Antibacterial Metal-Fiber Hybrid with Covalent Assembly of Silver and Palladium Nanoparticles on Cellulose Fibers

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Abstract—Cellulose fibers were bound with noble metal nanoparticles by covalent attachment of silver and palladium nanoparticles. It is achieved that some of hydroxyl groups in the cellulose fiber were converted to thiol groups known as binding to Au, Ag, Pt, Pd and etc. The thiolated cellulose fiber were then treated sequentially with colloidal silver and palladium nanoparticles. Field emission-scanning electron microscopy showed that the particles were well dispersed within the modified fibers. The antibacterial properties of the metal-cellulose fiber hybrid against S. aureus and K. pneumoniae were examined by the AATCC 100 antibacterial activity test method for fabric. The metal-cellulose fiber hybrid showed strong biocidal effects in excess of 99.9% growth inhibition of the bacteria. Because the method of fabrication for the metal-cellulose hybrid involved covalent bonding between the metal nanoparticles and fibers, the loss of metal nanoparticles from the fiber was fundamentally blocked. Therefore, the high antibacterial property of the metal nanoparticles in the resulting fiber is expected to show long-term stability.

Keywords—silver nanoparticles; palladium nanoparticles; cellulose fiber; covalent bonding; metal nanoparticles

I. INTRODUCTION

Cellulose fibers have hydrophilic surfaces and a porous structure, which afford excellent air permeability and sweat absorption properties. However, the excellent sweat-absorbing properties of cellulose fibers concomitantly provide a favorable environment for microorganisms. Numerous chemicals, such as halogen ion complexes, metal salt, and metal derivatives, have been used to provide antibacterial activity to cellulose fibers. [1-2] Unfortunately, the antibacterial properties of fibers treated with these compounds decrease with time, and these compounds may be toxic to humans. [3]

In recent years, noble metal nanoparticles have used to antibacterial textile finishing. The ions which are produced from metal nanoparticles interact with sulfur-containing proteins in bacterial cell, which influence bacterial cell viability. [4] The noble metal nanoparticles slowly oxidize to release ions that then react with the bacterial cells. This process conveys strong antibacterial effects toward pathogenic microorganisms with a long period.

To fabricate metal nanoparticles loaded fibers, the fibers immersed in metal nanoparticles containing aqueous solutions and then, it was treated with conventional pad-dry-cure process. [5-8] Another approach for fabricated metal nanoparticles loaded fiber, it was prepared by reduction of metal salt which was absorbed in fiber. [9] However, the practical use of metal nanoparticles in these methods was limited because the metal nanoparticles possibly dropped off from the fibers owing to the absence or weakness of the nanoparticle-fiber interaction.

In this study, in order to block the detachment of metal nanoparticles from fiber, we attempted to provide covalent bonding between metal nanoparticles and fibers. To achieve this, some of hydroxyl groups in the cellulose fiber were converted to thiol groups, which are able to bind to noble metal such as gold, silver, platinum, and palladium. The silver and palladium nanoparticles bound to the thiolated cellulose fiber. By stably and covalently immobilizing the metal nanoparticles on the fiber surfaces, the prepared metal-cellulose fiber hybrid have strong resistant to detachment of metal nanoparticles and high antibacterial property over long period.

II. EXPERIMENTAL

A. Materials

Cellulose fiber was obtained from the Korea Apparel Testing & Research Institute (KATRI). Silver nitrate (AgNO₃), sodium tetrachloropalladate (Na₃PdCl₄), trisodium citrate (C₆H₅Na₃O₇), triblock Pluronic copolymer P123 (poly(ethylene oxide)₉₇-poly(propylene oxide)₉₇-poly(ethylene oxide)₉₇), sodium borohydride (NaBH₄), sodium tetrachloropalladate, sodium tetrachloropalladate, and mercaptoacetic acid (C₅H₇O₂S) were purchased from Sigma-Aldrich. Acetic anhydride (C₄H₆O₃), sulfuric acid (H₂SO₄) were supplied from Daejung Chemicals & Metals. All chemicals were used as received without further purification.

B. Preparation of metal-cellulose fiber hybrid

The cellulose fiber was modified by mercaptoacetic acid. [10] Firstly, 100 mL mercaptoacetic acid, 60 mL acetic anhydride, 40 mL acetic acid (36%), and 0.3 mL concentrated sulfuric acid were added in turn to the round bottle. Second, the mixture was stirred thoroughly and cooled to room temperature, followed by addition of 30 g fat-free cellulose fiber, which was impregnated thoroughly with the solution. Finally, the bottle was covered with a lid and heated in an oven at 40 °C for 4 days. After completion of the thiolated reaction, the thiolated cellulose fiber was washed several times with deionized water and dried in an oven.
The colloidal silver nanoparticles were prepared by the addition of 0.6 mL of a 5 mM sodium borohydride solution as the reducing agent to 40 mL of an aqueous solution containing an equal concentration (1.0 mM) of silver nitrate and trisodium citrate with vigorous stirring at room temperature.[11]

The colloidal palladium nanoparticles were synthesized by mixing an aqueous solution of the palladium salt and the triblock Pluronic copolymer P123.[12] In this study, 0.4 mL of a 0.1 M Na₂PdCl₄ aqueous solution were added to 40 mL of a 3.4 mM P123 of aqueous solution prepared by dissolving 0.8 g of P123 in 40 mL deionized water, which served the dual roles of stabilizer and reducing agent. The resulting solution was vigorously stirred at room temperature for a day.

Each type of metal nanoparticle was introduced to the thiolated cellulose fiber by immersion of the fiber in a metal nanoparticle colloidal solution. In a typical procedure, the thiolated cellulose fiber was placed in round bottle. Next, 40 mL of silver and palladium nanoparticle colloidal solutions were added to the bottle, respectively. Finally, the bottles stored in a pre-heated oven at 60 °C for 4 days. After the thiolated cellulose fiber was sufficiently impregnated with the metal nanoparticle colloidal solutions, it was rinsed several times with deionized water and dried in an oven.

C. Antibacterial activity of metal-cellulose fiber hybrid

The antibacterial activity of the metal-cellulose was assessed by the American association of textile chemists and colorists (AATCC) 100 test method for fabric. *Staphylococcus aureus* and *Klebsiella pneumoniae* were selected as gram-positive and gram-negative test bacteria, respectively. 0.4 g of the control specimen, standard cellulose fiber, and the metal-cellulose specimens were placed in a sterilized container. An aqueous suspension containing test bacteria was dropped onto the surface specimen. After exposure of test bacteria, the inoculated control specimens or the metal-cellulose fiber hybrid specimens were placed in 100 mL deionized water containing container. The container was shaken vigorously for 1 minute. And then 0.1 mL of microorganism suspension was drawn and transferred to a nutrient agar plate. The number of survival microorganism was determined after 18 hours incubation at 37 °C for 4 days. After the thiolated cellulose fiber was successfully converted to thiol groups.

D. Characterization

The modification of cellulose fiber was monitored with attenuated total reflection Fourier-transform infrared (ATR/FT-IR) spectroscopy, which was employing a Thermo Scientific Nicolet 6700 FT-IR spectrometer with a spectral resolution of 8 cm⁻¹ in the scan range from 4000 to 650 cm⁻¹. In order to determine the sulfur element contents of the thiolated cellulose fiber, elemental analysis was carried out using CE Instruments EA 1112 elemental analyzer.

High-resolution transmission electron microscopy (HR-TEM) images of colloidal metal nanoparticles were obtained using a JEOL JEM-3010 instrument operating at 300 kV. Morphological images of the metal-cellulose fiber hybrid were obtained by field-emission scanning electron microscopy (FE-SEM) performed using a JEOL JSM-6700F. The specimens were coated with a thin layer of Pt prior to FE-SEM imaging. Energy-dispersive X-ray spectroscopy (EDS) was used for elemental characterization of the metal-cellulose using a spectrometer equipped with a JSM-6700F. Inductively coupled plasma-atomic emission spectrometry (ICP-AES, PerkinElmer Optima-4300 DV) was used to quantitatively analyze the metal content of the metal-cellulose fiber hybrid.

III. RESULTS AND DISCUSSION

A. Metal-cellulose fiber hybrid

Thiolated cellulose fiber was prepared by esterification reaction between a mercaptoacetic acid and a hydroxyl group in cellulose fiber. According to Pearson's hard soft acid and base (HSAB) theory,[13, 14] thiol groups would easily react with the soft metal elements. This theory defines a soft base as having a low electronegativity and a large radius such as thiols, sulfides, and phosphorus compounds. Soft bases tend to bind covalently with soft acids, which are defined as having a relatively high electronegativity, low charge (+1 or +2), and a relatively large radius, for example, Au²⁺, Ag⁺, Pt²⁺, and Pt⁴⁺.

The aim of the experiment was to ascertain whether IR spectroscopy could provide information on the thiol modification mechanism, which was expected to involve the esterification of the hydroxyl groups. Fig. 1 shows that The ATR/FT-IR spectra of the thiolated cellulose fiber discloses a carbonyl (C=O) stretch corresponding to an ester group at 1730 cm⁻¹ formed by an esterification reaction of mercaptoacetic acid with hydroxyl group in cellulose fiber. In addition, 2.1 wt% sulfur was detected in the thiolated cellulose fiber by EA. These results indicated that 0.11 units of hydroxyl groups per glucose unit in the cellulose fiber were successfully converted to thiol groups.

Figure 1. ATR/FT-IR spectra of (a) the cellulose fiber and (b) the thiolated cellulose fiber.
Silver and palladium nanoparticles were prepared by chemical reduction of metal salts, which is commonly used method for the solution-phase synthesis of metal nanoparticles. The synthesis involves a soluble metal salt as a metal nanoparticle precursor, a stabilizer agent, and a chemical reducing agent. In the preparation of silver nanoparticles, they were stabilized by trisodium citrate group. Otherwise, the palladium nanoparticles were synthesized using triblock Pluronic copolymer which serves in the dual roles of both reducing agent and stabilizer. Fig. 2 shows HR-TEM images of silver and palladium nanoparticles. Both silver and palladium nanoparticles formed spherical in shape particles with a size of less than 10 nm.

Figure 2. The TEM image of (a) silver nanoparticles and (b) palladium nanoparticles.

In order to assembly of metal nanoparticles on the fiber, the thiolated cellulose fiber had been immersed into silver and palladium nanoparticle colloidal solutions. After immersion process, as shown in Fig. 3 (inset image in (c) and (d)), the color of silver-cellulose fiber hybrid and palladium-cellulose hybrid changed from white into dark yellow and dark brown, respectively. These results were influenced by plasmon resonance absorption of the immobilized silver and palladium nanoparticles on fiber. To evaluate the changes in surface morphology upon assembly of the metal nanoparticles, surface morphology of the specimens were obtained by FE-SEM. Fig. 3(a) and 3(b) show that the FE-SEM images of the cellulose and thiolated cellulose fibers. The FE-SEM images disclose similar surface morphology without any presence of particles on the fiber surface. As can be seen Fig. 3(c) and 3(d), Otherwise the FE-SEM images of silver and palladium nanoparticles assembled on the fiber specimens clearly showed attachment of spherical-type particles on the fiber surface. In addition, the energy dispersive spectra (see Fig. 4) clearly confirmed the presence of silver and palladium peaks in the metal-cellulose fiber hybrid. These results indicated that the particles imaged were composed of silver and palladium elements. The ICP-AES results show that quantity of silver and palladium element in the fibers exceeded 99.9%. The measured values were 37.0 mg g⁻¹ (Ag) and 18.6 mg g⁻¹ (Pd) in the prepared fibers, respectively.

B. **Antibacterial activity of metal-cellulose fiber hybrid**

Fig. 5 shows the antibacterial properties of the metal-cellulose fiber hybrid. Inoculated specimens were incubated with the test bacteria, *S. aureus* and *K. pneumoniae*, for 18 hours at 37 ± 1 °C. At the initial stage (at ‘0’ contact time), the counting number of CFU for *S. aureus* and *K. pneumonia* is 2.2 × 10⁴ and 2.1 × 10⁴, respectively. After 18 hours incubation, the test bacteria in the blank specimens proliferated at a rate of more than 100 times rate of the initial stage. Otherwise the test bacteria in the Ag-cellulose fiber hybrid and Pd-cellulose fiber hybrid specimens observed growth of almost zero colonies (below 10 CFU). The reduction rate (R) of the test bacteria in the prepared fibers exceeded 99.9%.

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Figure 4. EDS spectra of (a) the Ag-cellulose fiber hybrid and (b) the Pd-cellulose fiber hybrid.
Figure 5. Antibacterial results of cellulose fiber (blank, left), and of Ag-cellulose fiber hybrid and Pd-cellulose fiber hybrid against S. aureus and K. pneumoniae after incubation. The extraction of microorganism solutions were incubated on a nutrient agar plates at 37 ± 1 °C for 18 hours.

IV. CONCLUSION

In this study, we developed a novel method for fabricating metal-cellulose fiber hybrid, in which the metal nanoparticles are covalently bound to the fiber. FE-SEM and EDS results indicate that the assembled silver and palladium nanoparticles are well-dispersed in the natural cellulose fiber. Furthermore, the prepared fibers showed high antibacterial activity due to the assembled silver and palladium nanoparticles. This preparation method for metal-cellulose fiber hybrid is not limited to silver and palladium nanoparticles. Any metal nanoparticle that displays soft acidic properties such as Au, Pt, or Cu may be applied to cellulose fibers. And this method is also suitable for introducing metal nanoparticles onto substrate with hydroxyl groups, not only cellulose fibers. Thus, the novel fabrication method for combining metal nanoparticles and flexible substrates via covalent bonding is simple and easy to apply in a conventional fiber processing facility and can be used directly in various antibacterial applications.

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REFERENCES