(3), 670–679.

Lin, H., Yao, L. R., Chen, Y. Y., & Wang, H. (2008). Structure and properties of silk fibroin modified cotton. *Fibers and Polymers*, *9*(2), 113–120.

Lu, Y. H., Lin, H., Chen, Y. Y., Wang, C., & Hua, Y. R. (2007). Structure and performance of *Bombyx mori* silk modified with nano-TiO_2 and chitosan. *Fibers and Polymers*, *8*(1), 1–6.

Mahapatra, S. S., & Karak, N. (2008). Silver nanoparticle in hyperbranched polyamine: Synthesis, characterization and antibacterial activity. *Materials Chemistry and Physics*, *112*(3), 1114–1119.

Manna, A., Imae, T., Aoi, K., Okada, M., & Yogo, T. (2001). Synthesis of dendrimer-passivated noble metal nanoparticles in a polar medium comparison of size between silver and gold particles. *Chemistry of Materials*, *13*(5), 1674–1681.

Mary, G., Bajpai, S. K., & Chand, N. (2009). Copper (II) ions and copper nanoparticles-loaded chemically modified cotton cellulose fibers with fair antibacterial properties. *Journal of Applied Polymer Science*, *113*(2), 757–766.

Menjoge, A. R., Kannan, R. M., & Tomalia, D. A. (2010). Dendrimer-based drug and imaging conjugates: Design considerations for nanomedical applications. *Drug Discovery Today*, *15*(5–6), 171–185.

Miao, A. J., Luo, Z. P., Chen, C. S., Chin, W. C., Santschi, P. H., & Quigg, A. (2010). Intracellular uptake: A possible mechanism for silver engineered nanoparticle toxicity to a freshwater. *PLoS ONE*, *5*(12), e15196.

Montazer, M., & Seifollahzadeh, S. (2011). Enhanced self-cleaning, antibacterial and UV protection properties of nano TiO_2 treated textile through enzymatic pretreatment. *Photochemistry and Photobiology*, *87*(4), 877–883.

Nikolic, T., Kostic, M., Praskalo, J., Pejic, B., Petronijevic, Z., & Skundric, P. (2010). Sodium periodate oxidized cotton yarn as carrier for immobilization of trypsin. *Carbohydrate Polymers*, *82*(3), 976–981.

Richter, T. V., Schüler, F., Thomann, R., Mülhaupt, R., & Ludwigs, S. (2009). Nanocomposites of size-tunable ZnO-nanoparticles and amphiphilic hyperbranched polymers. *Macromolecular Rapid Communications*, *30*(8), 579–583.

Saravanan, D., Vasanthi, N. S., & Ramachandran, T. (2009). A review on influential behaviour of biopolishing on dyeability and certain physico-mechanical properties of cotton fabrics. *Carbohydrate Polymers*, *76*(1), 1–7.

Scott, R. W. J., Wilson, O. M., & Crooks, R. M. (2005). Synthesis, characterization, and applications of dendrimer-encapsulated nanoparticles. *Journal of Physical Chemistry B*, *109*(2), 692–704.

Sun, H. Y., Li, J., Qiu, X. L., & Qing, F. L. (2005). Synthesis and structure-activity relationship (SAR) of novel perfluoroalkyl-containing quaternary ammonium salts. *Journal of Fluorine Chemistry*, *126*(9-10), 1425–1431.

Sun, Y. G., & Xia, Y. N. (2003). Gold and silver nanoparticles: A class of chromophores with colors tunable in the range from 400 to 750 nm. *Analyst*, *128*(6), 686–691.

Tomšič, B., Simončič, B., Orel, B., Černe, L., Tavčer, P. F., Zorko, M., et al. (2008). Sol–gel coating of cellulose fibres with antimicrobial and repellent properties. *Journal of Sol–Gel Science and Technology*, *47*(1), 44–57.

Vasilev, K., Sah, V. R., Goreham, R. V., Ndi, C., Short, R. D., & Griesser, H. J. (2010). Antibacterial surfaces by adsorptive binding of polyvinyl-sulphonate-stabilized silver nanoparticles. *Nanotechnology*, *21*(21), 215102.

Xia, N., Cai, Y., Jiang, T., & Yao, J. (2011). Green synthesis of silver nanoparticles by chemical reduction with hyaluronan. *Carbohydrate Polymers*, *86*(2), 956–961.

Xu, H., Qu, F., Xu, H., Lai, W., Andrew Wang, Y., Aguilar, Z. P., et al. (2011). Role of reactive oxygen species in the antibacterial mechanism of silver nanoparticles on *Escherichia coli* O157:H7. *Biometals*, *25*(1), 45–53.

Zhang, F., Chen, Y. Y., Lin, H., & Lu, Y. H. (2007). Synthesis of an amino-terminated hyperbranched polymer and its application in reactive dyeing on cotton as a salt-free dyeing auxiliary. *Coloration Technology*, *123*(6), 351–357.

Zhang, F., Chen, Y., Lin, H., Wang, H., & Zhao, B. (2008). HBP-NH_2 grafted cotton fiber: Preparation and salt-free dyeing properties. *Carbohydrate Polymers*, *74*(2), 250–256.

Zhang, F., Zhang, D. S., Chen, Y. Y., & Lin, H. (2008). The antimicrobial activity of the cotton fabric grafted with an amino-terminated hyperbranched polymer. *Cellulose*, *16*(2), 281–288.

Zhang, F., Chen, Y. Y., Ling, H., & Zhang, D. S. (2009). Synthesis of HBP-HTC and its application to cotton fabric as an antimicrobial auxiliary. *Fibers and Polymers*, *10*(2), 141–147.