In situ synthesis of silver nanoparticles onto cotton fibres modified with plasma treatment and acrylic acid grafting

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Published in Micro & Nano Letters; Received on 19th March 2013; Accepted on 17th April 2013

Silver nanoparticles were synthesised on the modified cotton fibres using an in situ method. Acrylic acid was grafted on the surface of cotton using plasma technology as a means to enhance the loading efficiency of nanoparticles. The loading efficiency of silver nanoparticles into the cotton fabric was examined by an atomic absorption spectrometer. The surface of the fibres was characterised by low-voltage scanning electron microscopy and attenuated total reflection-Fourier transform infrared spectrometry. The cotton fabrics loaded with Ag nanoparticles were examined by thermogravimetric analysis. In addition, the antibacterial activity of loaded samples was determined according to the AATCC test method 147-2004. Grafting of acrylic acid on cotton fibre leads to increase in the loading efficiency of silver nanoparticles and this sample showed the highest antibacterial activity.

1. Introduction: Natural fibres are excellent media for growth of microorganisms because of the presence of nutrients, moisture, oxygen and appropriate temperature. In addition, the moisture content of natural fibres assists the microorganisms' growth on the fabric. Thus, there is a great demand to impart antimicrobial properties into textile materials made of natural fibres by incorporating various functional antibacterial agents. This textile finishing can control the growth of microorganisms, and prevent the textile from deterioration of strength and quality, staining, odours and health concerns [1–5]. Applying nanoparticles is an interesting approach to fabricate functionalised textiles. To create new properties, a considerable amount of research has been carried out for immobilisation of various nanoparticles on textile materials. Silver nanoparticles (AgNPs) are widely used to impart antibacterial properties to medical textiles because of their wide-spectrum antibacterial activity [6–10]. Especially, Ag presents non-toxic properties to human cells at a reasonable amount [11].

There are several methods for synthesis of AgNPs in various shapes and sizes [12–16]. To obtain functional antimicrobial textiles with a broad antibacterial spectrum and good washing fastness, the synthesising method of nanosilver must correspond to its application [17]. There are several methods for deposition of AgNPs on textile substrates including coating, exhaustion and in situ methods [6, 11, 18–20]. Hydroxyl groups of cotton molecular structure are able to bind to positively-charged species of organic or inorganic materials. Therefore the presence of these characteristic groups makes them ideal for selective binding of metal ions.

Plasma treatment is employed as an effective means to modify the surface of textile materials to enhance certain properties [21]. According to this, the cotton fibre was pretreated with oxygen plasma to activate and facilitate the deposition of silver particles [22].

This reported study is aimed at exploring the possibility of using oxygen plasma pretreatment and acrylic acid (AA) grafting on cotton fabric to activate the surface of cotton fibre and enhance AgNPs loading. In this case, treated cotton fibre can act as a template for synthesising and growing the AgNPs. Sodium borohydride ($NaBH_4$) was used as reducing agent. All samples loaded with AgNPs were examined by thermogravimetric analysis (TGA) and attenuated total reflectance infrared Fourier transform (ATR-FTIR) spectroscopy.

2. Materials and methods

2.1. Materials and chemicals: All chemicals used in this study were of analytical grade and distilled water was used throughout the work. Silver nitrate ($AgNO_3$ extra pure, >99.8%), sodium borohydride ($NaBH_4$) and AA ($C_3H_4O_2$) were purchased from Merck Company (Germany).

A plain woven cotton fabric (100%) with an area weight of 240 g/m^2 was used in this study. Before being used, all samples were scoured with a non-ionic detergent (1 g/l) for 30 min at 60°C (L: G = 40:1), then rinsed with tap water and dried at room temperature.

2.2. Methods

2.2.1 Plasma treatment: The cotton fabric samples were pretreated using radiofrequency (13.56 MHz) low-pressure plasma equipment (model: Junior advanced, Europlasma, Belgium) with oxygen gas. The sample chamber was evacuated to 100 mTor and maintained at this pressure during the process. Then, oxygen was introduced with a flow rate of 20 sccm (standard cubic centimetres per minute). Plasma was generated at 100 W for different predefined times. After that, air was introduced into the chamber and the plasma-treated sample was removed. The time between the plasma treatment and the beginning of the next step was 5 min to ensure the formation of peroxide radicals necessary to initiate the grafting reaction [23].

2.2.2 Grafting: The plasma pretreated cotton samples were immersed into 50 ml of solutions of AA in water (different concentrations). To remove the air trapped inside the reaction flask, nitrogen gas was purged into the solution during the grafting process. The reaction flask was heated for different times at different temperatures. To remove any non-reacted AA and homopolymers adhering to the sample surface, the grafted fabric samples were drained and soxhlet extracted for 2 h with boiling distilled water. The samples were then dried in an oven at 50°C for 2 h and cooled over a silica-gel desiccator and weighed. The grafting percentage was calculated according to the following equation

$$G\% = \left[\left(W_f - W_i\right)/W_i\right] \times 100 \quad (1)$$

where W_i and W_f are the weights of the plasma pretreated and grafted cotton fabric at specific condition (25°C, 60% RH).

2.2.3 Synthesis of AgNPs: The cotton fabric samples (pristine and AA grafted cotton) were immersed in $AgNO_3$ solution (400 ppm) with a liquor ratio of 1:50 for 30 min at room temperature. Then, the wet fabric was introduced into the reducing bath at room

temperature. Reducing agent concentration was adjusted twice of silver ions concentration of impregnation solution. Hence, it is a guarantee for reducing all the absorbed Ag^{+} to $Ag^{\bullet}$ on the treated cotton fabric. Converting Ag^{+} to $Ag^{\bullet}$ atom and synthesising AgNPs caused the colour of cotton fabric to change to brownish yellow.

2.2.4 Characterisation of loaded sample: The surface of unloaded and AgNPs loaded cotton fabric was characterised with low-voltage scanning electron microscopy (LVSEM). The effect of the plasma pretreatment and grafting procedure on loading efficiency of AgNPs into the cotton fabric was examined by an atomic absorption spectrometer (Unicam 939). Therefore roughly 1 g of loaded sample was weighed and burned in a porcelain crucible. Then, ash of burnt samples was cooled in a desiccator and its weight was recorded. After that, it was dissolved in hot concentrated nitric acid and the silver concentration was determined with the atomic absorption spectrometer.

TGA of unloaded and AgNPs loaded cotton fabrics was performed with a Perkin-Elmer 7 thermal analyser. Hence, the sample (roughly 7 mg pieces of fabric) was heated from 25 to 650°C with a heating rate of 10°C/min in the presence of nitrogen gas.

The surface of plasma pretreated and grafted cotton was analysed by the ATR-FTIR (Perkin Elmer Spectrum 100 series). The spectra were recorded at a resolution of 1 cm^{-1} and the scanning range was 650–4000 cm^{-1} and an average of 20 scans was recorded.

The antibacterial efficiency of AgNPs loaded samples was determined against *Staphylococcus aureus* ATCC 6538 as a Gram-positive and *Escherichia coli* ATCC 8739 as a Gram-negative bacterium. This test was carried out according to AATCC test method 147-2004.

3. Results and discussion

3.1. Oxygen plasma pretreatment and grafting

3.1.1 Effect of plasma treatment on grafting efficiency: Cotton samples were plasma treated at different times (power = 100 W) and grafted with a 20% V/V of AA for 1 h at 60°C. Table 1 shows the effect of plasma treatment time on grafting yield of AA on cotton. As we see, the graft efficiency increases with increase in plasma treatment time. The reason is the creation of more free radicals and active sites as the plasma treatment increases. With the plasma treatment time extending beyond 120 s, grafting degree decreases. This decrease can be because of over-etching of the surface of the fibre and reducing the accessible free radicals on the surface. So a plasma treatment time of 120 s seems to be the optimum time for plasma treatment to reach the maximum grafting yield.

Plasma treatment can lead to the production of some radical sites. These radical sites will be oxidised with oxygen molecules in air and produce peroxides and graft reaction will take place between cellulose and AA monomer. About the optimal plasma treatment time, there are already some explanations. Before the optimal time, plasma treatment mainly produces radical sites; after the time, some existing radicals will disappear because of chemical degradation and lastly reach a dynamic equilibrium. Besides,

Table 1 Effect of plasma treatment time on grafting per cent

Plasma treatment time, s	Grafting, %
0 (blank)	0
30	0.81
60	1.74
90	2.66
120	3.54
150	3.47

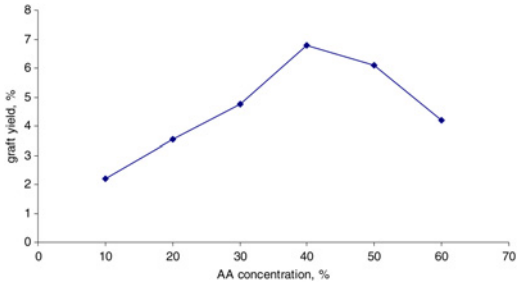

Figure 1 *Effect of AA concentration on graft yield*

longtime plasma treatment can lead to the cross-linking between some radicals [24]. The grafting per cent on the blank sample (grey cotton fabric) is approximately zero, which approves the positive effect of plasma treatment on grafting yield.

3.1.2 Effect of AA concentration on grafting efficiency: Plasma-treated cotton samples (2 min, 100 W) were grafted using different concentrations of AA. Fig. 1 shows that grafting per cent increased as the AA concentration increased from 10 to 40%, thereafter decreasing with further increase in AA concentration. This decrease can be because of more chance of AA monomers to form homopolymer instead of copolymer with cellulose at increased concentrations [23]. So the viscosity of the reaction medium increases significantly, which causes the monomer depletion and hence diminishing monomer accessibility to the grafting sites [23].

3.1.3 Effect of grafting time on graft yield: As we can see from Fig. 2, the grafting yield increases with increase of grafting time from 30 to 120 min, thereafter more increase in grafting time has no significant effect on grafting yield. It can be because of the reduced amount of AA monomer in the solution and free radicals at the fibre surface after a prolonged time. It may be stated that the growing chains are exhausted within 2 h and lead to the equilibrium degree of grafting [23].

The ATR-FTIR spectra of the pristine sample (untreated sample), plasma-treated (2 min, 100 W) and AA grafted sample (20% V/V of AA for 1 h at 60°C) have been characterised to confirm the grafting of AA onto the cotton fabric (Fig. 3). Small peaks at 1650 and 1710 cm^{-1} in the FTIR spectrum of the plasma-treated fabric confirms the creation of carbonyl groups after oxygen plasma treatment. Comparing the ATR-FTIR spectra of the grafted and the untreated sample, the –COOH group peak appeared at 1710 cm^{-1} on the grafted sample, which indicated the formation of polyacrylic acid onto the cotton fibres. The grafting percentage was calculated according to (1), and was 3.54% for this treatment condition on the cotton sample.

3.2. Synthesis of AgNPs: The surface of cotton fibres presents a negative charge in neutral and alkaline aqueous solutions [25] because of acidic groups in their chemical structure such as

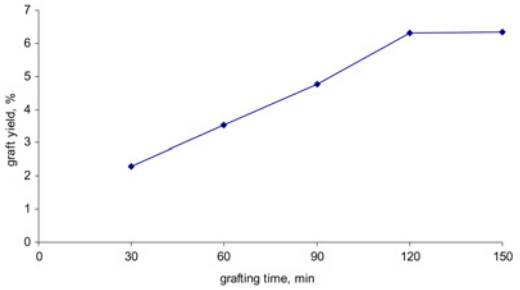

Figure 2 *Effect of grafting time on graft yield (plasma-treated, 20% AA, 60°C)*

doi: 10.1049/mnl.2013.0157

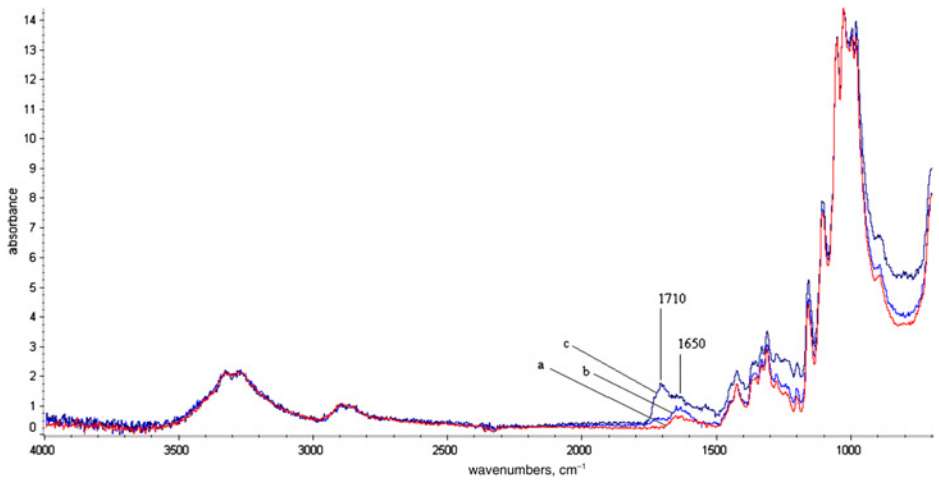

Figure 3 *ATR-FTIR spectra of (c) raw, (b) plasma-treated (2 min, 100 W) and (a) AA grafted cotton fibres (G % = 3.54)*

carboxyl or hydroxyl groups [26]. Oxygen plasma pretreatment and AA grafting increase this negative charge by the creation of carbonyl and carboxylic acid groups on the surface of cotton fibres [27, 28]. Hence, the silver ions (Ag^+) in the impregnating solution can be absorbed by these groups because of electrostatic interactions [11]. The absorbed silver ions were converted to silver atoms and grown to create nanoparticles when immersed in the reducing solution. Equations (2)–(4) present the mechanism of absorption of silver ions by cotton fibre and reduction in presence of $NaBH_4$.

$$\text{Cotton} - \text{XH} \xrightarrow[\text{aq}]{} \text{Cotton} - X^-,\ \text{XH} = \text{OH and COOH} \quad (2)$$

$$\text{Cotton} - X^- + \text{Ag}^+ \rightarrow \text{Cotton} - \text{X}^-\text{Ag}^+ \quad (3)$$

$$\text{Cotton} - X^-(n\text{Ag}^+) + \text{NaBH}_4 \rightarrow \text{Cotton} - X(\text{Ag})_n \quad (4)$$

3.3. Low-voltage scanning electron microscopy: The SEM images of unloaded and AgNPs loaded cotton fibres are presented in Fig. 4. The morphological changes in the surface of cotton fibres made by the synthesis of AgNPs are obvious and led to change of the uniform and homogeneous cotton surface to a rough surface (Fig. 4*b*) [19]. AA grafting on cotton fibres led to absorption of higher amounts of silver ions and finally presented higher AgNPs than the untreated cotton fabric. In addition, the plasma pretreatment and grafting process caused better dispersion of AgNPs on the fibre surfaces (Fig. 4*c*). The AA grafting on cotton fabric led to increasing AgNPs density on the surface of cotton fabrics.

3.4. Silver content of loaded cotton fabric: The loading efficiencies of AgNPs onto untreated, plasma-treated (2 min, 100 W) and AA grafted (20% V/V of AA for 1 h at 60°C) cotton fabrics are

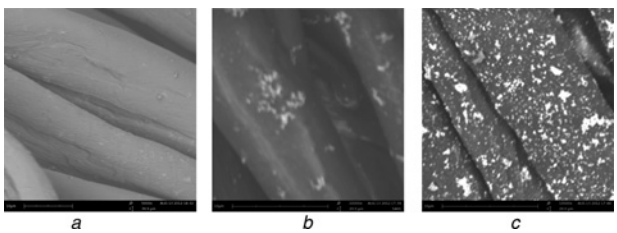

Figure 4 *LVSEM images*
a Pristine sample
b Pristine cotton loaded with Ag
c AA grafted cotton loaded with Ag

Table 2 Loading efficiency of AgNPs on cotton fabrics determined by atomic absorption spectrometer

Sample code	Ag concentration, ppm	Silver content, g/kg
Un-Ag	400	4.32
Pl-Ag	400	4.76
Pl-gr-Ag	400	9.86

presented in Table 2. The results indicated that the loading efficiency of AgNPs on the AA grafted sample (Pl-gr-Ag) is much greater than the untreated (Un-Ag) and plasma-treated (Pl-Ag) samples. It is obvious that the plasma pretreatment and AA grafting on cotton fabric results in greater silver content and the silver content of fabrics increased from 4.32 g/kg for the untreated sample (Un-Ag) to 9.86 g/kg$^-$ for the AA grafted sample (Pl-gr-Ag).

Oxygen plasma pretreatment and AA grafting on cotton fabric cause increase in the negative charge of the cotton surface. Hence, the electrostatic interaction of Ag^+ to the negative surface charge of the treated sample resulted in higher silver content.

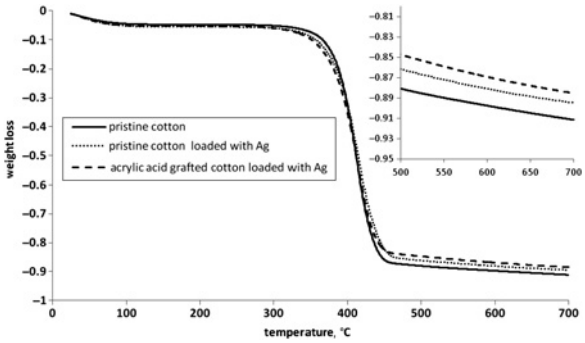

Figure 5 *TGA curves of the pristine sample and pristine and AA grafted samples loaded with AgNPs*

Table 3 Inhibition zone widths (mm) of different samples

Bacterial strain	Pristine sample	Un-Ag loaded	Pl-gr-Ag loaded
S. aureus	–[a]	0.75	1
E. coli	–	0.5	0.75

[a]No inhibition zone width was found with this sample

Consequently, the amount of synthesised AgNPs on treated cotton fabrics increased. This result was confirmed by SEM images showing that oxygen plasma pretreatment and AA grafting on cotton fabric led to the formation of higher nanoparticles density on the surface of loaded cotton.

3.5. Thermogravimetric analysis: Loading of AgNPs can change the thermal properties of cotton fabrics, hence they were analysed and compared with the untreated sample as a means to estimate the amount of AgNPs on the loaded samples. The TGA curves of the pristine sample besides pristine and AA grafted samples loaded with AgNPs are presented in Fig. 5. The AA grafted sample loaded with AgNPs presented more weight loss compared with other samples at the initial temperature range, which corresponds to the vaporisation of H_2O [29], because the presence of the carboxyl group because of AA grafting led to a more hydrophilic nature and a higher water content of the sample. However, these functional groups led to higher AgNPs loading and lower weight loss compared with other samples.

3.6. Antibacterial properties: The inhibition zone widths of different samples are presented in Table 3. The sample with the highest silver content, showed a larger inhibition zone, because the antibacterial activity depends on the silver content [30, 31]. Therefore the AA grafted sample loaded with AgNPs presented a better antibacterial activity because of higher loading efficiency.

4. Conclusion: The negative surface charge of cotton fibres can absorb silver ions with positive charge because of the electrostatic interaction. Grafting of AA increased the amount of surface active sites to absorb more silver ions. $NaBH_4$ reduced the absorbed silver ions to silver atoms and formed AgNPs. Formation of AgNPs on the surface of cotton fibres changed the uniform and homogeneous cotton surface to a rough surface, although well-dispersed on the surface of the cotton fibre. Higher loading efficiency led to enhancement of the thermal properties of AgNPs loaded fabric. The AA grafted sample loaded with AgNPs presented a better antibacterial activity because of higher loading efficiency.

5. Acknowledgment: The authors thank the Islamic Azad University, Birjand Branch, for financial support of the research project.

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doi: 10.1049/mnl.2013.0157