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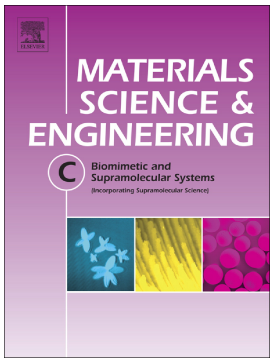

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In situ synthesis of silver or selenium nanoparticles on cationized cellulose fabrics for antimicrobial application

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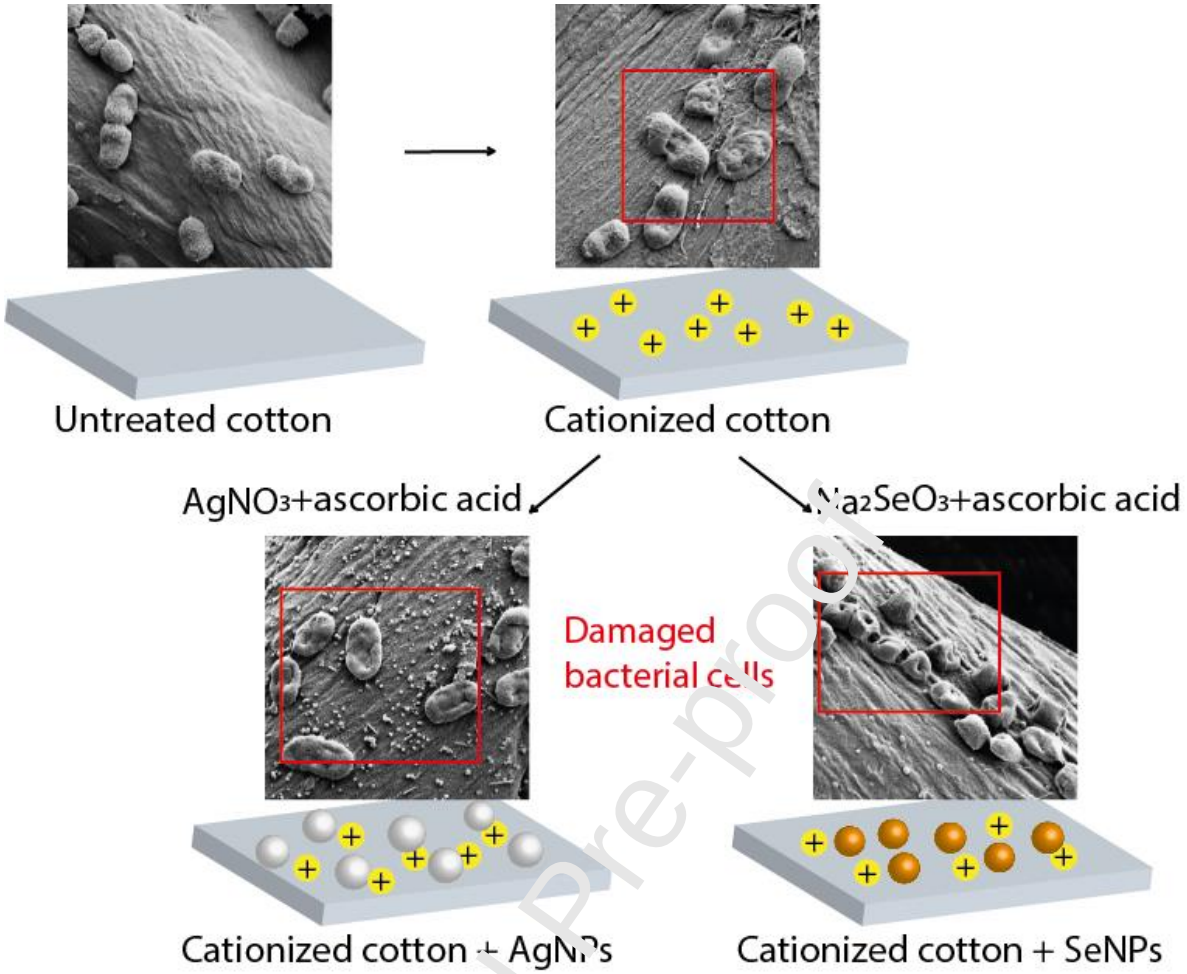

Graphical abstract

ABSTRACT

In this study, we developed a method to prepare inorganic nanoparticles *in situ* on the surface of cationized cellulose using a rapid microwave-assisted synthesis. Selenium nanoparticles (SeNPs) were employed as a novel type of antimicrobial agent and, using the same method, silver nanoparticles (AgNPs) were also prepared. The results demonstrated that both SeNPs and AgNPs of about 100 nm in size were generated on the cationized cellulose fabrics. The antibacterial tests revealed that the presence of SeNPs clearly improved the antibacterial performance of cationized cellulose in the similar way as AgNPs. The functionalised fabrics demonstrated strong antibacterial activity when assessed using the challenge test method, even after repeated washing. Microscopic investigations revealed that the bacterial cells were visually damaged through contact with the functionalised fabrics. Furthermore, the functionalised fabrics showed low cytotoxicity towards human cells when tested *in vitro* using an indirect contact method. In conclusion, this study provides a new approach to prepare cationic cellulose fabrics functionalised with Se or Ag nanoparticles, which exhibit excellent antimicrobial performance, low cytotoxicity and good laundry durability. We have demonstrated that SeNPs can be a good alternative to AgNPs and the functionalised fabrics have great potential to serve as an anti-infective material.

1. Introduction

From beddings, drapes and uniforms, to bandaging materials and wound dressings, textiles play vital roles in healthcare facilities. Due to the large surface areas, textiles have superior abilities to retain warmth, moisture, and nutrients from spillages and exudates, making them ideal substrates for microorganisms to grow on[1]. Some studies have suggested that

healthcare textiles can act as reservoirs and vehicles for the spread of microorganisms in hospitals[2–4]. Healthcare-associated infections (HAIs) have become a serious threat to patients' health and result in significant economic burdens to healthcare systems[5]. It is estimated that in Europe, approximately 4.1 million patients acquire at least one HAI each year, causing 37,000 deaths directly and contributing to an additional 110,000 deaths each year[6]. Furthermore, the emergence of antibiotic resistance is increasing the urgency with which we must find alternative ways to control the growth and transmission of pathogens in hospitals. With the development of nanotechnology, some inorganic nanoparticles (NPs) such as silver, copper and zinc, have been identified as promising candidates in combatting pathogenic microorganisms, including antibiotic-resistant strains[7]. Although the exact antimicrobial mechanisms of the NPs remain unclear, it is believed that they act differently from conventional antibiotics. NPs may exhibit multiple modes of action simultaneously, including physical damage of the microbial cell structures, release of toxic ions, and catalysed formation of reactive oxygen species (ROS) which can cause severe damage to the cell components[8,9], whereas antibiotics normally have only one mechanism of action, for example, the inhibition of either cell wall synthesis, protein synthesis, or DNA replication[10]. The multiple modes of action by NPs are believed to make it more difficult for the bacteria to develop resistance because simultaneous mutations in the bacterial cells will be needed[11]. Antimicrobial nanoparticles have been studied to functionalise different surfaces such as textiles[12,13], polymeric medical devices[14,15], and metal orthopaedic implants[16] as a means of infection control.

Silver nanoparticles (AgNPs) are one of the most extensively studied antimicrobial inorganic nanoparticles, due to their potent and broad-spectrum antimicrobial activities[17]. Silver nanoparticles have been used commercially for over a decade in cosmetics, textiles, pharmaceutical and medical products[18]. Despite this, there have been concerns regarding

their toxicity towards mammalian cells, their environmental impact, and the possible development of resistance due to the wide usage of AgNPs[19–21]. Therefore, efforts have been made to explore new inorganic nanomaterials for antimicrobial applications. Recently, selenium nanoparticles (SeNPs) have received attention for their antimicrobial, antitumor and antioxidant properties[22–24]. As an essential trace element, selenium deficiency can lead to health problems such as a weakened immune system, muscle weakness and fatigue, while high concentrations of Se may be toxic to the human body[25]. Compared with other forms of selenium, elemental SeNPs have been found to show low toxicity towards mammals through both *in vitro* and *in vivo* studies[26–29]. Biswas *et al.*[30] prepared silver or selenium nanoparticles on polymeric scaffolds and compared the cytotoxicity of the scaffolds towards mouse fibroblasts using an indirect contact method; the results indicated that the Ag-loaded scaffolds showed high cytotoxicity, while the Se-loaded scaffolds were not toxic to the cells. The low cytotoxicity of SeNPs indicates their great potential for use in biomedical applications.

The research on SeNPs as antimicrobial agents is still limited and some seemingly conflicting results can be found within the literature. For example, it has been demonstrated that SeNPs exhibit antibacterial and anti-biofilm effects towards both Gram-positive (e.g. *Staphylococcus aureus*, *Streptococcus pyogenes* and *Staphylococcus epidermidis*) and Gram-negative bacteria (e.g. *Escherichia coli* and *Pseudomonas aeruginosa*), including some multidrug-resistant strains[29,31–33]. However, it has also been reported that the colloidal SeNPs stabilised by polyvinyl alcohol[34] or polysorbate 20[35] effectively inhibited the growth of *S. aureus* but did not show similar effect against *E. coli*. It was hypothesised by Guisbiers *et al.*[31] that the antibacterial activity of SeNPs against some bacterial species can be hindered by the presence of chemical contaminants on the particle surface (e.g. polymer and surfactant stabilisers). Unlike metal nanoparticles such as silver and copper, elemental selenium is not

normally considered to be soluble in aqueous environments[36]. It is believed that the SeNPs can be transformed into organic forms (e.g. seleno amino acids and selenoproteins) through the interactions with microorganisms[34,37]. Due to the chemical similarity, selenium may be able to displace the sulphur for sulphur-containing ammonic acids such as cysteine and methionine[38]. Excessive amounts of selenoproteins can lead to the generation of ROS, causing DNA damage, structural changes of proteins and enzyme dysfunction[39]. Therefore, the presence of some stabilisers on the particle surface may result in inadequate interaction between the nanoparticles and the bacterial cells and impede the antimicrobial activity.

Search of the literature has produced very few published studies using elemental SeNPs as the antimicrobial agent to functionalise textile materials, and in these studies, the SeNPs were prepared *ex situ* before being applied onto the fabrics[40–42]. Yip *et al*.[40] prepared SeNPs using a natural polysaccharide-protein complex (PSP) extracted from mushrooms as the stabiliser and padded the PSP-SeNPs onto the fabrics; the SeNP-functionalised fabrics showed strong antifungal activity against *Trichophyton rubrum*; unfortunately, the authors only reported moderate antibacterial activity of the colloidal PSP-SeNPs against *S. aureus*, and did not test other bacterial strains or the antibacterial performance of the functionalised fabrics. Based on the hypothesis that the presence of some stabiliser on the surface of SeNPs may hinder their antimicrobial activity, in this study we developed a method to prepare SeNPs directly *in situ* on the surface of cationized cellulose without the inclusion of any stabiliser. Cellulose is the most abundant natural and renewable polymer on earth; the large number of hydroxyl groups on the cellulose chains provide plenty of sites for the graft of functional groups or ionic interactions[43]. This method may be easily adapted and applied to prepare other types of inorganic nanoparticles on other cellulose materials. Since AgNP is one of the most studied and well-documented antimicrobial nanoparticles, here we report the

preparation and evaluation of both AgNP- and SeNP-functionalised cationic cellulose fabrics using the same approach.

2. Experimental Section

2.1 Materials

Bleached woven cotton fabric (250 g/m^2) was purchased from a local fabric store (Brighton, UK) and used as the cellulose substrate. The as-purchased cotton was pre-treated to remove impurities resulting from cotton growth and manufacturing processes that may leach out during testing, as described in Supporting Information (SI). Sodium selenite (Na_2SeO_3), silver nitrate ($AgNO_3$), 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC) aqueous solution (wt 60%), and ascorbic acid were purchased from Sigma Aldrich (UK). NaOH solution (10 M), acetic acid (pure), Tween 80 (polysorbate 80), concentrated sulphuric acid, hydrogen peroxide (>30%), lecithin, peptone and absolute ethanol were purchased from Fisher Scientific (UK). All bacterial culture media including Nutrient Broth (NB), Tryptone Soya Broth (TSB), Standard Plate Count Agar (PCA), and Phosphate-buffered Saline (PBS) tablets were purchased from Oxoid (UK). Reverse osmosis water (RO water) with a resistance of 15 mΩ cm was used throughout the experiments.

2.2 Cationization of cellulose

The cationized cotton was prepared by chemical modification of cellulose molecules with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC)[44–47]. In this study, the cationization method was based on a cold pad batch protocol[46] with a molar ratio of NaOH and CHPTAC of approximately 2:1, and batching time of 24 h. The reaction solution

containing NaOH (1 M) and CHPTAC (100 g/L, 0.53 M) was prepared with 10 M NaOH solution and CHPTAC aqueous solution (wt 60%). Unmodified cotton (UC) was immersed into the solution at a material-to-liquor ratio of 1:20. The reaction bath was shaken constantly at 150 rpm for 1 h at room temperature. Subsequently, the samples were removed from the bath, dried briefly by squeezing to remove excess liquid (wet pick up approximately 120%), placed into polypropylene sample bags, and sealed for 24 h at room temperature. After 24h, the samples were neutralized using 1% acetic acid (material-to-liquor ratio of 1:20) and washed thoroughly with RO water. Finally, the air-dried cationized cotton (CC) was autoclaved at 121 °C for 15 minutes, after which the following preparation of nanoparticles *in situ* was performed using aseptic technique to avoid contamination (See SI for details).

2.3 *In situ* preparation of Ag and Se nanoparticles on cationized cotton fabrics

The CC samples (4.8 g) were immersed in different concentrations of silver nitrate or sodium selenite solutions (0.2, 0.5, and 1 mM) at a material-to-liquor ratio of 1:20 in 200 mL beakers. The beakers were shaken at 150 rpm for 1 h in the dark at room temperature to allow the precursor ions to be adsorbed onto the fabric surfaces. Subsequently, ascorbic acid (100 mM) was added resulting in concentrations of 2, 5, and 10 mM respectively. The reactants and fabrics were mixed thoroughly with a glass rod and then microwaved using a domestic microwave oven at 700 w for 90 s and taken out to cool and age for 2 h at room temperature. The cotton fabrics turned from white to beige or orange colours, indicating the formation of silver or selenium nanoparticles respectively. The samples were rinsed with RO water, soaked in 0.1% non-ionized surfactant Tween 80 for 30 min while shaken at 150 rpm to wash off any unattached NPs, and finally washed thoroughly with sterile RO water again before

drying in a laminar air flow hood. The products were designated AgNPs modified cotton (Ag-C) and SeNPs modified cotton (Se-C).

2.4 Sample characterisation

Microscopy investigations of the fabric samples were carried out using a Zeiss SIGMA Field Emission Gun Scanning Electron Microscopy (FEG-SEM) at an accelerating voltage of 2 kV. The microscope was equipped with an Energy-dispersive X-ray Spectroscopy (EDS) system, which was used to analyse the surface chemistry of the samples. The samples were sputter-coated with 4 nm platinum to increase the conductivity using a Quorum Q150T ES Turbo-Pumped Coater. The sizes of the NPs were determined manually with ImageJ software. Three batches of samples were prepared on individual occasions and approximately 300 particles from 10 – 15 images were analysed for each type of sample.

To determine the total amounts of Ag or Se nanoparticles loaded onto the cationized cotton fabrics, the cotton samples were digested in piranha solution and the solutions were analysed with Microwave Plasma-Atomic Emission Spectroscopy (4100 MP-AES, Agilent Technologies). The cotton samples were carefully disassembled and shredded into short loose fibres. Piranha solution was prepared in Pyrex test tubes by slowly adding one portion of H_2O_2 (30% wt) to three portions of concentrated H_2SO_4. Approximately 100 mg of the loose fibres were weighed accurately and then wet oxidised by 2 mL of the Piranha solution. After the fibres were fully dissolved, the solution was slowly added to 18 mL of cold RO water to dilute and prepare for MP-AES analysis. Three batches of samples prepared on individual occasions were analysed.

The XPS spectra were acquired on an Axis Ultra DLD spectrometer (Kratos Analytical) using a monochromatic AlKα source (hν = 1486.7 eV, 180 W). The pass energies of the analyzer were 160 eV for survey spectra and 40 eV for high resolution scans. The Kratos charge neutralization system was used and the position of the low energy component in C1s spectra (Figure S1) was referenced to 284.8 eV, which corresponded to C−C bonds of hydrocarbon contamination.

2.5 Evaluation of antibacterial performance using a challenge test

Antimicrobial activity was assessed using a challenge test method based on the Absorption Method from ISO 20743:2013 (Textiles — Determination of antibacterial activity of textile products)[48]. Antibacterial properties of the functionalized cotton fabrics were tested against *Staphylococcus aureus* (NCTC 10788) *Klebsiella pneumoniae* (NCTC 11228) and *Escherichia coli* (NCTC 10418). *S. aureus* and *K. pneumoniae* are Gram-positive and Gram-negative strains, respectively, recommended for testing by ISO 20743:2013. In this study *E. coli* was employed as an additional test strain, as multiple reports have described conflicting results on the antibacterial efficacy of SeNPs against *E. coli*[31,34,35]. The maintenance of the bacterial cultures and preparation of culture media are described in SI. Single colonies of the test bacteria were picked off the PCA agar plate, inoculated into fresh TSB (10 mL) and incubated at 37 °C at 120 rpm overnight. A bacterial suspension was then prepared by inoculating fresh TSB (10 mL) with 0.2 mL of the overnight TSB culture and incubating at 37 °C at 120 rpm for 2 – 3 h. When the bacterial concentration reached approximately 1×10^9 CFU/mL (estimated using optical density at 600 nm), the culture was diluted to a concentration of $1 – 3 \times 10^5$ CFU/mL by serial dilution in dilute NB (0.65 g/L) to serve as the inoculum for the tests.

Six specimens (4 × 4 cm, 0.4 ± 0.05 g) were prepared for each type of fabric sample (UC as control, and CC, Se-C and Ag-C as test samples). Aliquots of the bacterial inoculum (0.2 mL) were pipetted over the surfaces of the specimens in sterile universal bottles. Care was taken to ensure that no inoculum touched the walls of the vial. Immediately after the inoculation, 20 mL of Soyabean-Casein Digest broth with Lecithin and Polysorbate 80 medium (SCDLP, containing 30 g/L TSB, 1 g/L lecithin and 7 g/L polysorbate 80) was added to 3 specimens of each type of sample. The vials were shaken vigorously on a vortex mixer for 5 × 5 s cycles to remove attached cells. The resulting suspensions were subject to serial dilution in peptone salt solution (containing 1 g/L peptone and 8.5 g/L NaCl) and a viable count determined using pour plates with PCA, prepared in duplicate for each dilution. These specimens are referred to as the time 0 (t_0) group. The remaining 3 specimens of each type of sample were incubated at 37 °C for 24 ± 3 h after the inoculation. Subsequently, these samples were processed in the same way as the t_0 group and referred to as the t_{24} group. Where there was no colony observed on the plate, the number was recorded as 1 colony, according to the standard. The experiment was repeated three times using three batches of samples on individual occasions (n=3).

Antibacterial value (A) can be calculated using Equation (1) below:

$$A = (\log_{10} C_t - \log_{10} C_0) - (\log_{10} T_t - \log_{10} T_0) \quad (1)$$

where C_t and C_0 are the CFU of the control samples (UC) at t_{24} and t_0; T_t and T_0 are the CFU of the functionalised test samples (CC, Se-C or Ag-C) at t_{24} and t_0. In the case of $C_0 > T_0$, substitute C_0 for T_0. According to Annex F of ISO 20743:2013, the antibacterial efficacy of the test fabric can be considered as “significant” when $2 \leq A < 3$ and “strong” when $A \geq 3$.

Apart from the antibacterial value 'A' which is recommended by the standard, growth reduction (R%) in the numbers of viable/live bacteria after incubation was also determined using Equation (2) below:

$$R\ (\%) = (C_t - T_t)/C_t \times 100 \qquad (2)$$

2.6 Determination of bacterial viability on fabric surfaces by confocal microscopy

The viability of the bacteria after incubation with the fabric samples was visualised by using a LIVE/DEAD Baclight Bacterial Viability Kit (Thermo Fisher Scientific, UK) and confocal microscopy. Since the fabrics have a complex 3-dimensional structure which makes it difficult to locate the bacterial cells under the microscope with high magnification, a high inoculum concentration (approximately 10^8 CFU/mL) was used for microscopic examination to ensure bacterial coverage on the fibres. Moreover, the inoculum was prepared in saline to avoid broth constituents interfering with components of the LIVE/DEAD stain[49]. A liquid culture in TSB (OD_{600nm} approximately 1), prepared as described above, was centrifuged in Eppendorf tubes at 5 000 g for 5 mins. The supernatant was discarded, and the cells were re-suspended in 0.85% physiological saline. The washing procedure was carried out twice.

Fabric samples were cut into square swatches of 0.5 cm × 0.5 cm and placed into individual Eppendorf tubes. Bacterial suspension (10 µL) was then inoculated onto the fabric surfaces and incubated at 37 °C for 24 ± 3 h. After incubation, the fabric samples were disassembled carefully with sterile forceps into loose yarns and fibres and placed onto microscope slides. The staining reagent, containing SYTO 9 and propidium iodide (PI), was prepared according to the manufacturer's instructions and 10 µL applied to the samples. Glass cover slips (22

mm × 22 mm) and DPX mountant (SureChem, UK) were used to seal the samples which were subsequently incubated at room temperature, in the dark, for at least 15 mins before being examined using a Leica SP5 Confocal Laser Scanning Microscope. Excitation was performed using an Argon laser (488 nm) for both dyes with power set to 25%. SYTO 9 emission was measured at 510 to 550 nm and PI emission at 610 to 650 nm. Z-stack images were acquired at 1 μm intervals (20 – 30 μm thick) and orthogonal projections were constructed.

2.7 Effect of functionalised fabrics on bacterial morphology

Control (UC) and test (CC, Se-C and Ag-C) fabric samples were inoculated with a bacterial suspension in saline as described above for confocal microscopy. NP-functionalised samples prepared with the highest precursor concentration (1 mM) were employed in order to make sure that the effects caused by the quaternary groups and the nanoparticles could be differentiated. After 24 h incubation, the samples were washed twice with 1 mL sterile PBS and fixed with 2.5% glutaraldehyde (in PBS) for 2 h at room temperature. After the fixation, the samples were washed with PBS twice and then dehydrated with a series of graded ethanol solutions (35%, 50%, 75%, 95%, 100%, for 15 mins each and twice for 100%). Finally, the samples were air dried for two days and left in a desiccator overnight. Prior to the SEM examination, the samples were coated with 4 nm platinum by sputter coating and examined as previously described.

2.8 Cytotoxicity evaluation of functionalised fabrics towards human cells

Human bronchial epithelial cells (16HBE14o-) were purchased from Sigma Aldrich (UK) and human keratinocytes (HaCaT) were purchased from AddexBio (UK). Details of cell culture and maintenance is described in the SI. The sample preparation method for indirect contact cytotoxicity tests was based on ISO 10993-12:2012 (Biological evaluation of medical devices. Part 12: Sample preparation and reference materials)[50]. Se-C and Ag-C prepared with the highest precursor concentration (1 mM) were used in the cytotoxicity tests. Fabric samples were cut into 2 cm × 2 cm squares (0.1 ± 0.01 g). The samples were placed in sterile glass vials and sterile RO water was added at a ratio of 0.1 g/mL. The glass vials were incubated at 37 °C with 100 rpm agitation for 72 h. After 72 h, the extracts were centrifuged in Eppendorf tubes at 3000 g for 5 mins to remove the short loose fibres from the extracts. The extracts were then mixed with an equal amount of double strength cell culture medium to form single strength medium to treat the cells (see SI for details).

The cells were washed with PBS and harvested using 0.05% trypsin-EDTA (Gibco, UK). After trypsinisation, the cells were counted using a haemocytometer and seeded at a density of 4×10^3 cells/well in 96-well plates. The cells were prepared in two sets of triplicate wells. One set was for each type of the sample extract or medium-only negative control, and the other set for a total lysis positive control. Cells were allowed to attach to the surface of the wells for 24 h at 37 °C prior to extract exposure. The culture media for the seeded cells were discarded after 24-h incubation, and 100 µL of the 72-h extracts were then added to the wells. The extracts were also added to empty wells without any cells as cell-free controls. The plates were incubated at 37 °C in a humidified atmosphere with 5% CO_2 for 24 h before the cell activity was assessed.

Lactate dehydrogenase (LDH) Cytotoxicity Assay Kit (Thermo Fisher Scientific, UK) was used to measure the LDH release following the 24-h exposure of the cells to the fabric extracts. LDH is a soluble enzyme that is released into the culture medium as a result of

compromised membrane integrity and, therefore, it can be used as an indicator of cell death. CellTiter-Glo Luminescent Cell Viability Assay Kit (Promega, UK) was used to determine the cell viability after exposure to the fabric extracts. CellTiter-Glo is a luminescent cell viability assay to determine the number of viable cells based on quantification of the adenosine triphosphate (ATP) present, which is related to the number of metabolically active cells. The assays were performed according to the manufacturer's instruction (see SI for details). The experiment was repeated three times on individual occasions (n=3). A Student's t test was performed to determine the difference between the medium-only negative control and other samples.

2.9 Washing durability of the functionalised textiles

In the UK, the Department of Health requires healthcare linens to be washed at 65 °C for no fewer than 10 mins or at 71 °C for at least 3 mins[51]. In this study, the washing durability was evaluated by a method based on the accelerated laundering test method recommended by American Association of Textile Chemists and Colorists (AATCC) Test 61-2013 Colorfastness to Laundering: Accelerated[52]. The washing apparatus comprised 300 mL polypropylene wide-mouth bottles (Thermo Fisher Scientific), stainless steel balls (6 mm), and a TURBULA T2F Shaker Mixer (WAB, Switzerland). The laundry detergent Persil Colour Care Biological Washing Powder was purchased from a local supermarket. Bottles were filled with 150 mL RO water along with 50 stainless steel balls and 0.225 g washing powder (0.15% w/v), which was then heated in a water bath to 75 °C, and a 2.5 g fabric sample (5 cm × 20 cm) added. The bottle was wrapped in oven gloves, to insulate for heat loss, and then shaken (96 rpm) for 30 mins (one accelerated washing cycle). According to

AATCC 61-2013[52], one washing cycle with this accelerated method is equivalent to 5 typical home launderings. Four accelerated washing cycles were performed for each type of sample. After each accelerated washing cycle, a small piece (approximately 5 cm × 2 cm) was cut from the fabric for MP-AES elemental analysis using the method described previously. The washing procedure was carried out three times using samples prepared on three individual occasions for the analysis.

3. Results and discussion

3.1 Sample preparation and characterisation

Here we report a rapid microwave-assisted *in situ* synthesis method that can be used to directly prepare both metal (Ag) and non-metal (Se) inorganic nanoparticles on cellulose textiles without the use of any additional capping agent (Figure 1). In the first step, a cationization agent, 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC), was used to functionalize the cotton fabrics prior to the preparation of nanoparticles. CHPTAC is a low-toxicity agent that is widely used for the cationization of starch and cellulose[46]. During the cationization, NaOH was used to transform the CHPTAC into 2,3-epoxypropyl trimethyl ammonium chloride (EPTAC) to react with cellulose, while the excessive NaOH activated the primary –OH groups on the cellulose chain into alkali cellulose (Cell–O^-Na^+). This resulted in a fabric surface with both cationic quaternary ammonium groups (-$N^+(CH_3)_3$) and activated –O^-Na^+ groups. The –O^-Na^+ groups on activated alkali cellulose can attract silver ions. Yazdanshenas and Shateri-Khalilabad[53] prepared silver nanoparticles *in situ* on the surface of alkali cellulose. They suggested that the sodium salt of Cell–O^-Na^+ was exchanged to the silver salt of Cell–O^-Ag^+ due to the higher electronegativity (Pauling's scale) of silver (1.93) towards sodium (0.93) in the aqueous

solution of $AgNO_3$. In our study, when the $AgNO_3$ was added and before the *in situ* reduction took place, it was noticed that the reaction solution became slightly milky white in appearance. This was probably due to the presence of chloride ions as the counter-ion of the quaternary ammonium groups. Some AgCl precipitated in the solution and there might also be a small amount of AgCl generated on the fabric surface. On the other hand, the cationic quaternary ammonium groups can attract the anionic selenite groups (SeO_3^{2-}) onto the fabric surface and, subsequently, SeNPs can be generated by *in situ* reduction using ascorbic acid. Thus, the cationization process with NaOH and CHPTAC prepares the cellulose fabric for the *in situ* synthesis of both metal (e.g. silver) and non-metal (e.g. selenium) nanoparticles.

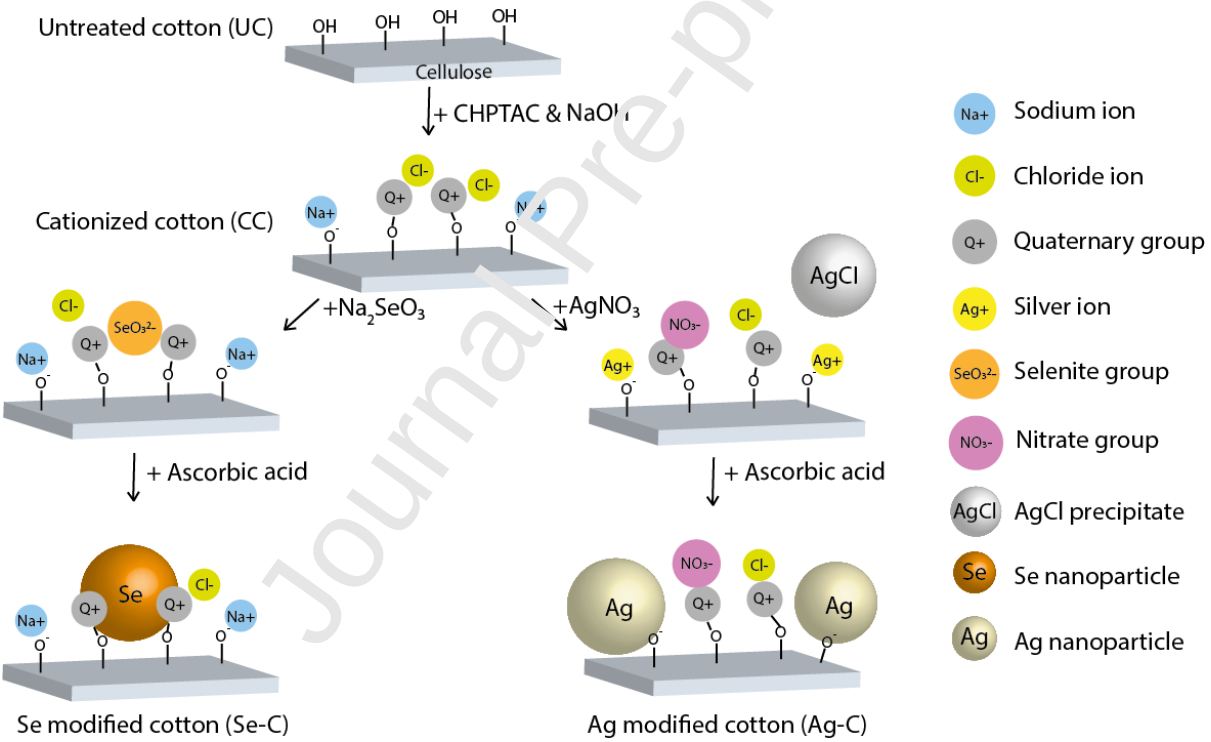

Figure 1. Preparation of Se or Ag nanoparticles *in situ* on a cellulose surface.

The photographic and SEM images of the control, unmodified (UC) and cationized, silver and selenium modified (CC, Ag-C and Se-C) cotton fabrics are shown in Figure 2. As can be seen from Figure 2A, the cationization process did not result in colour change of the cotton

fabric, while the formation of Se or Ag nanoparticles changed the colour of the fabrics from white to orange or beige, with the intensity of the colour dependent on the concentration of precursor salt. Several reports have described the orange colour of SeNPs[30,54], and the colours of AgNPs, ranging from yellow to beige/grey, depending on the sizes of particles[55,56]. The cationized cotton (Figure 2C) seemed to be slightly rougher than the unmodified control (Figure 2B); however, as a plant material, cotton fibres have natural surface roughness, making it difficult to conclude significant morphological change from the SEM images shown in Figure 2. Similar results were reported by some previous studies on the cationization of cotton using CHPTAC[57,58]. No cracking or etching of the fibres can be seen, indicating the cationization process did not result in significant physical damage of the fibres. The presence of SeNPs (Figure 2D-2F) or AgNPs (Figure 2G-2I) can be clearly seen on the surface of the fibres. The particles were predominantly quasi-spherical in shape, although small numbers of silver nano rods can also be seen. The numbers of SeNPs and AgNPs and the amount of Se or Ag per gram of cotton increased with increasing precursor concentrations (0.2, 0.5 and 1 mM) (Table 1), which is in agreement with the colour changes shown in Figure 2A. The nanoparticles had relatively narrow size distributions, falling predominantly into the range of 40 nm – 140 nm (Table 1). The average sizes of SeNPs prepared with different concentrations of Na_2SeO_3 were relatively similar, at around 100 nm. It can also be seen from the size distributions of SeNPs that the peaks of the histograms were also relatively stable, at around 100 nm. On the other hand, when looking at the average size and size distributions of the AgNPs, the particle sizes seemed to increase as the concentration of $AgNO_3$ increased. The different trends could be due to various reasons including the different nucleation and particle growth mechanisms between the AgNPs and SeNPs.

Table 1. Average nanoparticle sizes and loading of Se or Ag per gram of cotton on the functionalised cotton fabrics.

Sample	Average size (nm)	Loading of Se or Ag (mg/g)
Se-C (0.2 mM)	106 ± 32	0.327 ± 0.027
Se-C (0.5 mM)	98 ± 28	0.658 ± 0.023
Se-C (1 mM)	94 ± 25	1.069 ± 0.122
Ag-C (0.2 mM)	64 ± 21	0.167 ± 0.016
Ag-C (0.5 mM)	85 ± 36	0.481 ± 0.119
Ag-C (1 mM)	97 ± 34	1.383 ± 0.179

* Data represented as mean ± SD, n=3.

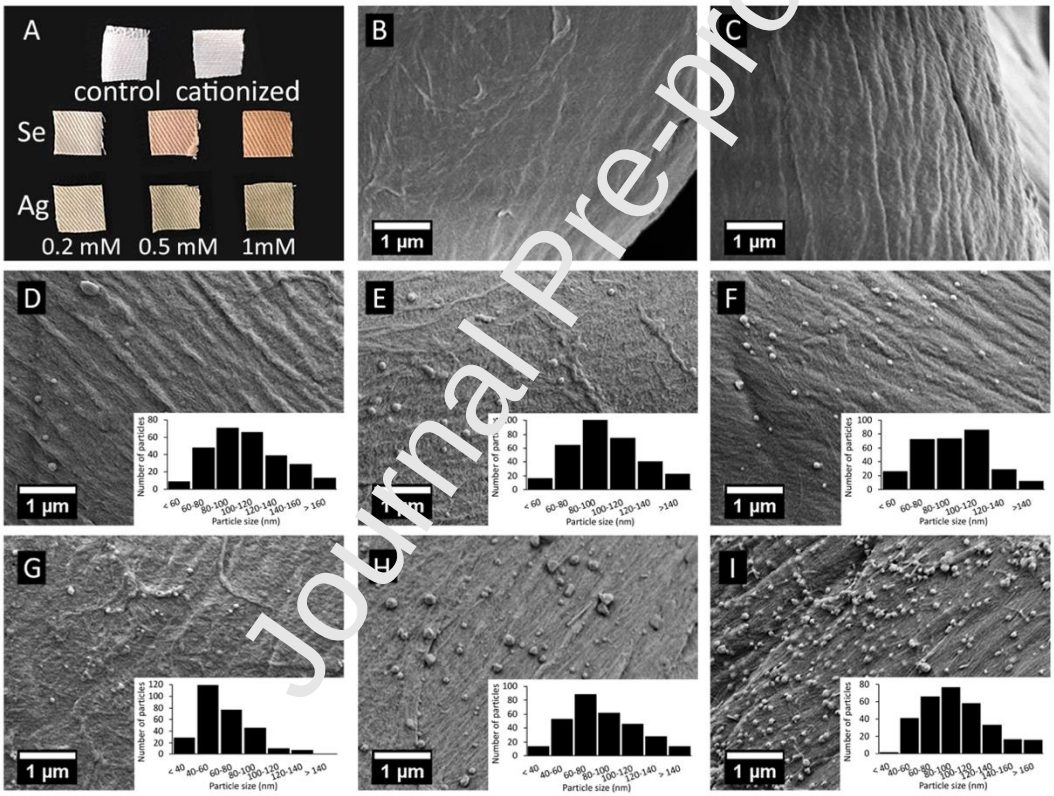

Figure 2. (A) Photographic image of the cotton samples; SEM images and corresponding particle size distributions of (B) UC, (C) CC, (D) 0.2 mM Se-C, (E) 0.5 mM Se-C, (F) 1 mM Se-C, (G) 0.2 mM Ag-C, (H) 0.5 mM Ag-C and (I) 1 mM Ag-C.

The sample surface was analysed by XPS (Figure 3). The detailed XPS spectra and binding energies can be found in Supporting Information (Figure S3 and Table S1). The EDS spectra of the samples are presented in Figure S2 as supportive data. In Figure 3 and Figure S3, the peak at about 399.8 eV observed in the N1s spectra of all samples can be attributed to NR_3 species, which exist naturally in cotton fibres. The additional peak at 402.6 eV in the spectra of CC, Ag-C and Se-C corresponds to quaternary nitrogen species (NR_4^+). No chlorine was detected on the surface of UC, while the binding energy of Cl $2p_{3/2}$ peak at about 197.6 eV observed in other samples is typical for Cl^- ions. These new peaks on the modified samples demonstrate the successful grafting of quaternary ammonium groups onto the cotton fabrics. On Ag-C, the binding energy of the $Ag3d_{5/2}$ line and the Auger parameter calculated for Ag $M_4N_{45}N_{45}$ transition are close to that for non-oxidized silver[59], indicating the silver on the surface of Ag-C was mostly metallic silver. The $Se3d_{5/2}$ line for Se-C is centred at 55.3 eV, which is typical for non-oxidized elemental selenium[60]. These results confirm that the AgNPs and SeNPs formed *in situ* on the surface of CC were non-oxidized elemental nanoparticles.

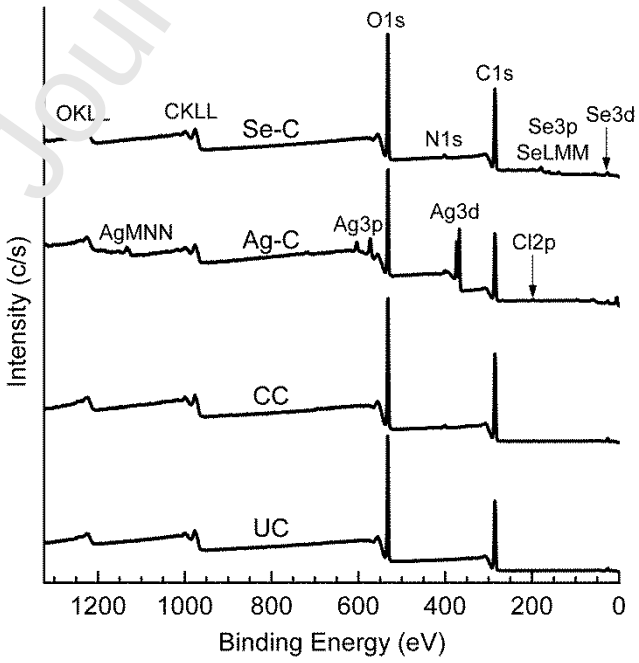

Figure 3. Survey XPS spectra of UC, CC, Ag-C and Se-C.

3.2 Antibacterial performance of the functionalised cotton

3.2.1 Quantitative analysis using the challenge test

Antibacterial performance of the functionalised cotton was assessed quantitatively using a challenge test method as described in the Absorption Method of ISO 20743:2013. Two associated values, antibacterial value 'A' and growth reduction rate R(%), were calculated and summarised in Table 2. They both describe the difference in the number of viable bacteria on the test samples compared to the control samples after incubation. The number of viable bacteria post incubation on the control samples should increase compared to time zero. If the test samples have antibacterial activity, the number of viable bacteria attached on the surface after incubation should be fewer than the number on the control. An 'A' value of 2 represents a 2 $\log_{10}$ reduction, which is equivalent to 99% of growth reduction R%.

Table 2. Growth reduction rate (R %) and antibacterial value 'A' of the modified cotton samples after 24 h contact time

Sample	*S. aureus*		*K. pneumoniae*		*E. coli*	
	R (%)	'A'	R (%)	'A'	R (%)	'A'
CC	97.51	1.61	>99.99	4.52	>99.99	3.24
Se-C (0.2 mM)	>99.99	5.30	>99.99	5.83	>99.99	5.66
Se-C (0.5 mM)	>99.99	5.36	>99.99	5.83	>99.99	5.66
Se-C (1 mM)	>99.99	5.36	>99.99	5.83	>99.99	5.66
Ag-C (0.2 mM)	>99.99	5.33	>99.99	5.83	>99.99	5.66

Ag-C (0.5 mM)	>99.99	5.36	>99.99	5.83	>99.99	5.66
Ag-C (1 mM)	>99.99	5.36	>99.99	5.83	>99.99	5.66

As can be seen from Table 2, the cationized cotton (CC) without the addition of any nanoparticles showed antibacterial activities against all of the three bacterial species tested, with 'A' values 1.61, 4.52 and 3.24 for *S. aureus*, *K. pneumoniae* and *E. coli*, respectively. The antibacterial effects of CHPTAC-modified cellulose materials have been reported by several recent studies[61–63]. It is thought that the negatively charged bacterial cells are absorbed onto the cationic surface and their cell membranes could be physically damaged due to the electrostatic interactions and the penetration of lipophilic alkyl groups, causing the leakage of cell constituents[64,65]. The cationic groups could also lead to the uneven distribution of moisture and nutrients[66]. Eventually, the bacteria could die from altered osmotic pressure, membrane damage and lack of nutrients[64–66]. It was found that the antibacterial efficacy of the cationized cotton against *S. aureus* was lower than against the two Gram-negative strains, although the growth reduction rate against *S. aureus* was still as high as 97.51%. *S. aureus* may be less susceptible to the cationic cellulose due to the fact that the Gram-positive bacterial cell wall has a comparatively thicker and more rigid peptidoglycan layer than Gram-negative strains[67], and the net negative surface charge of Gram-positive bacteria is also less than Gram-negative species[34]. Furthermore, the contact area between the spherical *S. aureus* cells and the cellulose surface is likely to be less than between the rod-shaped *K. pneumoniae* and *E. coli* cells and the surface. Therefore, the cationized cotton showed stronger antibacterial efficacies against *K. pneumoniae* and *E. coli* than against *S. aureus*. Overall, the CC samples without NPs showed good antibacterial performance against all three species tested. However, the employment of the NPs is of additional value as alternative antimicrobial modes of action are introduced, reducing the

potential for the bacterial cells to develop resistance, which is clearly a desirable characteristic[68].

It was found that both Se-C and Ag-C prepared with all of the three different concentrations of precursor salts (0.2, 0.5 and 1 mM) showed strong antibacterial performance, with growth reduction rates all above 99.99% and 'A' values all above 5 for both Gram positive and Gram negative strains, higher than for the cationized cotton. After 24 h contact time, the numbers of viable bacteria recovered from almost all of the NP-functionalised fabrics, with the exception of 0.2 mM Se-C and Ag-C against *S. aureus*, were lower than the limit of detection (Figure S4), making it difficult to differentiate the antibacterial activities of the Se-C and Ag-C with different concentrations of SeNPs and AgNPs. A supplementary qualitative test based on a chromogenic agar (Figure S5) showed some qualitative concentration-dependent effects; for example, the 1 mM Se-C and Ag-C showed the strongest antibacterial effect against *S. aureus* when the samples were immediately placed on chromogenic Nutrient Agar after inoculation (t= 0 h group on Figure S5).

The incorporation of SeNPs or AgNPs, even at a low concentration, further improved the antibacterial efficacies of the cationized fabrics. It has been widely reported that the positive surface charge of nanoparticles can enhance their antibacterial performance by facilitating the interaction between the negatively-charged bacterial cells and nanoparticles[69]. In our study, although the positive charge was not directly applied onto the nanoparticle surface, the presence of cationic groups on the cotton surface could also force the contact between the bacterial cells and the nanoparticles. It is believed that inorganic nanoparticles have multiple modes of action, which makes it difficult for bacteria to simultaneously evolve resistance against these actions. Huang *et al.*[32] investigated the potential antimicrobial mechanisms of SeNPs and detected promoted ROS production in the *S. aureus* cells treated with SeNPs compared to the control cells without SeNPs. Additionally, they found that the *S. aureus*

treated with SeNPs suffered from depletion of adenosine triphosphate (ATP), as well as the depolarisation of bacterial membranes and altered cell morphology (i.e. wrinkled cell wall). As a widely studied antimicrobial agent, AgNPs have also been found to have multiple antimicrobial mechanisms, including physical damage to the cell membranes, binding to proteins and DNA to interfere with the cellular functions, as well as inducing the generation of ROS. With the presence of both cationic quaternary groups and nanoparticles, the functionalised materials offer combined antimicrobial effects, which in theory can prevent the development of antimicrobial resistance.

3.2.2 *In situ* observation of bacterial cells on cotton samples using LIVE/DEAD staining

LIVE/DEAD staining was used to directly observe the status of the bacterial cells in contact with the fabric samples (Figure 4). Using confocal microscopy to conduct *in situ* observation avoids the uncertainty inherent in a bacterial removal procedure; for example, when conducting an *ex situ* observation, the dead cells may be removed more easily from the fabrics than the live cells, which may lead to erroneous results. As can be seen from Figure 4, on the UC, there were considerable numbers of live cells (green) of all the three bacterial strains, while there were also some dead cells present (red). Some cells will die naturally due to nutrient limitation on the untreated cotton samples.

When examining the cationized cotton (Figure 4), it is noticeable that the number of dead cells increased for all three of the strains compared with the UC. It is also evident that there were many yellow/orange coloured cells, especially of *S. aureus*. The intermediate colours (yellow and orange) of the cells are due to the varying amounts of PI entering the cells,

indicating different degrees of damage to the cell membrane, and thus these cells are often considered to be sub-lethally injured[70,71]. The results of the challenge test showed an increase in the number of *S. aureus* cells on CC over the 24 h incubation period (Figure S4). Therefore, it can be postulated that the cationic quaternary groups of the cationized cotton can compromise the membrane integrity of the *S. aureus* cells, but the effects may not always be lethal.

It is clear that almost all of the bacterial cells on the Se-C and Ag-C samples were dead after 24 h contact time. Small numbers of *K. pneumoniae* cells appeared to be yellow on the Se-C and Ag-C samples, indicating that the integrity of these cells was at least compromised. It is worth noting that in the challenge test, the bacterial inoculum was prepared in dilute broth and, therefore, the dynamics between bacterial cell growth and antibacterial effects would be different from the LIVE/DEAD assay where the inoculum was prepared in saline. In dilute broth, overall cell growth could occur when the damage was not significant or not as fast as the cell reproduction. It must be taken into consideration that the initial concentration of the inoculum used in the challenge test was between $1 - 3 \times 10^5$ CFU/mL and, even after 24 h incubation, the highest final concentration on the untreated cotton was approximately 10^8 CFU/mL (Figure S4). In contrast, in order to obtain a suitable number of bacteria to observe under the microscope, the inoculum concentration used in the LIVE/DEAD assay was over 10^9 CFU/mL. When the concentration of antibacterial agents remains the same on the sample but the bacterial concentration is increased, this may result in an insufficient antibacterial effect towards some of the cells. However, in this LIVE/DEAD assay, it can be clearly seen that the Se-C and Ag-C killed the majority of bacteria despite such a high inoculum level, demonstrating excellent antibacterial performance of the NP-modified fabrics.

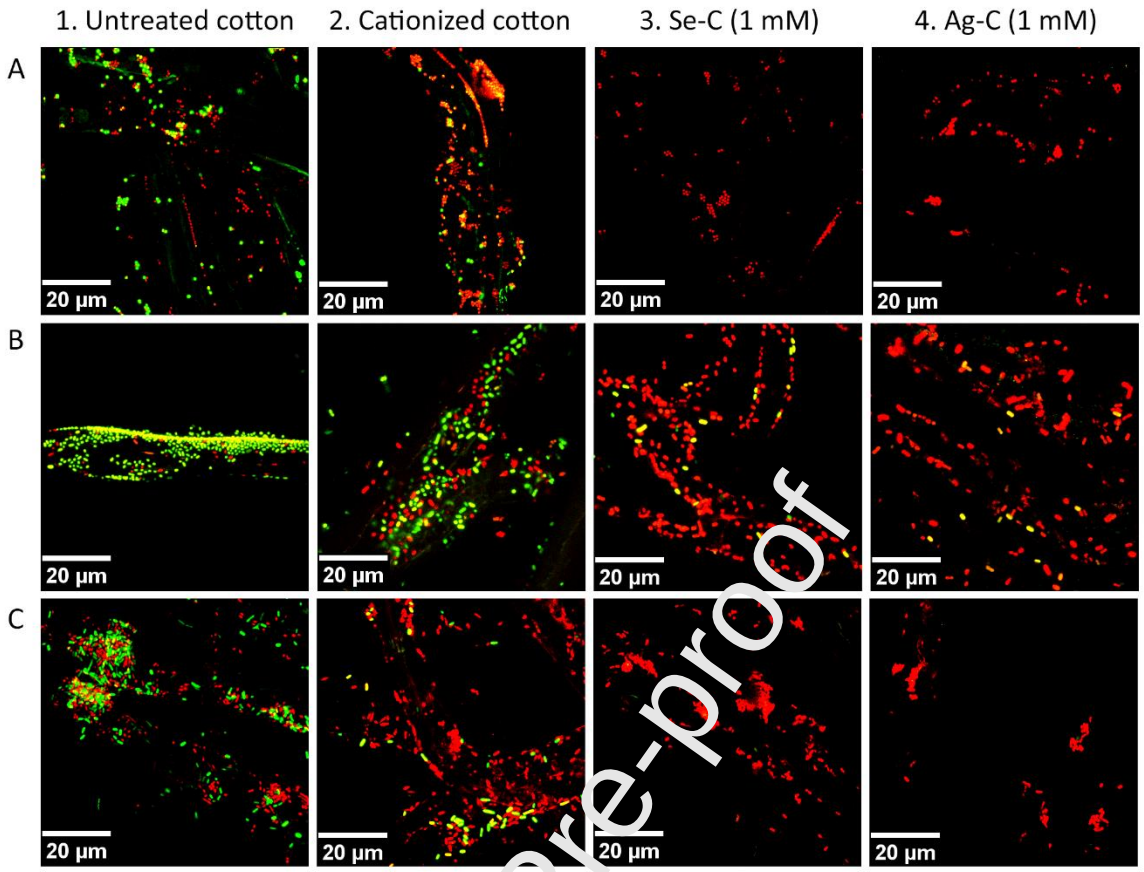

Figure 4. Confocal microscopy images of bacterial cells incubated on the cotton samples for 24 h before being stained with Baclight™ LIVE/DEAD™ staining kit; (A) *S. aureus*, (B) *K. pneumoniae*, and (C) *E. coli*; green= live, red=dead.

3.2.3 Morphology of bacterial cells in contact with the fabrics

The morphologies of the bacterial cells in contact with the fabric samples were observed with SEM (Figure 5). It can be seen that on the control UC, most of the cells display their expected morphologies; *S. aureus* being spherical, *K. pneumoniae* being short rods and *E. coli* being long rods. The LIVE/DEAD assay showed that many cells died naturally on the untreated cotton control sample and in the SEM images it can be seen, that most of the control cells did not exhibit significant morphological changes, with a small number of cells appearing

shrunken slightly. This may indicate that natural death of the cells does not result in significantly altered morphology. In contrast, morphological abnormalities can be seen on all three bacterial species incubated on the modified cotton surfaces. The *S. aureus* cells on the CC and the Ag-C were observed to have some indentations on the surface and were not as rounded as the control cells on the untreated cotton. The effects seemed to be more pronounced on the Se-C where some cells were clearly shrunken and wrinkled. *K. pneumoniae* cells on the CC and the Ag-C had similar morphologies, appearing collapsed. Interestingly, the *K. pneumoniae* cells on the Se-C were not flattened in the same manner, but deep holes were visible, which might indicate that the damage caused by the SeNPs occurred faster than the effects caused by the cationic quaternary groups, as such features were not visible on the *K. pneumoniae* – CC sample. The *E. coli* cells were also observed to be collapsed on all the modified cotton samples, with the effects more pronounced on Se-C and Ag-C than on the CC. Similar morphological changes including collapsing, shrinking, and dents/holes in the cells, have been observed in other studies where bacterial cells have been treated with antimicrobials such as silver nanoparticles[72], selenium nanoparticles[73], copper nanoparticles[74], and cationic antimicrobial peptides[75]. In summary, the bacterial cells on the modified cotton fabrics had significant morphological abnormalities, which indicated the damage of cell structures caused by the cationic quaternary ammonium groups and the nanoparticles. The SeNPs seemed to have caused more pronounced effects on the bacterial cells.

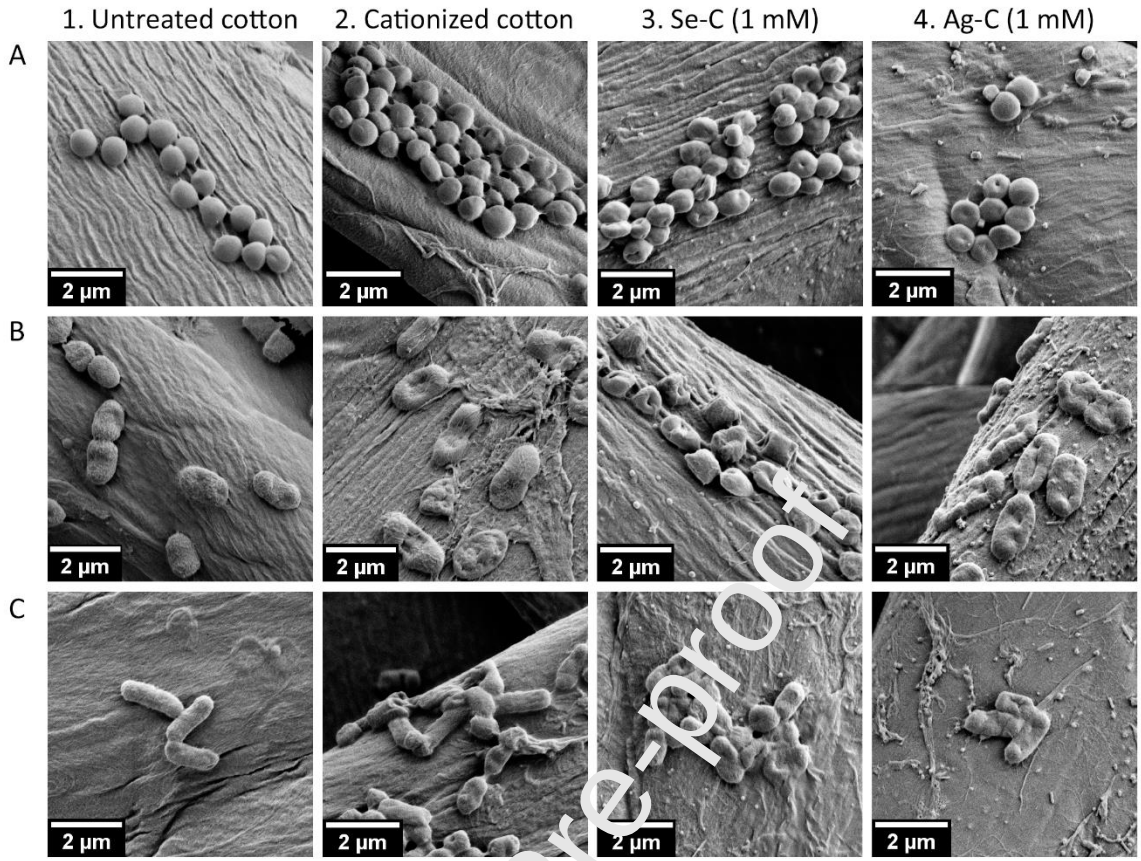

Figure 5. SEM images of bacterial cells incubated on the cotton samples for 24 h; (A) *S. aureus*, (B) *K. pneumoniae*, and (C) *E. coli*.

3.3 Washing durability of the functionalised fabrics

One of the major challenges of textile functionalisation with nanoparticles is the durability of the modification. In order to address this issue, we analysed the amounts of Se or Ag on the samples as well as antibacterial performance after laundering. The washing method was based on both the accelerated laundry method described in AATCC Test 61-2013 (Colorfastness to Laundering: Accelerated)[52] and the elevated washing temperature for healthcare linens recommended by the Department of Health[51]. As can be seen from Figure 6 (Table S2), all of the samples retained over 80% of the Se or Ag after 4 accelerated laundry

cycles (equivalent to 20 typical home laundry cycles), indicating excellent washing durability of the nanoparticle-fabric interaction. This may be due to the fact that particles formed *in situ* on the fibre surface fit the natural topography and therefore were physically lodged within the fibre. Moreover, the microwave treatment for the synthesis of nanoparticles may have resulted in the swelling of cotton fibres, which facilitated the penetration of nanoparticles into the intramolecular structure of the fibres[76,77]. Another interesting observation is that after repeated washing in hot water (>70 ^{o}C), the colour of Se-cotton turned from bright orange into darker colours (Figure S6), indicating some changes might have taken place to the SeNPs. SEM images were taken for the Se-cotton samples that were washed in hot water and it was noticeable that the SeNPs lost the smooth and spherical shape and became irregular and pointed; some Se nanowires can even be observed in the images (Figure S6). Many reports have discussed the transformation of red/orange amorphous or monoclinic nano-selenium into the grey/black trigonal selenium after thermal treatment[78]. Therefore, although the repeated washing did not lead to a significant loss of nanoparticles, retention of antibacterial properties was investigated.

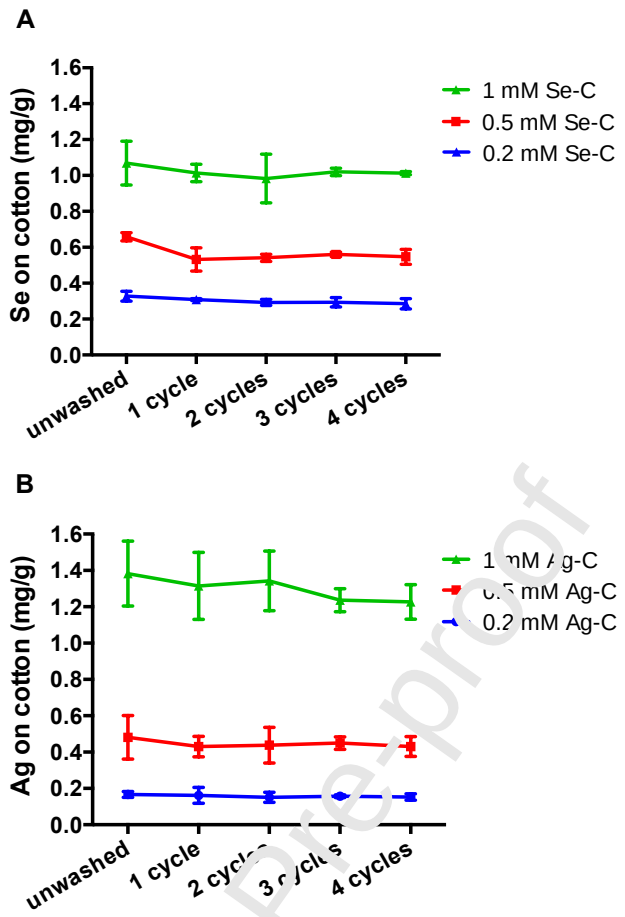

Figure 6. Concentration of (A) Se and (B) Ag on the modified cotton samples (mg/g) prepared with 0.2, 0.5, and 1 mM precursor salts, determined by MP-AES before and after repeated washing. Data are represented as mean with SD (n=3).

The antibacterial activity of the modified cotton fabrics before and after being washed for 4 accelerated laundry cycles are summarised in Figure 7. As can be seen, the 'A' values of the cationized cotton against all three bacterial species reduced slightly ('A' value reduction<0.5). The growth reduction rate (R%) of CC against *S. aureus* reduced from 97.51% to 95.76%; the R% values of all other groups were still higher than 99.99%. The reduction of antibacterial values may be due to the fact that the detergent contains large amount of anionic surfactants, which may have neutralised some of the cationic groups after repeated washing.

For both Se-C and Ag-C, the samples prepared with 0.2 mM precursor salt exhibited lower antibacterial activities after being washed; while the samples prepared with higher concentrations of precursors (0.5 and 1 mM) did not show reduced antibacterial activities. The decreased 'A' values of 0.2 mM Se-C and Ag-C may indicate that concentrations of nanoparticles on these samples were at a critical level for the antibacterial activities that could inactivate all of the bacteria. As discussed previously, the antibacterial activities were the combined effects of cationic quaternary groups and nanoparticles. The slight decrease in the cationic effects was evidenced by the reduced 'A' values of cationized cotton; and the slight decrease of Se or Ag contents on the 0.2 mM Se-C or Ag-C was evidenced by the MP-AES results. These two factors together led to the decreased 'A' values of 0.2 mM Se-C and Ag-C.

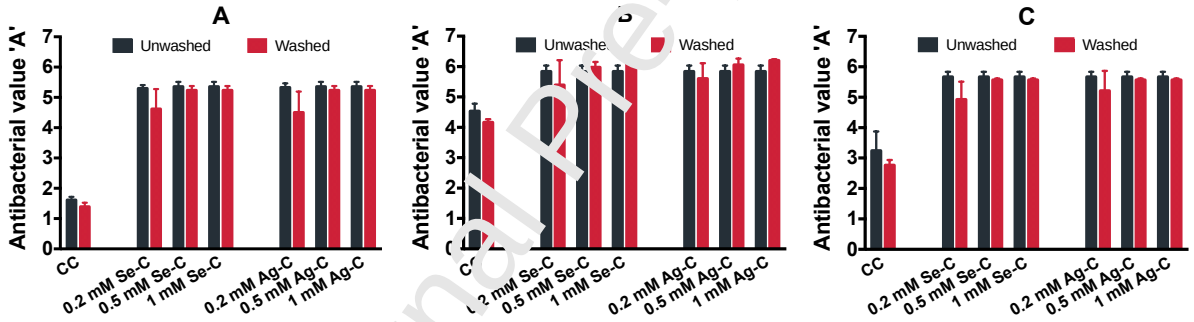

Figure 7. Antibacterial value 'A' of the modified cotton fabrics before and after being washed for 4 accelerated laundry cycles against (A) *S. aureus*, (B) *K. pneumoniae*, and (C) *E. coli*. Data are represented as mean with SD (n=3).

3.4 Cytotoxicity of functionalised fabrics towards human cells

The studies into the cytotoxicity of NP-functionalised textiles have been discussed in various reports[79–81], where an indirect contact evalution method has been employed since mammallian cells are not expected to grow directly on the fabrics. In our study, the fabric

samples were immersed in sterile RO water for the extraction and the extracts were then mixed with double strength cell culture medium to treat the cells. Considering the common usage of textile materials, a respiratory epithelial cell line (16HBE14o-) and a dermal keratinocyte cell line (HaCaT) were chosen for the *in vitro* cytotoxicity tests. An LDH assay and an ATP assay were employed to determine the cell death rate and cell viability respectively. As can be seen from Figure 8 (A&B), no significant difference was found between any of the samples with the medium-only negative control for both of the cell lines, indicating none of the fabric samples induced significant cell death. Moreover, cell viability was calculated using the amount of ATP detected from the culture, which is related to the number of metabolically active cells. The viability of the cells treated with the fabric sample extracts did not show significant difference from the negative control either (Figure 8 C&D), which is in accordance with the results of the LDH assay. The concentration of Ag or Se released from the NP-functionalised fabrics was found to be 0.94 ± 0.24 ppm and 0.69 ± 0.15 ppm (mean ± SD) respectively. After mixing with double strength cell culture medium, the concentration of Ag or Se in the extracts was halved. Many reports have discussed the cytotoxicity of AgNPs on mammalian cells. The concentration range of nanoparticles that can induce cytotoxicity is dependent on various factors, including particle size, particle surface decoration, particle shape/crystallinity, dispersion media, and cell type[82]. Therefore, it is difficult to make direct comparisons with other data reported in the literature. Although, various reports have shown that AgNPs at a concentration of 1 ppm did not result in significant cytotoxicity towards mammallian cells *in vitro*[83,84]. Reports have also suggested that the SeNPs were not toxic to mammalian cells at concentrations up to 37.8 ppm[30], 128 ppm[34], and 500 ppm[29]. The low concentration of Ag or Se found in the extracts probably explains the non-toxic results of the test and, additionally, demonstrates the good durability of the nanoparticles attached to the fabric surfaces.

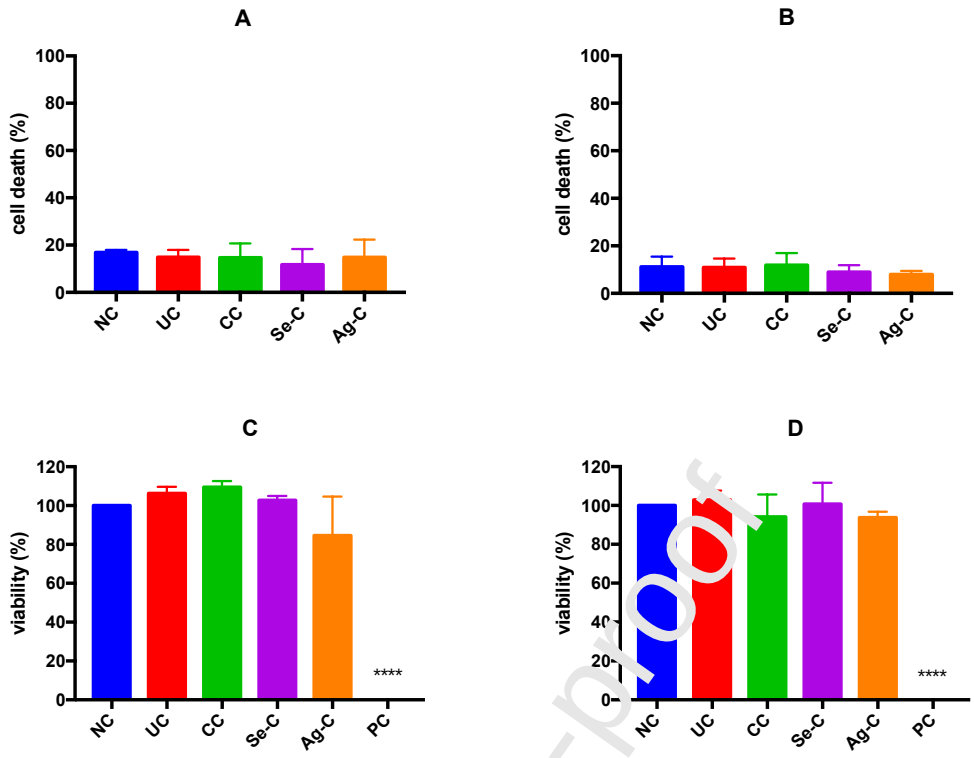

Figure 8. Cell death rate of (A) 16HBE14o- and (B) HaCaT cells after 24-h exposure to the extracts of fabric samples; viability of (C) 16HBE14o- and (D) HaCaT cells after 24-h exposure to the extracts of fabric samples. NC=negative control (medium only); PC=positive control (medium supplemented with Triton-X 100). The viability of NC was set as 100%. Data are represented as mean with SD (n=3; **** $p<0.0001$).

4. Conclusions

A rapid and simple method for preparation of selenium and silver nanoparticles on the surfaces of cationized cotton based on the microwave assistant reduction of precursor salts with ascorbic acid has been reported in this work. To the best of the authors' knowledge, this is the first time that selenium nanoparticles, a relatively new and understudied antimicrobial agent, have been prepared *in situ* on cationized cellulose without any stabilising agent. Moreover, this is the first report showing that both metal and non-metal nanoparticles can be

prepared on a cellulose substrate using the same approach. The characterisation of the modified fabrics demonstrated that both AgNPs and SeNPs provided a good coverage over the fibre surfaces, and the particles had a narrow size distribution of between 40 nm to 140 nm. The antibacterial evaluation revealed that the cationization treatment alone exhibited some antibacterial effect, while the addition of nanoparticles greatly increased the antibacterial performance of the fabrics. The bacterial structures appeared to be severely damaged by the cationic quaternary groups and the nanoparticles. Although there have been controversial results regarding the antibacterial performance of SeNPs against some bacterial species[34,35], in our study, the antibacterial efficacies of all the NP-modified samples were so high that no viable bacteria could be detected post-incubation when testing using the challenge test (Absorption Method of ISO 20743:2013). The laundry tests indicated that the nanoparticles had excellent durability and were securely attached to the cotton surfaces. The preliminary *in vitro* cytotoxicity studies conducted using the indirect contact method did not show significant cytotoxicity of the modified fabrics towards 16HBE14o- and HaCaT cells, addressing the safety concerns of using nanoparticle-functionalised textiles. Future development of cellulose-based biomaterials using this method may require more comprehensive toxicity studies such as *in vitro* studies employing a direct contact method, bacterial endotoxin testing, or perhaps *in vivo* studies.

Considering the excellent antimicrobial performance, low cytotoxicity and resilience to the laundry process, the functionalised textiles have the potential to be used in healthcare environments to reduce the transmission and spread of pathogens. The simple and versatile method presented in this article can be easily adapted for preparation of modified cellulose materials that benefit from the combined antimicrobial effects of cationic quaternary groups as well as antimicrobial nanoparticles, for diverse applications such as wound care, tissue scaffold or antimicrobial filtration.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Highlights

- *In situ* microwave-assisted synthesis of Se or Ag nanoparticles on cationized surface
- Se nanoparticles were effective against Gram-positive and Gram-negative strains
- Cationic groups and inorganic nanoparticles offer combined antimicrobial activities
- Antibacterial activity of Se and Ag modified fabrics retains after repeated washing
- Se nanoparticles a good alternative to Ag for developing an anti-infective material