Antibacterial and Antifungal Thioglycolic Acid-Capped Silver Nanoparticles and Their Application on Wool Fabric as a Durable Antimicrobial Treatment

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Abstract

Currently used silver nanoparticle-based antimicrobial treatments are effective against bacteria and certain fungi but they have limited durability to washing. In this work, the surface of silver nanoparticles was modified with thioglycolic acid (TGA) to further enhance their antimicrobial activities and also to enable their binding to the surface of wool fibre. Silver nanoparticles were

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characterised by FTIR, UV-vis spectroscopy and TEM. The TGA-capped silver nanoparticles were covalently bonded to wool fibre surface by using 1-ethyl-3-[3-dimethylaminopropyl]-carbodiimide hydrochloride in combination with N-hydroxysuccinimide to provide enhanced durability to multiple washings, which is an issue for the nanosilver-based treatments used in wool textiles. The antimicrobial activities of this treated wool fabric were compared with the wool fabric treated with trisodium citrate (TSC)-capped silver nanoparticles (bonded by a silicone resin). The TGA-capped silver nanoparticle-treated wool fabric not only showed superhydrophilicity and excellent durability to washing but also excellent antibacterial activity along with moderate to excellent antifungal activity. The wool fabric treated with TSC-capped silver nanoparticles showed strong hydrophobicity and antibacterial activity but no antifungal activity. This work demonstrates that silver nanoparticles can be made antifungal by the capping with TGA and also the durability of the treatment to washing can be considerably enhanced.

Introduction

Textile materials need antimicrobial treatment for various reasons, such as to protect the wearer from pathogenic microbial attack, to suppress odour formation in textiles by killing odour-forming microbes, and also to protect the textile itself. Cellulosic and protein textiles are prone to microbial attack that can degrade them causing considerable loss of tensile strength. Textile materials also can act as carriers for transmitting diseases from the patients to the surgeons and also to other hospital staff. In our daily life our body comes in contact with clothing and various materials that are contaminated with various microbes; some which could be deadly but the

majority of them are harmless. A large number of published literature demonstrate that microbes can survive and grow in textiles, which could be a vector for health risk.[1,2]

A range of bioactive agents including quaternary ammonium compounds, halamine polymers, polybiguanides, modified chitosan, etc., have been investigated for textile applications.[2-4] One of the most popular and effective antimicrobial agents for textiles is triclosan, which has been found to produce drug-resistant strains of microorganisms.[3] It is a major concern when using antibacterial agents in textile treatments as overuse of these antimicrobial agents may produce 'superbugs' that are resistant to conventional antibiotics.[4]

Silver, a broad spectrum antimicrobial agent, has a long history in the treatment of burns and wounds. Metallic silver and silver ions are effective against a wide range of bacteria.[5,6] When silver ions accumulate inside cells, they can bind to negatively charged components in proteins and nucleic acids, causing structural changes in bacterial cell walls, membranes, and nucleic acids affecting their viability.[5] Silver nanoparticles and compounds produce their antimicrobial effects by the time-dependent release of silver ions and their clinical efficiency is directly related to the constant presence of free silver ions in the local microbial environment.[6] Fabrics containing silver nanoparticles are entering the market rapidly and concerns have been raised about their effects on the environment and human health.[7-9] It was reported that during laundering not only silver ions but also silver nanoparticles are removed causing contamination of watercourses.[8,9] Application of silver nanoparticles for providing wash-durable antibacterial performance has been frequently investigated.[9-11] Silver nanoparticles embedded into silica matrix have been investigated to make wool fibre antibacterial and durable to laundering by binding them through a reactive binder.[10,11] Liu *et al.* coated cotton fabric with pomegranate-shaped poly(aminomethyl acrylate) wrapped silver nanoparticle aggregations by γ-irradiation.[12]

Alkane thiols have been extensively studied to modify the surface of gold and silver nanoparticles, where thiol groups covalently bind to the surface of silver nanoparticles.[13,14]. However, such a kind of treatment considerably reduces antimicrobial activity and also affects the handle properties of the fabric.[15,16]. The durability of this kind of treatment is dependent on the durability of the reactive binders. Covalent binding of silver nanoparticles could be a solution but they cannot be bonded to the wool surface because of lack of any functional group. Geisberger et al. found that thioglycolic acid derivatised chitosan killed 99.97% of *Candida albicans* fungus.[17] As thiol groups can bind to silver nanoparticles, therefore we thought that thioglycolic acid derivatised silver nanoparticles may enhance their antifungal activity.

We report, for the first time, covalent binding of silver nanoparticles to the wool fibre surface. For this purpose, the wool fabric was first chlorinated to remove the 18-methyl eicosanoic acid (18-MEA) by breaking the thioester bonds, which exposed other functional groups including amine. Silver nanoparticles were surface modified by capping with thioglycolic acid (TGA) that permits binding of the carboxyl groups of the TGA to the amino groups of wool by using a cross-linker.

Results and Discussion

Surface Charge of Silver Nanoparticles

In the TSC-capped silver nanoparticles, TSC is weakly bound to the surface of silver nanoparticles and gives them stability. On the other hand, in the formation of TGA-capped silver

nanoparticles, borohydride anions (BH^{-4}) formed on the surface of silver nanoparticles are replaced by TGA (Scheme 1). It is generally accepted that thiol adsorption onto the silver surfaces consists of many steps, starting with physical adsorption, followed by the sulphur–metal bonding reaction, the reorientation of the adsorbed thiol molecules, and finally the formation of a compact self-assembled layer.[10,19,20] To observe whether the thiols or the carboxyl groups interact with the surface of TGA-capped silver nanoparticles and also to evaluate the ionic property of the silver nanoparticles, they were exhausted into wool fibres at pH 3 and at 40 °C. It was observed that within a couple of minutes, all the TGA-capped silver nanoparticles were adsorbed by wool fabric and the solution became colourless. As at this pH wool fibre is strongly cationic, the absorption of TGA-capped silver nanoparticles by wool indicates that the surface of TGA-capped silver nanoparticles is anionic. Chung and Lee[21] investigated the acid-base behaviour of exposed carboxylic acid groups of the TGA-capped silver nanoparticles by forming a monolayer of TGA on the surface of silver nanoparticles and the separated nanoparticles were rinsed with absolute ethanol. After drying they were scanned by FT-IR and found that the level of TGA in the silver nanoparticles did not diminish, which prove that thiols are bonded to the surface of silver nanoparticles and the exposed groups on the surface of TGA-capped silver nanoparticles are the carboxylic acid groups.

Characterisation of TSC and TGA-capped Silver Nanoparticles

The UV-visible spectra of an aqueous dispersion of TSC and TGA-capped silver nanoparticles synthesised using two different ratios of borohydride to silver nitrate (2:1 and 1:5) are shown in Figure 1. The observed spectra are consistent with the spectra of silver nanoparticles shown by

other researchers.[22,23] The wavelength of maximum absorption (surface Plasmon band) for the TSC (2:1) and TGA-capped (2:1) silver nanoparticles was 398 and 389 nm respectively, which is identical to the surface Plasmon band of silver nanoparticle hydrosol.[23] This shift of the surface Plasmon band from 398 for the TSC-capped silver nanoparticles to 389 nm for the TGA-capped silver nanoparticles can be attributed to the reduction of the size of the produced silver nanoparticles. The presence of a broadband suggests that all of the synthesised silver nanoparticles are either polydisperse or they are in the aggregate state, leading to the coupling of Plasmon vibrations between neighbouring particles. The synthesised TSC and TGA-capped silver nanoparticles were stable for several months when the ratio of $AgNO_3$ to sodium borohydride was 1:2 and silver nanoparticles produced at this ratio were used in the rest of the work.

Zeta potential measurement provides an indication of the potential stability of a colloidal system. Surface zeta potential and electrophoretic mobility of the uncapped and the capped silver nanoparticles are shown in Table 1. The zeta potential of the uncapped silver nanoparticles was -33.5±0.6, which increased to -35.5±1.80 and -46.60±2.10 mV for the TSC and TGA-capped silver nanoparticles, respectively. The results indicate that all the silver nanoparticles are anionic but the TGA-capped silver nanoparticles had much higher anionic surface charge compared to the TSC-capped silver nanoparticles, which is in agreement with the exhaustion experiment results mentioned above.

FTIR spectral analysis was used to prove the bonding between –COOH terminated TGA and the surface of silver nanoparticles. The spectrum of TSC-capped silver nanoparticles shows bands at 3462, 1591, 1385, and 1072 cm^{-1} corresponding to hydroxyl bands of water bound to carboxyl groups, the anti-symmetric stretching of carboxylate anion (–COO$^-$), symmetric

stretching of carboxylate anion (–COO⁻), C-H bending and C-O stretching respectively (Figure 2). The spectrum of TGA shows typical peaks at 1114, 1346, 1782 and 2562 cm⁻¹ and they could be associated with the absorption peaks of C-S, C-H, C=O and S-H respectively. The broad peak shown at 3100 to 3650 cm⁻¹ could be attributed to hydroxyl groups, which is absent in the spectra of TGA and TGA-capped silver nanoparticles.[24] On the other hand, TGA-capped silver nanoparticles show a new peak at 584, 653, 1188, 1232, 1567, 1715, 3132, 3575 cm⁻¹. The band shown at 3132 cm⁻¹ could be attributed to the stretching vibration of –COOH of TGA. If the thiol groups of TGA didn't react with silver nanoparticles, there should be a peak at 2500 to 2600 cm⁻¹. However, no such peak was observed for the TGA-capped silver nanoparticles, although that absorption band was present in the spectrum of TGA. In the case of TGA-capped silver nanoparticles, the disappearance of the absorption peak of thiol groups of TGA at 2562 cm⁻¹ indicates the cleavage of S-H bond that led to the formation of a new bond, i.e. Ag-S bond. Battocchio *et al.*[25] analysed silver nanoparticles coated with various thiol compounds using synchrotron radiation techniques and found that thiol groups form Ag–S–R (R is alkyl) bond with the silver nanoparticle.

TEM micrographs of TSC and TGA-capped silver nanoparticles show that TSC and TGA-capped both types of silver nanoparticles are mostly spherical in shape (Figure 3). The TSC-capped silver nanoparticles were evenly dispersed without forming any agglomeration. Although TGA-capped nanoparticles formed a small level of aggregation (two nanoparticles bonded together) but the size of the aggregates was very small (less than 15 nm). The results show the effectiveness of TSC and TGA as capping agents. TEM micrographs reveal that the maximum size of the TGA-capped silver nanoparticles was 20 nm and the minimum size was 4.0 nm, the corresponding values for TSC-capped silver nanoparticles are 22.0 nm and 6.0 nm respectively.

TEM micrographs show that TGA-capped silver nanoparticles are slightly smaller than the TSC-capped silver nanoparticles. Dynamic light scattering data reveals that the average size of TSC and TGA-capped silver nanoparticles was 9.7 and 5.9 nm respectively.

Antibacterial Activity of Wool Fabric Treated with Silver Nanoparticles

Table 2 shows detailed results of antibacterial tests of wool fabrics treated with TSC (bonded by Basolan MW-P) and TGA-capped (bonded by NHS/EDC) silver nanoparticles. The untreated wool fabric did not show any antibacterial activity. There was growth of bacteria up to the edge and also under the tested samples for all three types of bacteria investigated (Figure S1 in Supplementary Information). No inhibition zone was observed for any bacteria. The wool fabric treated with TSC-capped silver nanoparticles showed excellent antibacterial performance and showed a clear zone of inhibition of bacterial growth. The size of inhibition zone for *Staphylococcus aureus*, *Klebsiella pneumoniae* and *Escherichia coli* was 2, 3, and 5 mm respectively. Obviously, no growth of bacteria under the sample was observed for all bacteria. The wool fabric treated with TGA-capped silver nanoparticles also showed excellent antibacterial performance but the size of the zone of inhibition was smaller than that achieved for the fabric sample treated with TSC-capped silver nanoparticles.

Table 3 shows the bacterial reduction in the presence of untreated wool fabric and wool fabric samples treated with TSC and TGA-capped silver nanoparticles. In the presence of wool fabric samples treated with TSC-capped silver nanoparticles, 98.0, 97.2 and 95.6% of *Staphylococcus aureus*, *Klebsiella pneumoniae* and *Escherichia coli* was killed respectively. On the other hand, in the presence of wool fabric samples treated with TGA-capped silver nanoparticles, the killing

rate of bacteria was increased to 99.6, 98.0 and 98.3% respectively. The TGA-capped silver nanoparticles showed marginally better antibacterial activity compared to the TSC-capped silver nanoparticles. The achieved results suggest that the toxicity of the silver nanoparticles probably increased by capping with TGA.

The release of silver ions from silver nanoparticles is considered to be the main factor that is associated with their toxicity.[26] The toxicity of silver nanoparticles is dictated by various factors including their size, size distribution, shape and concentration, time of ageing, surface area, surface charge, surface functionalities, their stability, and also the environment and in the media they are dispersed.[7,26] There was a direct correlation between the cytotoxicity of dispersed silver nanoparticles and their overall surface charge and or surface coating.[26] With decreasing size of silver particles, the potential for releasing silver ions increases and the particle coating also plays a role in the process.[27] In this work, the size of the TGA-capped silver nanoparticles was smaller than the size of the TSC-capped silver nanoparticles. Geisberger *et al.*[20] investigated the antimicrobial performance of variously modified chitosan and they found that chitosan conjugated with TGA showed markedly better activity against *Streptococcus sobrinus* (Gram-positive bacteria), *Neisseria subflava* (Gram-negative bacteria) and *Candida albicans* (fungi) than the chitosan alone. Tang *et al.*[28] found that compared to unmodified CdSe quantum dots, TGA-coated CdSe quantum dots showed genotoxicity as they interacted with DNA through groove-binding. Several published literature also reported that TGA-modified chitosan and 3-(1,2,4-triazol-3-yl)-4-thiazolidinones showed some levels of antifungal activity.[29,30] Therefore it can be concluded that the capping of silver nanoparticles with TGA increased their toxicity, resulting in an improvement in their antibacterial and antifungal performance.

Antifungal Activity of Wool Fabric Treated with Silver Nanoparticles

It has been long known that silver nanoparticles have antibacterial properties but their effectiveness on fungi has not been well investigated. From Figure 4, it can be seen that the control wool fabric did not show any antifungal activity against *Aspergillus brasiliensis* and *Aspergillus fumigatus* and the same is true in the case of TSC-capped silver nanoparticles. Fungi started to grow on the tested samples even after 2 days of incubation. After 14 days of incubation, extensive growth of both of the fungi is visible on the whole agar gel plate and also on the tested control and the TSC-capped silver nanoparticle-treated fabric samples. On the other hand, the wool fabric samples treated with TGA-capped silver nanoparticle initially showed growth of *Aspergillus brasiliensis* similar to the sample treated with SBS silver nanoparticles but after 5 days incubation the TGA-capped silver nanoparticle-treated fabric showed much smaller growth compared to the growth observed for the control and the TSC-capped silver nanoparticle-treated fabric. After 14 days incubation, the TGA-capped silver nanoparticle-treated fabric was fully covered by the fungi but the density of fungal growth was considerably smaller compared to the growth observed in the cases of control and the TSC-capped silver nanoparticle-treated fabric. The TSC-capped silver nanoparticle-treated fabric showed only slightly better antifungal activity against *Aspergillus fumigatus* than the antifungal activity shown by the control fabric. However, the TGA-capped silver nanoparticle-treated wool fabric showed no growth of *Aspergillus fumigatus* even after 14 days of the incubation.

Pulit *et al.* found that silver nanoparticles stabilised with polyphenols extracted from raspberry at the concentration of 50 ppm inhibited the growth of *Aspergillus niger* by 70%.[31] It was reported that chitosan stabilised-silver nanoparticles inhibited growth of *Cordyceps militaris*

and *Antrodia cinnamomea* fungi.[32] Silver nanoparticles stabilised with sodium dodecyl sulphate also showed antifungal activity against *Candida albicans II*.[33] This present work demonstrates that the antifungal activity of silver nanoparticles can be further enhanced by capping with TGA.

Durability of the Antimicrobial Treatment

As shown in Table 3, before washing all TSC and TGA-capped wool fabrics demonstrated excellent antibacterial activity. However, after five washings, the wool fabric treated with TGA-capped silver nanoparticles showed no change in antibacterial activity while the fabric treated with TSC-capped silver nanoparticle showed a reduction in antibacterial performance. After 10 washings, the wool fabric treated with TSC-capped silver nanoparticles considerably lost the antibacterial activity as the percentage of bacterial reduction dropped from 96.8, 97.0 and 95.2 % against *Staphylococcus aureus*, *Klebsiella pneumoniae* and *Escherichia coli* respectively to 70.0, 77.0 and 85% respectively. However, the wool fabric treated with TGA-capped silver nanoparticles did not lose any antibacterial performance even after 10 washings. The results achieved indicate that covalent binding with EDC/NHS cross-linkers reduced nanoparticle loss during laundering, which will reduce silver nanoparticle-induced contamination of washing effluent.

In the case of unbound or loosely bound silver nanoparticles by a resin, sometimes not only silver ions but also whole silver nanoparticles are released into the environment resulting in poor durability to laundering.[29] In this work, TGA-capped silver nanoparticles were covalently bonded to wool fibre surface, which prevented leaching of silver nanoparticles from wool fibre

but permitted leaching of silver ions. As a result the durability of the treatment to laundering considerably improved.

Contact Angle and Surface Topographies

Table 4 shows contact angle of the surface of control wool fabric, SBS silver nanoparticle-treated control wool fabric, TGA-capped silver nanoparticles ionically bonded to the wool fabric, and also control wool fabric treated with TGA-capped silver nanoparticles using EDC in combination with NHS cross-linker. The control wool fabric showed some level of hydrophobicity initially but the water droplet disappeared within 30 s. TSC-capped silver nanoparticles bonded to the wool fabric by Basolan MW-P showed strong hydrophobicity as the contact angle shown was 134.6° and the contact angle only decreased to 132.2° after 30 s. On the other hand, wool fabrics treated with TGA-capped silver nanoparticles by ionic and also NHS/EDC bonding both showed strong hydrophilicity and the water droplet disappeared immediately. The results suggest that the surface of TGA-capped silver nanoparticle is superhydrophilic indicating the presence of hydrophilic carboxyl groups on the surface. It is known that a surface deposited with nanoparticles or a surface with nanoindentation shows 'Lotus Effect' with strong superhydrophobicity.[30,34] In this work, we found that wool fabric surface coated with TSC-capped silver nanoparticles in combination with Basolan MW-P showed strong hydrophobicity. FTIR spectrum of TSC-capped shows the presence of hydroxyl groups on their surface (Figure 2). These hydroxyl groups reacted with silane groups of the Basolan MW-P thorough condensation reaction and formed a nanostructured hydrophobic layer on the surface of the wool fibre. On the other hand, wool fabric coated with TGA-capped silver

nanoparticles showed very strong hydrophilicity, which indicates that only few carboxyl groups reacted with EDC and the rest were exposed, which conferred strong hydrophilicity.

The surface morphology of the wool fabric samples treated with TSC and TGA-capped silver nanoparticles is shown in Figure 5. The TGA-capped silver nanoparticles on the surface of wool fibre are clearly visible and appear to be adhered to the fibre surface and distributed over the surfaces. It is evident that agglomerated TSC silver nanoparticles are covered by silicone resin but the TGA-capped silver nanoparticles are more uniformly distributed on the surface (although few small aggregations could be visible) compared to the TSC-capped silver nanoparticle-treated wool fabric.

Conclusions

We have demonstrated that silver nanoparticles could be successfully bonded to the wool fibre surface with appropriate surface modifications. The bonding of TSC-capped silver nanoparticles onto wool fabric surface with silicone resin increased their durability to washing, although the level of improvement achieved was poor and may not be enough for industrial applications. Moreover, the surface of the treated fabric exhibited strong hydrophobicity. On the other hand, the TGA-capped silver nanoparticles showed slightly better antibacterial properties compared to the TSC-capped silver nanoparticles and the treated fabric surface exhibited superhydrophilicity. The TSC-capped silver nanoparticles did not show any antifungal activity against *Aspergillus brasiliensis* and *Aspergillus fumigatus* but TGA-capped silver nanoparticles showed excellent antifungal activity against both types of fungi. The TGA-capped silver nanoparticle-based

treatment was found to be durable to at least 10 washings as no loss of antibacterial activity was noticed after 10 washings. The developed treatment could be a sustainable antibacterial treatment for wool fabrics.

Supplementary Information

The supplementary information contains the experimental details and a figure containing optical images that show the growth of bacteria under the untreated wool fabric, wool fabric treated with TSC-capped silver nanoparticles and wool fabric treated with TGA-capped silver nanoparticles after 48 hours of incubation with *Escherichia coli*, *Staphylococcus aureus*, and *Klebsiella pneumoniae*.

Acknowledgment

Keywords: Antibacterial properties . Antifungal properties . EDC cross-linking . TGA-capped silver nanoparticles . Wool keratin fibre

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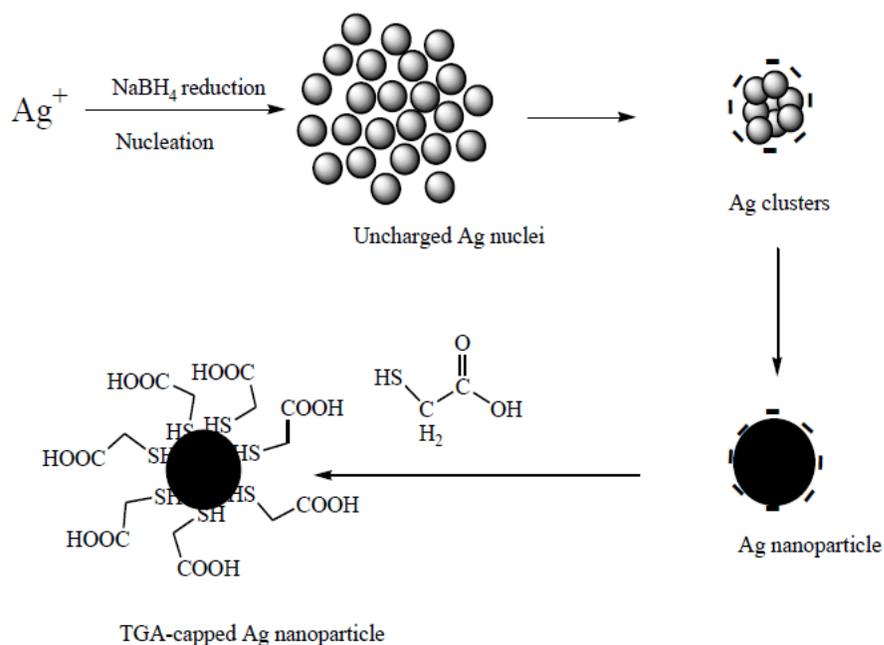
Figure 1. Mechanism of stabilisation of silver nanoparticles by capping with TGA.
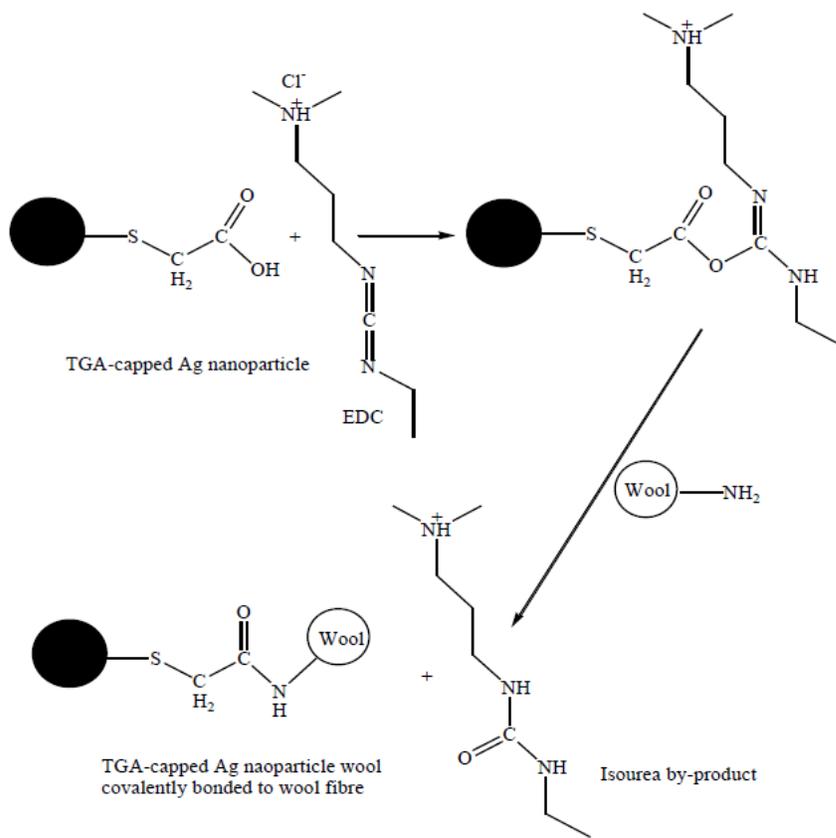
Figure 2. Mechanism of binding of TGA-capped silver nanoparticles to wool fibre surface.
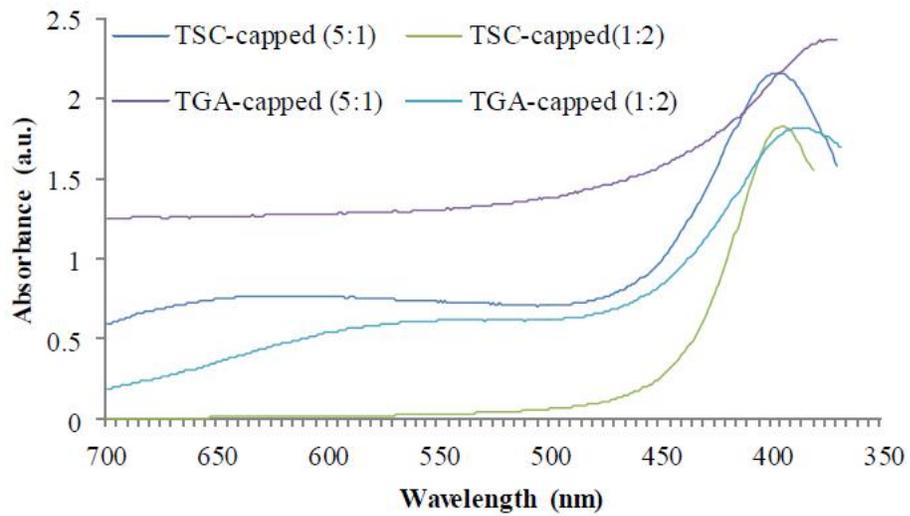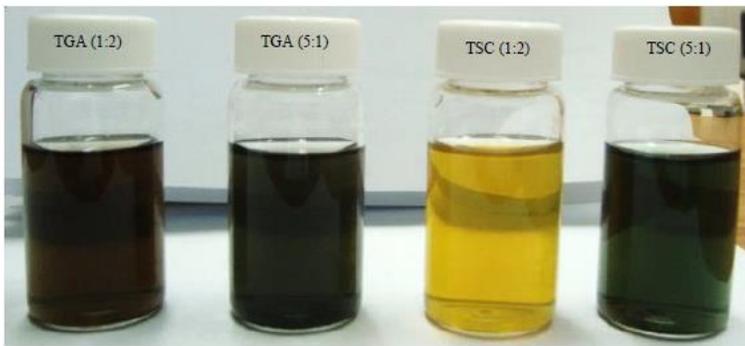
Figure 3. UV-vis spectra of aqueous dispersion of various SBS, TSC and TGA-capped silver
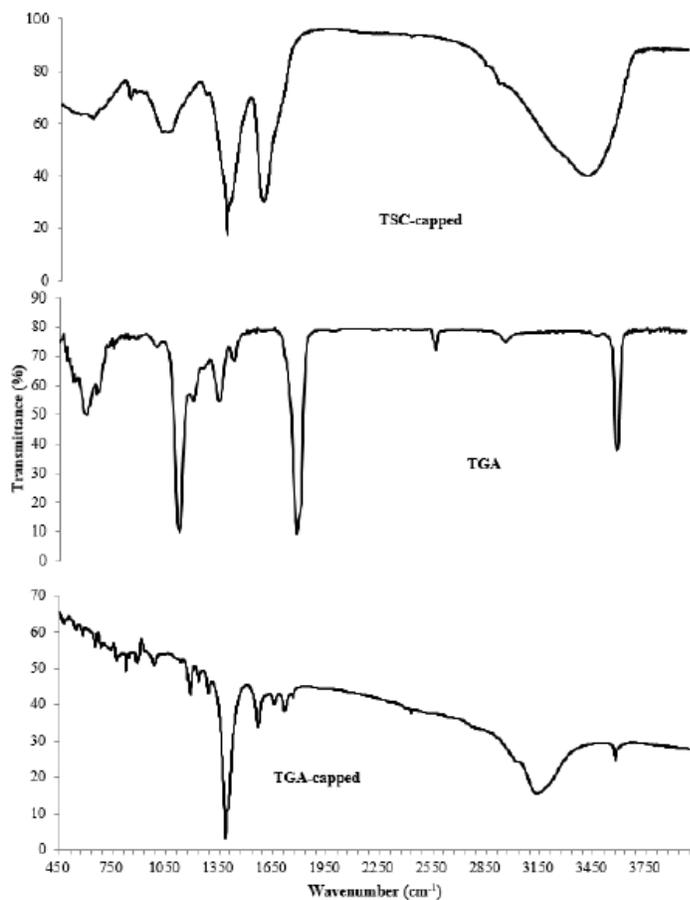
nanoparticles.

Figure 4. FTIR spectra of TGA, SBS and TGA-capped silver nanoparticles. KBr disc technique was used to record the FTIR spectra.
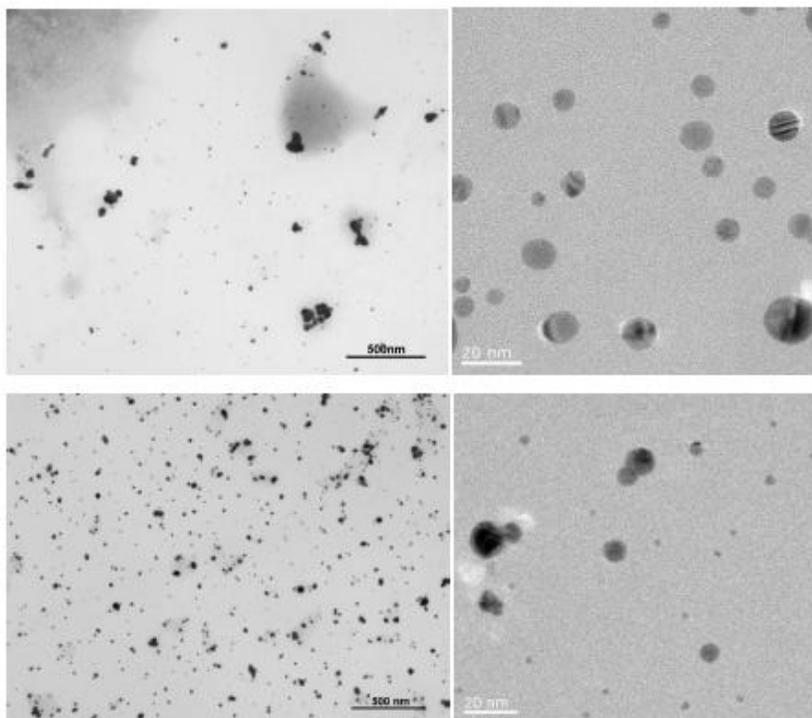
Figure 5. TEM (left) and HRTEM (right) micrographs of TSC (top) and TGA (bottom)-capped silver nanoparticles after three days of ageing.
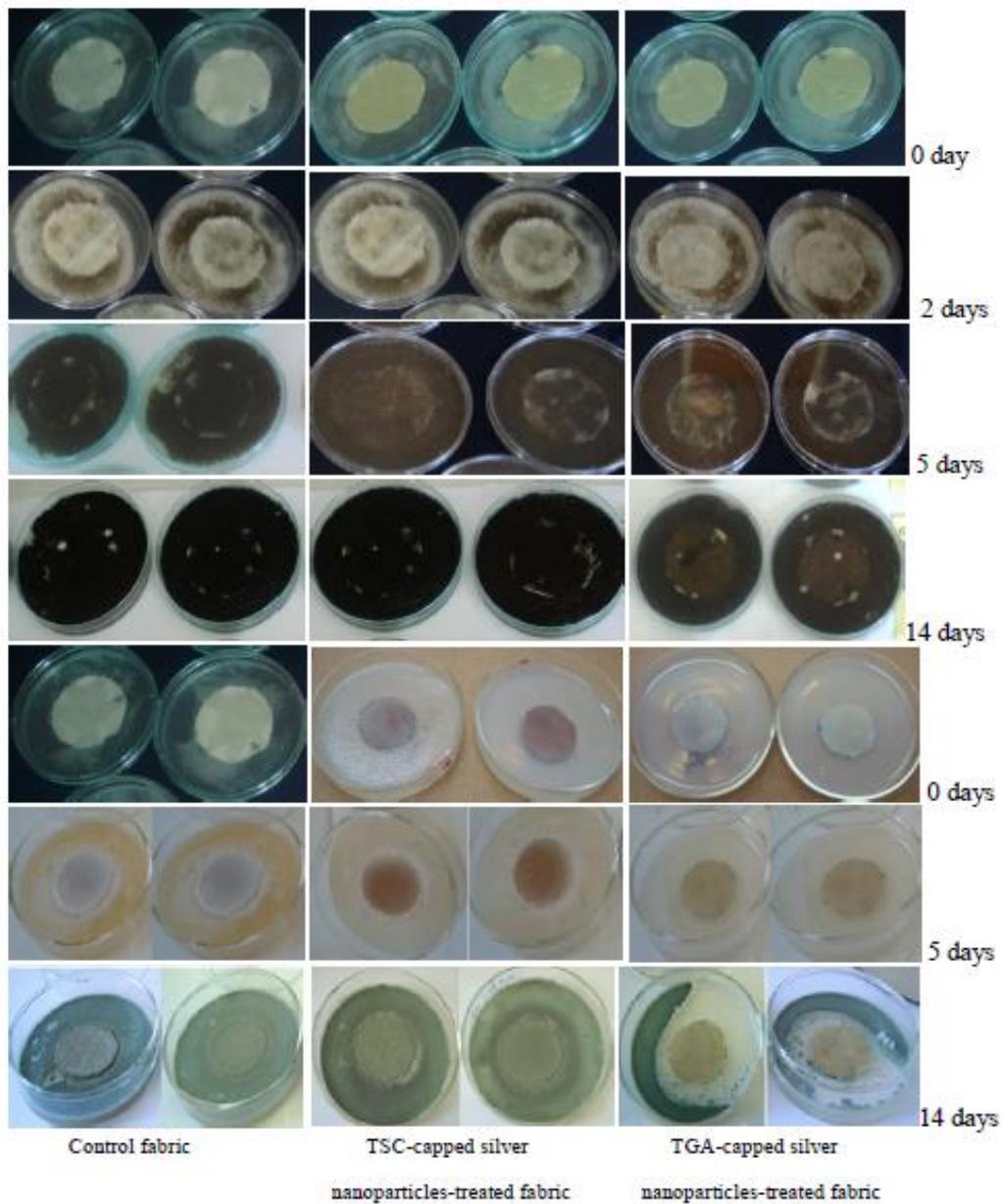
Figure 6. Images of samples of control wool fabric and also wool fabrics treated with TSC and TGA-capped silver nanoparticles after various days' incubation with *Aspergillus brasiliensis* (top) and *Aspergillus fumigatus* (bottom).
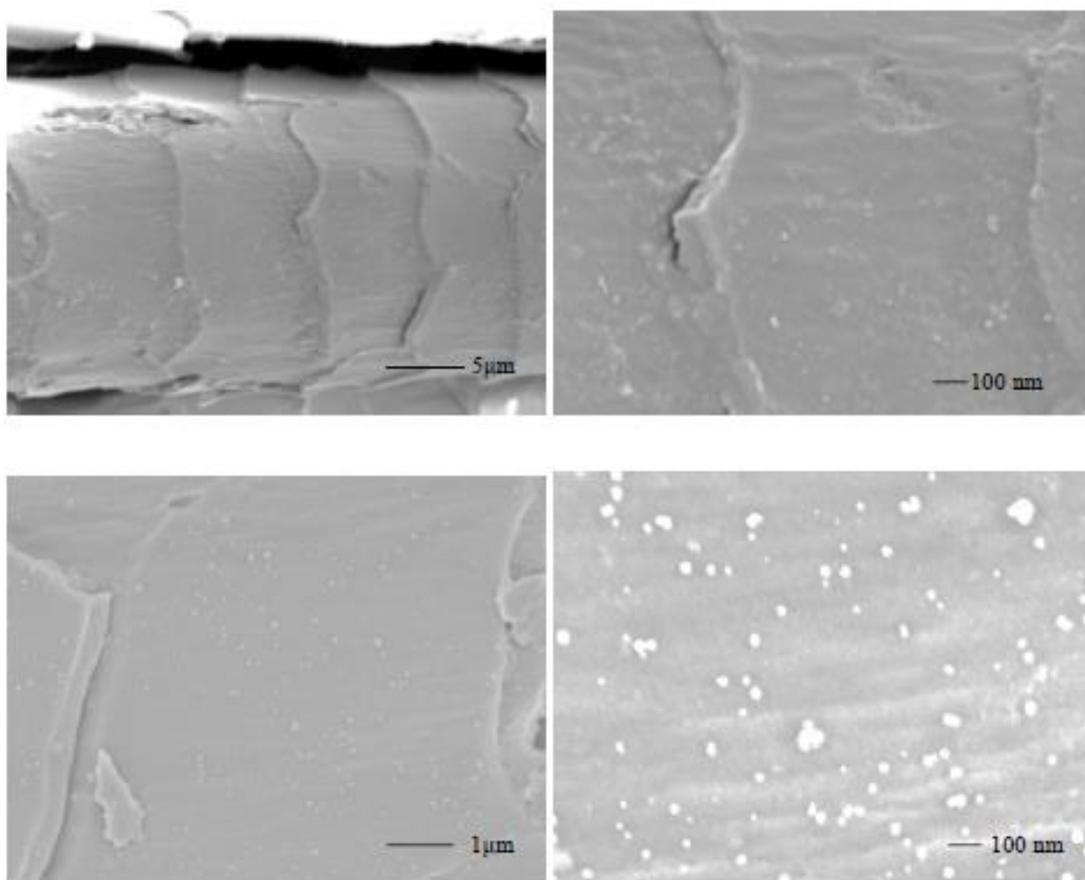
Figure 7. SEM images of wool fabrics treated with TSC (top) and also TGA-capped silver nanoparticles (bottom) before washing. Left = low magnification; right = high magnification.

Table 1. Surface zeta potential, electrophoretic mobility, conductivity and derived count rate of various silver nanoparticles.

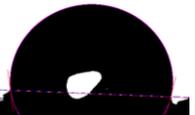| Samples	Surface zeta potential (mV)	Electrophoretic mobility (µmcm/Vs)	Conductivity (µS/cm)	Derived count rate (kcps)
Uncapped	-33.50±0.60	-2.62±0.01	0.05±0.01	3201.67±67
TSC-capped (pH 4.45)	-35.50±1.80	-2.83±0.02	0.33±0.01	330.23±52
TGA-capped (pH 4.45)	-46.60±2.10	-3.11+0.16	0.11±00	2795.65±59

Table 2. Antibacterial properties of wool fabrics treated with SBS and TGA-capped silver nanoparticles evaluated by AATCC Test Method 147-1998 (Parallel streak method).

Samples	Qualitative antibacterial performance					
	Staphylococcus aureus		*Klebsiella pneumoniae*		*Escherichia coli*	
	Bacterial growth	Inhibition zone (mm)	Bacterial growth	Inhibition zone (mm)	Bacterial growth	Inhibition zone (mm)
Control wool fabric	Visible growth directly under the fabric sample	0	Visible growth directly under the fabric sample	0	Visible growth directly under the fabric sample	0
Wool fabric treated with TSC-capped silver nanoparticles	No visible growth directly under the fabric sample	2	No visible growth directly under the fabric sample	3	No visible growth directly under the fabric sample	3
Wool fabric treated with TGA-capped silver nano-particles	No visible growth directly under the fabric sample	2	No visible growth directly under the fabric sample	1	No visible growth directly under the fabric sample	2

Table 3. Antibacterial properties of wool fabrics treated with silver SBS and TGA-capped silver nanoparticles evaluated by AATCC Test Method 100–1999

Number of washing	Quantitative antibacterial performance								
	Survival of Staphylococcus aureus cells (CFU/ml)			*Survival of Klebsiella pneumoniae* cells (CFU/ml)			*Survival of Escherichia coli* cells (CFU/ml)		
	Control	*Treated*	*% reduction*	*Control*	*Treated*	*% reduction*	*Control*	*Treated*	*% reduction*
TSC-capped silver nanoparticles									
Before washing	3.3×10^5	6.60×10^3	98.0	4.3×10^5	0.12×10^5	97.2	7.9×10^5	0.35×10^5	95.6
After five washings	3.3×10^5	4.95×10^4	85.0	4.3×10^5	0.54×10^5	87.3	7.9×10^5	1.15×10^5	85.4
After ten washings	3.3×10^5	7.49×10^4	77.3	4.3×10^5	0.78×10^5	81.8	7.9×10^5	1.27×10^5	83.9
TGA-capped silver nanoparticles									
Before washing	3.3×10^5	0.33×10^3	99.9	4.3×10^5	8.60×10^3	98.0	7.9×10^5	3.16×10^3	99.6
After five washings	3.3×10^5	4.29×10^3	98.7	4.3×10^5	9.46×10^3	97.8	7.9×10^5	2.37×10^3	99.7
After ten washings	3.3×10^5	3.30×10^3	99.0	4.3×10^5	9.46×10^3	97.8	7.9×10^5	5.53×10^3	99.3

Table 4. Dynamic contact angle of chlorinated control wool fabric and wool fabrics treated with SBS and TGA-capped silver nanoparticles.

Samples ID.	Average contact angle (°) at			
	0 s	10 s	20 s	30 s
Control chlorinated wool fabric	103.95	100.85	67.3	0
TSC-capped silver nanoparticles-treated wool	134.55	133.6	131.8	132.20
TGA-capped silver nanoparticles-treated wool (ionically bonded)	0	0	0	0
TGA-capped silver nanoparticles-treated wool (covalently- bonded)	0	0	0	0