

Can natural fibers be a silver bullet? Antibacterial cellulose fibers through the covalent bonding of silver nanoparticles to electrospun fibers

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Abstract

Natural cotton was dissolved in a room-temperature ionic liquid 1-ethyl-3-methyl acetate and wet-jet electrospun to obtain nanoscale cotton fibers with a substantially reduced diameter—and therefore an increased surface area—relative to natural cotton fibers. The resulting nano-cotton fibers were esterified with trityl-3-mercaptopropionic acid, which after selective de-tritylation afforded nano-cotton fibers containing reactive thiol functionality. Silver nanoparticles that were covalently attached to these sulfhydryl groups were assembled next. The microstructure of the resulting nanocomposite was characterized, and the antibacterial activity of the resulting nano-cotton Ag-nanoparticle composite was also studied. This nanocomposite showed significant activity against both Gram-negative and Gram-positive bacteria.

Keywords: nanoparticle, antimicrobial, cellulose, electrospinning

(Some figures may appear in colour only in the online journal)

1. Introduction

Natural cotton is one of the purest cellulose sources and is the most significant commercial source of natural fiber. As a material, cotton holds a number of attractive properties, including biocompatibility, biodegradability, and both thermal and chemical stability. Natural cotton fibers are 10 to 20 μm in diameter and 2–3 cm in length, and are not typically considered to be a nanomaterial [1]. However, it is possible to prepare nanoscale cotton fibers by dissolving natural cotton in room-temperature ionic liquid (RTIL), 1-ethyl-3-methylimidazolium acetate ([EMIM][Ac]), and then reforming the cotton cellulose as long continuous nanofibers of 100–1000 nm in diameter by wet-jet electrospinning in a water coagulation bath [2]. Such reformed cotton fibers offer

both enhanced surface area and the potential for improved physical properties.

Silver nanoparticles are conveniently prepared from silver nitrate and represent one of the most commonly studied nanoparticles [3]. The antimicrobial properties of silver nanoparticles (AgNPs) are well known [4], but the toxicity of nanoscale silver and its potentially adverse environmental impact has limited the use of AgNPs as antimicrobial agents [5]. One approach to ameliorating the adverse properties of nanoscale silver is to incorporate it into stable nanocomposites.

Polysaccharide nanocomposites, particularly those comprised of nanocellulosics, have recently seen widespread investigation for a variety of medical and nonmedical applications [6, 7]. AgNPs non-covalently linked to cellulose

reportedly demonstrate antimicrobial activity through the release of nanoscale silver [8]. Recently, our laboratory has investigated non-covalent cellulose nanocomposites prepared through wet-jet electrospinning [6]. However, in the current study, AgNPs with low polydispersity are covalently attached through thiol groups to electrospun cotton-based cellulose nanofibers. These cellulose-AgNP nanocomposites were physically characterized and their antimicrobial activities against both Gram-negative and Gram-positive bacteria were assessed. The potential applications for such nanocomposites include antimicrobial protective clothing for medical personnel, antimicrobial wound dressings, antibacterial food-packaging materials, and water treatment applications.

2. Materials and methods

2.1. Materials

Cotton balls were purchased from a local pharmacy. Sodium acetate was purchased from Mallinckrodt AR analytical reagents (St. Louis, MO, USA). 4-Dimethylaminopyridine (DMAP) was purchased from Acros Organics (Fair Lawn, NJ, USA). 3-Mercaptopropionic acid, the RTIL 1-ethyl-3-methylimidazolium acetate ([EMIM][Ac]), trityl chloride, *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (EDC), sodium borohydride, and other common reagents were purchased from Sigma-Aldrich Chemicals (St. Louis, MO, USA). Silver nitrate (AgNO_3) was purchased from Amresco (Solon, OH, USA). *N*-hydroxysuccinimide (NHS) was purchased from Thermo Scientific (Rockford, IL, USA). All solvents used were purchased from Fisher Scientific (Pittsburgh, PA, USA).

2.2. Covalent attachment of AgNPs onto electrospun cotton fibers

2.2.1. Electrospinning cotton fibers. Natural cotton (240 mg) was added to [EMIM][Ac] (19.76 g) to prepare a 1.2 wt% cotton solution in RTIL. The mixture was mechanically stirred using a magnetic stir bar on a digital stirring hotplate (Fisher Scientific™ Isotemp™ 11-300-49SHP) at 80 °C for 8 h until a homogeneous solution was formed.

A previously reported dry-jet wet electrospinning technique was used to produce nanoscale cotton fibers.⁶ The RTIL-cellulose solution was transferred to a 5 ml syringe connected to a spinneret (MECC, Ogori, Fukuoka, Japan) using PTFE tubing. The spinneret was fitted with a stainless steel needle with an internal diameter of 0.60 mm. The needle was connected to a high-voltage power supply (CZE1000R, Spellman, Hauppauge, New York, USA), which is capable of generating a DC voltage up to 30 kV. Electrospun cotton fibers were collected in a de-ionized aqueous coagulation bath to remove the [EMIM][Ac] and solidify the fibers. A small sheet of aluminum foil (20 μm thick) was electrically grounded and placed as a current collector on the bottom of the coagulation bath (inside the vessel). The distance between the needle tip and the surface of the water in the coagulation

bath remained constant at 10 cm. The electrospinning solution was fed at a constant rate using a mechanical syringe pump (NE-1000, New Era Pump System Inc., Wantagh, New York, USA) at 40 μl min⁻¹. The applied voltage ranging from 15–20 kV was optimized to obtain sufficient spinnability resulting in continuous fibers. Fibers collected in the coagulation bath formed an entangled web of flexible fibers. These fibers were recovered and washed with distilled water five times to remove the [EMIM][Ac], resulting in fully coagulated cellulose hydrogel fiber mats. The resulting fiber mats were used directly for the next modification step.

2.2.2. Synthesis of trityl-3-mercaptopropionic acid. A mixture of 3-mercaptopropionic acid (100 μl, 1.15 mmol) and trityl chloride (481 mg, 1.73 mmol) was stirred in 0.65 ml dimethylformamide (DMF) for two days at room temperature. Aqueous sodium acetate (7 ml of 10 wt% solution) was then added and the obtained precipitate was filtered and washed with distilled water. The recovered precipitate was suspended and stirred in acetone at 50 °C for 30 min and filtered after cooling. The residue was washed with acetone and then with diethyl ether to obtain a final product of 370 mg (yield 89%) of trityl-3-mercaptopropionic acid. The spectral data were consistent with the reported literature [9].

2.2.3. Covalent attachment of AgNPs onto electrospun nano-cotton fiber surface. 1-Ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride (EDC) (19.2 mg, 0.1 mmol) and NHS (16 mg, 0.14 mmol) were added to (34.8 mg, 0.1 mmol) trityl-3-mercaptopropionic acid dissolved in 3 ml *N,N'*-dimethylformamide (DMF) and stirred for 40 min at room temperature. Electrospun cotton fibers (10 mg) were added to the solution of pre-activated trityl-3-mercaptopropionic acid, and 4-dimethylaminopyridine (DMAP) (5.4 mg, 0.05 mmol) was then added. The reaction was shaken overnight in a shaking incubator at 220 rotations min⁻¹ at 37 °C. The nano-cotton fibers were taken out, washed with DMF three times and washed with water three times.

Deprotection of the trityl groups was accomplished using 80% trifluoroacetic acid (TFA) at room temperature [10]. When 80% trifluoroacetic acid (TFA) was added to the nano-cotton fibers, the solution changed color from transparent to yellow, indicating that the trityl groups had been removed from the cotton fiber (figure 1). The cotton fiber was washed with water several times until colorless. The activated free thiol-groups on the cotton fiber surface were now ready for the covalent immobilization of silver.

The nano-cotton fibers were immediately transferred to a 25 mM solution of AgNO_3 and gently shaken for 1 h to bind Ag^+ ions to the thiol groups on the surface of the modified nano-cotton fibers. The nano-cotton fibers were then carefully transferred to 20 ml vials with 5 ml water added to completely cover the fibers. The vials were placed in an ice bath (0 °C). Aqueous sodium borohydride (1 mol l⁻¹) was then added dropwise to the vials. The color of the cotton fibers changed to brown indicating the growth of AgNPs (figure 1(C)) [11].

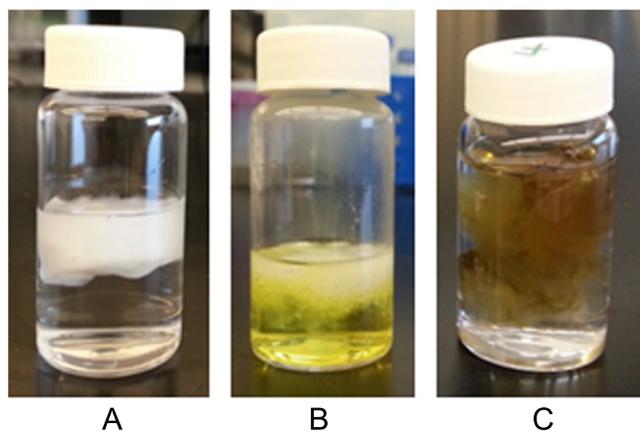


Figure 1. Optical images of (A) electrospun cotton fiber web, (B) thiol-surfaced cotton fiber web, and (C) AgNP covalently attached cotton fiber web.

The cotton fibers were washed with water several times to remove excess loosely bound AgNPs not covalently attached to the fiber surfaces and the cotton was freeze-dried to form a loose structure similar to a cotton ball.

2.3. Characterization

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were collected with a PerkinElmer Spectrum One spectrometer (PerkinElmer, Inc. Waltham, MA, USA) using the diffuse reflectance sampling accessory with a zinc selenide internal reflection element (IRE). These spectra were collected using the rapid-scan software spectrum v5.3.0 with eight scans and a resolution of 4 cm^{-1} . X-ray photoelectron spectroscopy (XPS) measurements were carried out in a PHI 5400 instrument with a 102 W AlK_α probe beam. The spectrometer was configured to operate at high-resolution with a pass energy of 20 eV . UV-vis spectroscopic measurements of the particles relied on a Perkin-Elmer Lambda 950 spectrometer operated with a step size of 2 nm . Samples were imaged using a field emission scanning electron microscope (FE-SEM) using a Zeiss SUPRA-55 instrument (Oberkochen, Germany). All samples were sputter-coated with 1 nm of Pt (Denton Vacuum Desk IV, Moorestown, NJ) prior to imaging. Images were obtained at a working distance of $5.0\text{--}5.2\text{ mm}$ using an acceleration voltage of 2 kV . The presence of AgNPs on the surface of the coated fibers was confirmed with a Bruker D8-discover x-ray diffractometer using graphite monochromated CuK_α radiation. Atomic absorption spectroscopy (AAS) was carried out using a Perkin-Elmer Model 3100 AAS, with AgNO_3 used as a standard and internal check throughout.

2.4. Antibacterial activity of the fiber surface

The antibacterial activity of the electrospun cotton fiber with AgNPs covalently attached (CF-AgNPs) was tested against *Bacillus cereus* 3551 (Gram-positive) and *Escherichia coli* BL21 (Gram-negative) by two different methods: (i)

qualitative evaluation with an agar diffusion assay and (ii) quantitative evaluation in a liquid medium.

For the qualitative evaluation, overnight cultures of *B. cereus* or *E. coli* were positioned in a Petri dish filled with NB or LB agar, respectively. CF-AgNP mats and unmodified electrospun cotton fiber (CF) mats (negative control) were placed over the colony and the cultures were incubated in an oven at 37°C for 24 h. After this period, the cultures were removed from the oven. The antibacterial activity was identified and estimated by a clear zone of bacterial inhibition around the samples.

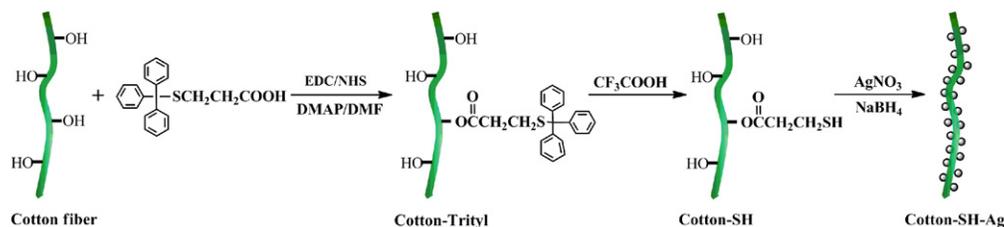
To quantitatively evaluate the antibacterial activity, CF-AgNP mats (80 mg) were added to 2 ml of phosphate-buffered saline (PBS) suspension of a stationary phase culture of *B. cereus* 3551 ($1.3 \times 10^6\text{ cfu ml}^{-1}$) (cfu stands for colony-forming units) or 149 mg CF-AgNP mats were added to 2 ml PBS suspension of *E. coli* BL21 ($3.7 \times 10^7\text{ cfu ml}^{-1}$). The corresponding equivalent weights of unmodified CFs were included in these assays as negative controls. The suspensions were incubated at 37°C with continuous shaking for 1 h. For the control, after 1 h of incubation in PBS, the viability of the bacteria was comparable to the initial inoculum. At the end of incubation, the bacterial suspensions that underwent proper serial dilution in PBS were plated on NB agar for *B. cereus* 3551 or LB agar for *E. coli* BL21 and incubated overnight at 37°C . The number of bacteria was counted to determine the presence or absence of viable bacteria. The values reported are the mean (\pm) standard deviation of three independent experiments with comparable results.

2.5. Release characteristics of AgNPs

The concentration of AgNPs released in a liquid medium (distilled water, or simulated body fluid (SBF)) from the CF-AgNPs was measured by atomic absorption spectroscopy (AAS). The results were reported as average values ($n = 3$). Prior to the release assay, the actual amount of AgNPs covalently bound on the cotton fiber surface was determined. The actual amount of Ag was quantified by treating each film specimen with 2 ml of 95% nitric acid (HNO_3), followed by the addition of a liquid medium (distilled water, or SBF) to obtain a total volume of 12 ml .

The silver released from the CF-AgNPs was assessed in distilled water and SBF as the releasing medium. The CF-AgNPs (12.2 mg) immersed in 12 ml of the SBF and the CF-AgNPs (9.1 mg) immersed in 12 ml of water were shaken in a shaking incubator at $220\text{ rotations min}^{-1}$ at physiological temperature, 37°C , to simulate local *in vivo* release conditions. Aliquots were withdrawn from these solutions at fixed time intervals of 1 h, 5 h, 10 h, 1 d, 5 d, and 10 d for the determination of silver release and the equivalent volumes of fresh deionized SBF or water were replaced in the containers after each sampling to maintain a constant medium volume. At each time point, the measurements were carried out in triplicate. The cumulative amount of silver released was calculated from the data obtained.

The control sample of CF-AgNPs, which was fully dissolved in concentrated HNO_3 , resulted in a solution with



Scheme 1. Schematic for the covalent attachment of AgNPs onto electrospun cotton fibers.

$[Ag^+] = 524.4 \text{ mg l}^{-1}$. Continuous shaking at body temperature (37°C) in distilled water did not result in any detectable release of silver from the CF-AgNPs. The same study in SBF resulted in a maximum release of 0.503 mg l^{-1} after 9 d continuous shaking at 37°C , approximately equivalent to a 0.1% loss of AgNPs from the cotton fiber surfaces.

3. Results and discussion

3.1. Covalent attachment of AgNPs onto an electrospun cotton nanofiber surface

Natural cotton was dissolved in RTIL and wet-jet electrospun in water to prepare nano-cotton fibers with an increased surface area relative to natural cotton fibers. The nano-cotton fibers (figure 1(A)) were then modified through EDC-activated esterification with trityl-3-mercaptopropionic acid (scheme 1). The trityl protecting group was removed by treatment with trifluoroacetic acid exposing the sulfhydryl groups of the modified nano-cotton fibers (figure 1(B)). Treatment with $AgNO_3$ in the presence of $NaBH_4$ results in the covalent attachment of AgNPs to the nano-cotton backbone (figure 1(C)). The chemistry in these reactions can be conveniently followed through the color changes observed in the modified nano-cotton fibers.

The ATR-FTIR spectra of the original nano-cotton fibers and nano-cotton esterified with trityl-protected thiopropionate show the same cellulose characteristic FTIR peaks (i.e., O-H, C-H and C-O stretching vibrations at 3670 cm^{-1} , 2905 cm^{-1} and 1060 cm^{-1} , respectively), as does the cotton source used (figure 2). The region between $1200\text{--}1500 \text{ cm}^{-1}$ shows several bands that correspond to the deformation of the primary and secondary -CH groups. After the covalent attachment of trityl-3-mercaptopropionic acid, new peaks appear at 1708 cm^{-1} (carboxyl stretching vibrations) and 1608 cm^{-1} and 1503 cm^{-1} (aromatic ring C=C stretching vibrations), confirming that esterification has taken place.

The cotton fiber, nano-cotton-trityl fiber, nano-cotton-SH fiber, and nano-cotton-SH-Ag fiber were analyzed by XPS (figure 3). The general scan spectrum shows the presence of the principal C1s, O1s, S2p, and Ag3d core levels for AgNP-coated cotton fiber with no evidence of impurities. Of the C1s, O1s, S2p, and Ag3d core levels from these fibers, the C1s core level peak for nano-cotton fiber was at 286 eV (figure 3(A)), while for nano-cotton-trityl fiber, one new C1s core level peak was observed at 285 eV resulting from the introduction of the trityl groups (figure 3(B)). In the nano-

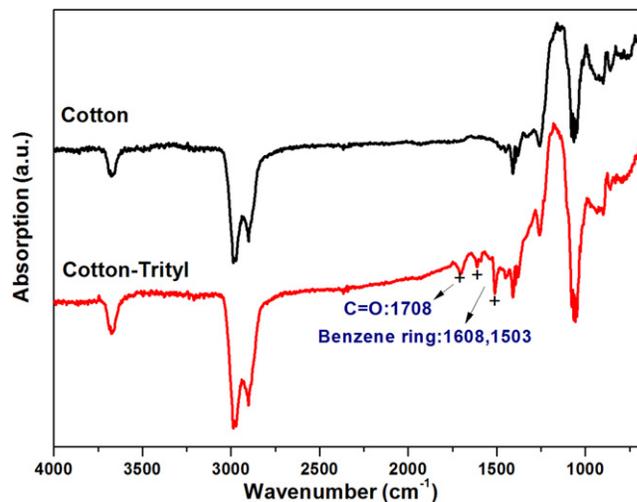


Figure 2. ATR-FTIR spectra of nano-cotton and nano-cotton-trityl fibers.

cotton-SH fiber, only one peak was again observed due to the deprotection of the trityl groups (figure 3(C)). The O1s core level peak (532 eV) showed no differences. In the case of the cotton-SH fiber, the S2p core level peaks were small and not easily detected. It was possible to fit the S2p core level satisfactorily to a peak at 163 eV (figure 3(C)). After the AgNPs were assembled, the peak shifted to 161 eV , which was most likely the result of C-S-Ag bonding (figure 3(D)). At the Ag3d core level, the binding energies of Ag in the AgNP covalently-attached cotton fiber were 367.4 eV ($3d_{3/2}$) and 373.4 eV ($3d_{5/2}$), which are lower than those of elemental silver (368.4 eV and 374.4 eV) because of the covalent bonding between sulfur and silver. Thus, XPS analysis clearly demonstrates that AgNPs are covalently immobilized on the surface of the nano-cotton fibers through a strong thiol-Ag bond.

The pristine natural cotton fibers are completely white, and the regenerated nano-cotton fibers are also very white as evidenced by the photograph in figure 1. The UV-visible spectrum of the brown-colored nano-cotton-AgNP composite is shown in figure 4. The absorbance maximum in the spectrum associated with the plasmon peak at 412 nm corresponds to the surface-bound AgNPs.

3.2. Film morphology

The morphology of the film consisting of the nano-cotton-AgNP composite was examined by FESEM (figure 5). The images clearly show an entangled mat of cellulose nanofibers with nanoparticles on their surfaces. These nanoparticles were

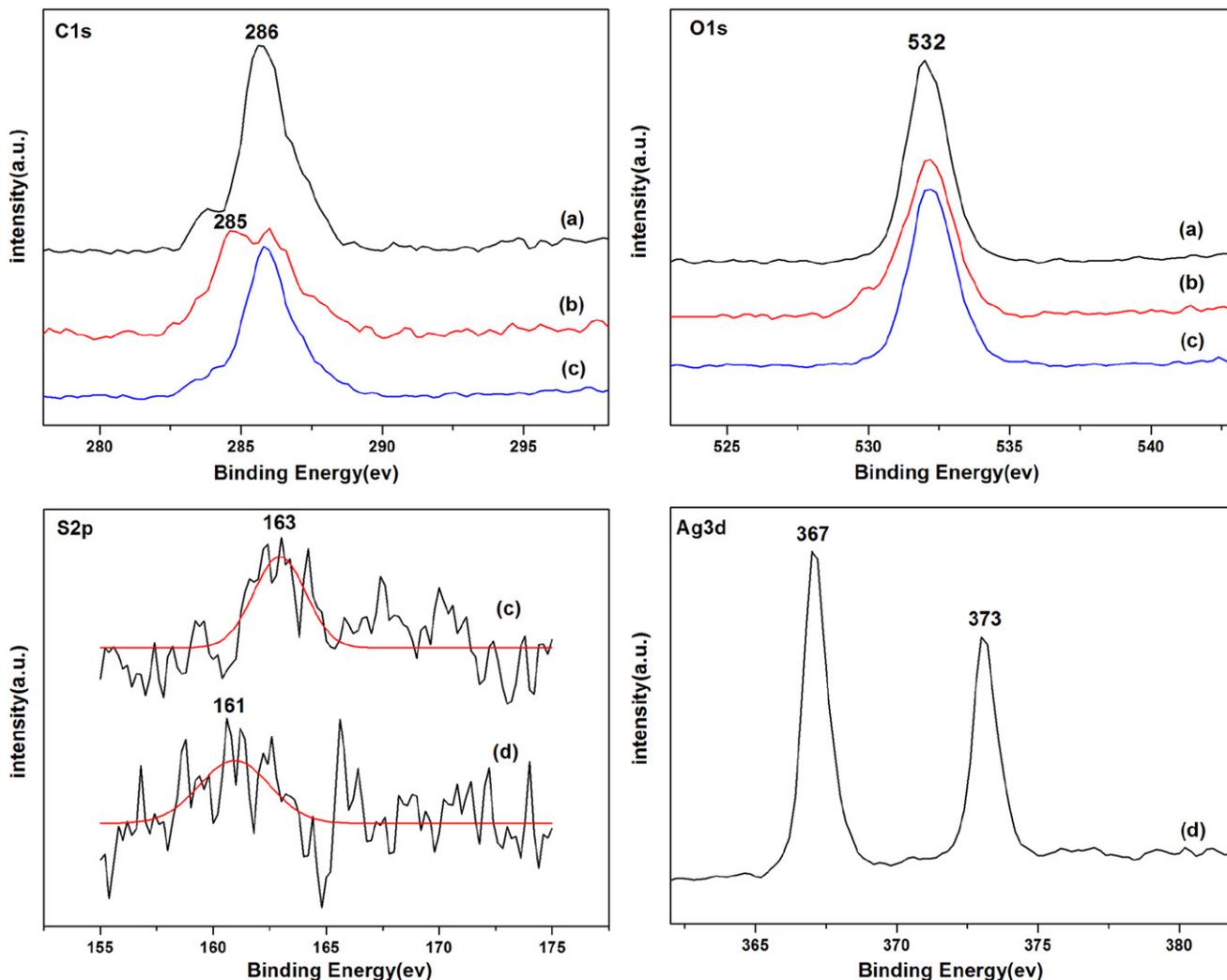


Figure 3. XPS spectra for carbon, oxygen, sulfur, and silver for (a) nano-cotton fiber, (b) nano-cotton-trityl fiber, (c) nano-cotton-SH fiber and (d) nano-cotton-SH-Ag fiber (arbitrary units).

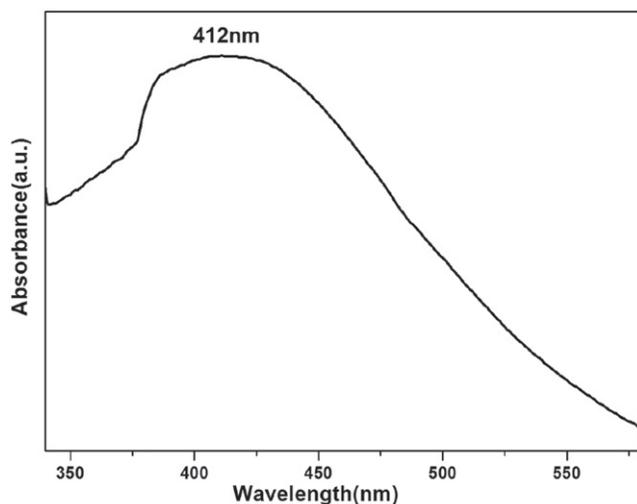


Figure 4. UV-visible spectra of AgNP-coated cotton fiber (arbitrary units).

confirmed to be covalently bound AgNPs through a variety of studies presented here.

3.3. Crystal structure of AgNPs

The nano-cotton fiber AgNP composite was examined by XRD (figure 6). The XRD showed the face-centered cubic lattice of silver with peaks at $2\theta = 38.116^\circ$ [111], $2\theta = 44.300^\circ$ [200], $2\theta = 64.445^\circ$ [220] and $2\theta = 77.399^\circ$ [311]. The prominence of the [111] peak indicates that these are polycrystalline NPs, which are typically larger than 20 nm [12]. A broad peak for regenerated cellulose was observed between $15\text{--}20^\circ$, with no discernible peaks that would suggest crystalline cellulose domains [13].

3.4. Antibacterial evaluation of film surface

The antibacterial activity of the nanocomposite was assessed using two different bacterial species, *B. cereus* 3551 (Gram-

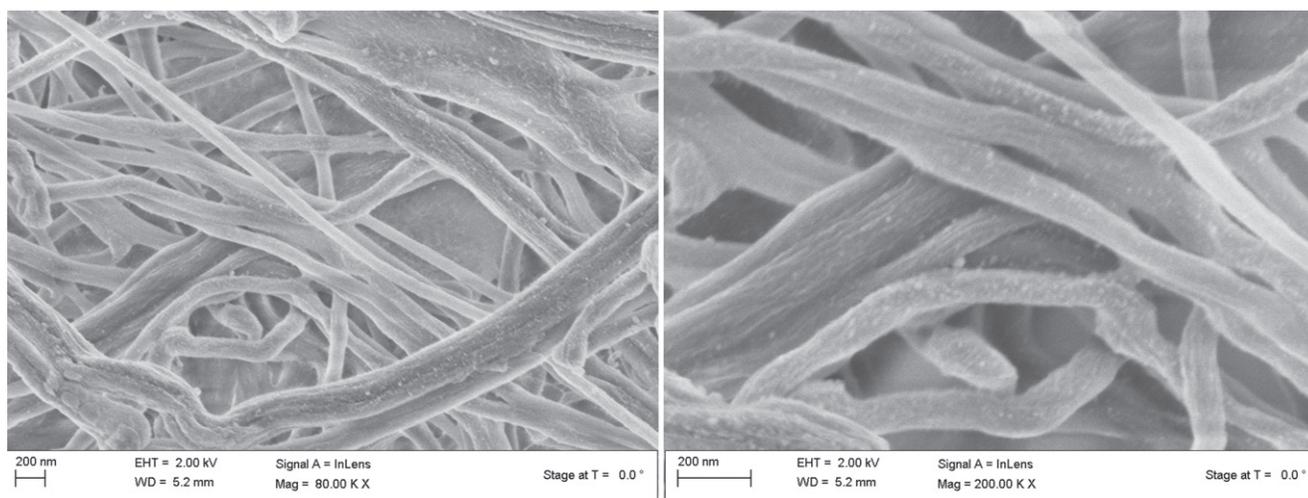


Figure 5. FE-SEM micrographs of AgNP-coated cotton fiber.

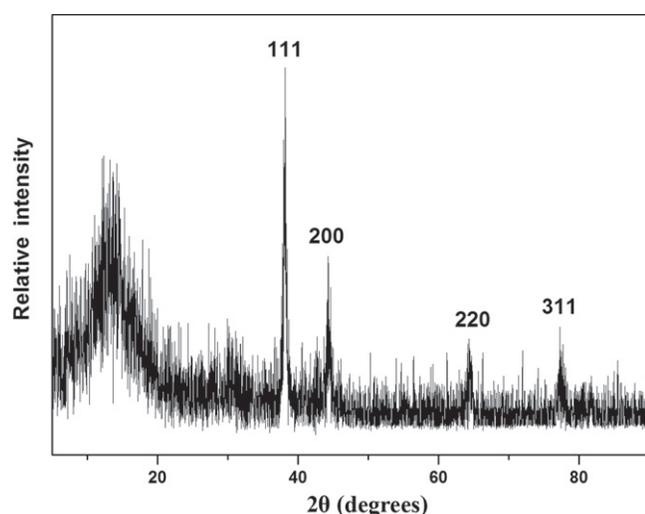


Figure 6. XRD spectrum of AgNP-coated cotton fiber.

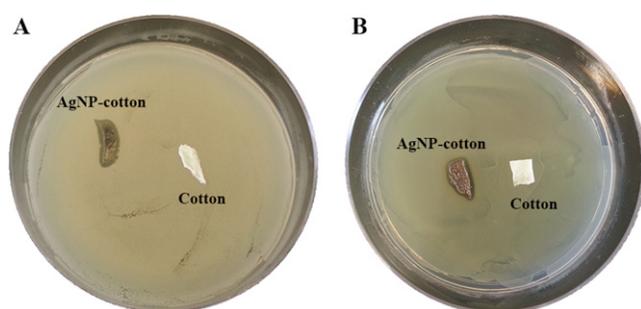


Figure 7. Antimicrobial activities of the AgNP covalently attached cotton fiber and unmodified cotton as the negative control. (A) *B. cereus* 3551 and (B) *E. coli* BL21.

positive) and *E. coli* BL21 (Gram-negative). First, a solid phase qualitative assay was performed (figure 7). At inhibitory concentrations around the nanocomposite, no growth of the microbes associated with a clearance zone was observed. A growth inhibition zone of >1 mm suggests good antibacterial properties.

A quantitative solution-phase assay was performed to determine the antibacterial activity of the nanocomposite against the same two bacteria (figure 8). After 1 h of contact with AgNP-coated cotton fibers, bacteria were taken out of the PBS and the number of cfu ml⁻¹ was evaluated. The nanocomposite killed 100% of both the *B. cereus* and *E. coli* within 1 h. The *in vitro* results show that the nanocomposite coating effectively kills both Gram-negative and Gram-positive bacterial strains causing nearly a six-log drop in cfu ml⁻¹ for *B. cereus* and a seven-log drop in cfu ml⁻¹ for *E. coli* BL21. The uncoated cotton controls displayed no antibacterial effect (figure 8). These results are consistent with the known antibacterial activity of AgNPs (Pinto *et al* 2009). The high activity of this nanocomposite can be explained by the small particle/fiber sizes, leading to a large surface area, and thus large antimicrobial effect.

3.5. Release of silver by nanocomposite

This nanocomposite contains AgNPs on nano-cotton fibers and has a high surface area per unit mass. Despite the covalent linkage between the AgNPs and the cellulosic nanofibers, a slow release of silver is expected due to the high surface area of this nanocomposite.

The optical image of the nanocomposite shows that after 20 d immersion and shaking in SBF or water, the fiber still has a uniform brown color (figure 9). This suggests that most of the AgNPs are retained in the nanocomposite. The UV-vis spectrum was also used to track the silver released from the filters after 20 d immersion and shaking. The spectra of the SBF solution or water solution after the AgNP-coated cotton fiber was immersed and shaken for 20 d did not show the characteristic Ag surface plasmon peak at approximately 412 nm.

4. Conclusion

Natural cotton was successfully electrospun in room temperature ionic liquid to obtain nanoscale cotton fibers that were

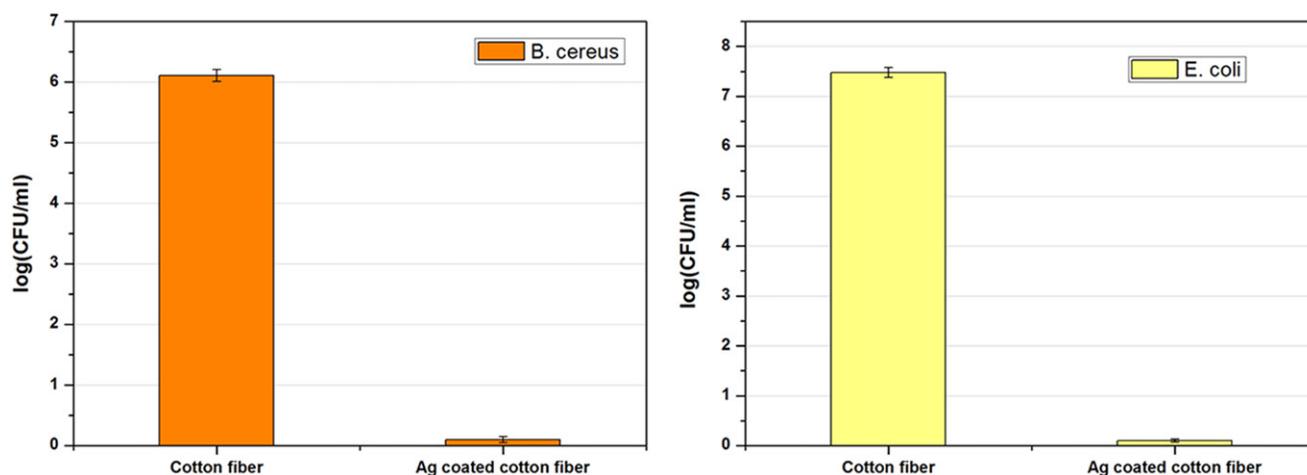


Figure 8. Antibacterial efficacy tests on *B. cereus* and *E. coli* in direct contact with Ag coated and uncoated cotton fiber. The values are the mean \pm standard deviation of three independent experiments (0.1 colonies were assumed when zero colonies were detected).

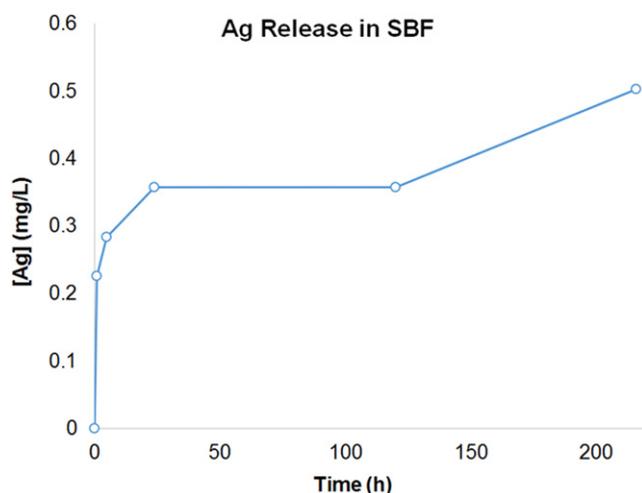


Figure 9. AAS data showing the release of AgNPs over several days of shaking at 37 °C in SBF. Total release of AgNPs from nano-cotton fibers over 9 d was approximately 0.1% by mass. Similar shaking in distilled water showed no detectable release of AgNPs from the fibers.

esterified with trityl-3-mercaptopropionic acid. Selective de-tritylation afforded nano-cotton fibers containing reactive thiol functionality to which silver nanoparticles were covalently attached. This nanocomposite showed significant activity against both Gram-negative and Gram-positive bacteria. The covalent linkage of functional nanomaterials to regenerated natural cotton fibers as presented here will allow for novel applications of one of the most versatile biopolymers known.

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