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One-pot fabrication of durable antibacterial cotton fabric coated with silver nanoparticles via carboxymethyl chitosan as a binder and stabilizer

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ABSTRACT

In this article, durable antimicrobial cotton fabric was prepared by a one-pot modification process using a colloidal solution of silver nanoparticles (Ag NPs) stabilized by carboxymethyl chitosan (CMC). Due to coordination bonds between the amine groups of CMC and the Ag NPs and the ester bonds present between the carboxyl groups of CMC and the hydroxyl groups of cellulose, the Ag NPs were tightly immobilized onto the cotton fiber surface. As a result, the Ag NPs that were adhered on the cotton fabrics have uniform dispersion and small size, ranging from 10 nm to 80 nm. This provides the cotton fabric with remarkable and durable antibacterial activity against both *S. aureus* and *E. coli*. After 50 laundering cycles, the bacterial reduction rate (BR) for the modified cotton fabric remained over 94%. This method is simple, and it is particularly suitable for the industrial finishing process.

1. Introduction

Cotton fabric plays key roles in our daily life due to its excellent properties: it is comfortable, flexible, water-absorbing, and air-permeable. To expand cotton fabric applications, numerous modifications to enhance antimicrobial properties (Fei, Liu, Zhu, Wang, & Yu, 2018; Rauytanapanit, Opitakorn, Terashima, Waditee-Sirisattha, & Praneenararat, 2018; Salat et al., 2018), UV protection (Hu et al., 2018; Ren et al., 2018), fire resistance (Yang, Zhang, Fu, & Liu, 2017) and water repellence (Feng, Sun, & Ye, 2017; Xi et al., 2016; Xi, Fan, Wang, Liu, & Endo, 2015; Wang, Xi, Wan, Zhao, & Liu, 2014) have been made. Among these, the preparation of antimicrobial cotton textiles based on modification with silver nanoparticles (Ag NPs), offers one of the simplest processes which would fit with the capabilities of most finishing plants (Zhang, Xu, Fu, & Liu, 2016).

As an antimicrobial reagent, Ag NPs have desirable properties that include high specific surface area and high activity against a wide scope of pathogens. However, there have been concerns that Ag NPs may have health risks and environmental issues (Hernández-Arteaga et al., 2017). Previous work has indicated that the toxicity of Ag NPs is mainly caused by Ag ions leached from Ag NPs, and the toxicity strongly depends on the concentration of the leached ions (Parham et al., 2017). These issues are worrisome to the cotton textile industry, limiting the adoption of Ag NPs by scientists and engineers (Limpiteeprakan, Babel, Lohwacharin, & Takizawa, 2016; Shaheen & Fouda, 2014).

To enhance adhesion between Ag NPs and the cotton fiber surface, numerous strategies have been reported in the last decade (He, Xin, Chen, & Liu, 2018; Karim, Anderson, Singh, Ramanathan, & Bansal, 2018; Zhang, Li, Huang, Ren, & Huang, 2018; Zhang, Shu, Su, & Zhu, 2018). Among these methods, many have focused on the use of polymeric binders because they can combine various functional groups in one polymer chain to accomplish two tasks simultaneously: linking with cotton fabric and immobilizing the Ag NPs. For example, polydopamine (Li et al., 2018) and amino-terminated hyperbranched polymers (HBP-NH_2) (Zhang, Zhang, Morikawa, & Chen, 2014) were reported to be very effective for binding Ag NPs onto the cotton surface. However, Ag NPs have large specific surface areas and high surface energies. Thus, they favor aggregation to form larger nanoparticles during the coating process. Generally, larger Ag NPs are easier to wash off of the fiber surface. Therefore, for Ag NPs, both immobilization and control of the size and dispersion are important.

Chitosan has a several amine groups that can form coordination bonds with Ag NPs, but it cannot form covalent bonds with cotton fibers. Many methods, such as ones using plasma technology, cross-

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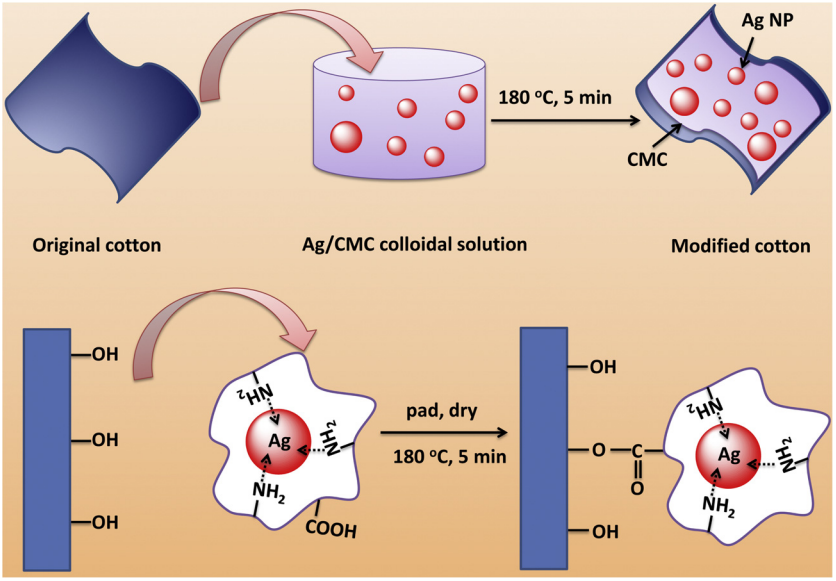

Scheme 1. The illustration of procedure to prepare the modified cotton fabrics.

linking techniques, and oxidation treatments, have been attempted (Dechojarassri et al., 2017; Liu, Nishi, Tokura, & Sakairi, 2001; Liu, Tokura, Nishi, & Sakairi, 2003) to link chitosan chains onto the cotton surface. Most of these treatments use toxic chemicals or complex processes.

In this study, a colloidal solution containing Ag NPs has been successfully prepared by using carboxymethyl chitosan (CMC) as a stabilizer. Because CMC has amine groups and carboxylic acid groups, it was expected to form coordination bonds with Ag NPs and to react with the hydroxyl groups of cellulose. Therefore, this modification could be carried out using a pad-dry-cure process (Dhineshbabu & Bercy, 2018; Ortelli et al., 2018).

In this effort, a colloidal solution of Ag NPs protected by CMC was first prepared and then used to immobilize the Ag NPs in a pad-dry-cure process within a few minutes. Notably, this one-pot method is operationally easy and could simplify the finishing process (Haraguchi, Hirai, Ozawa, Miyamoto, & Tanaka, 2012; Pedroza-Toscano et al., 2017). Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and field emission scanning electron microscopy (FE-SEM) were used to characterize the modified cotton fabrics. Moreover, the antimicrobial activity and laundering durability of these modified cotton fabrics were evaluated by using an improved AATCC 100–1999 method.

2. Experimental

2.1. Materials

CMC (Mw, 15 kDa; deacetylation degree, > 95%; substitute degree, 80%) was purchased from Zhejiang Golden-Shell Pharmaceutical Co., Ltd (China). The cotton fabric was obtained from Shaoxing Qidong Textile Co., Ltd (60 ends/cm, 30 picks/cm, 0.42 mm thickness, 120 g/m weight, 35.2 m^2/g specific surface area). Before chemical modification, cotton fabric was cleaned as previous works (Xu, Gu, Zhao, Ke, & Liu, 2017; Xu, Wu, Zhang, Fu, & Liu, 2016; Xu, Xie et al., 2017). The human immortalized keratinocytes (Hacat) cells were purchased from iCell Bioscience Inc (Shanghai, China). The Dulbecco's modified Eagle's medium (DMEM), fetal bovine serum (FBS), and penicillin/streptomycin solution were purchased from Gibco (CA, USA). The Annexin V-FITC Apoptosis Detection Kit was purchased from BD Biosciences (San Diego, CA, USA). The cell counting kit-8 (CCK-8) was purchased from Dojindo (Japan). Before assay, the Hacat cells were cultured in DMEM, supplemented with 10% FBS, 100 U/mL penicillin and 100 μg/mL streptomycin at 37 °C, 5% CO_2. Other reagents were bought from Shanghai Aladdin Co., Ltd (China) and without further purification.

2.2. Preparation of Ag NPs/CMC colloidal solution and modification of cotton fabrics

CMC solution (1 wt %) was firstly prepared, mixed with an aqueous solution of $AgNO_3$ (10 mL, 0.47 mol/L) and $NaBH_4$ solution (10 mL, 0.94 mol/L), stirred at 25 °C for 30 min to obtain Ag NPs/CMC colloidal solution. A piece of cotton fabric (3.0 cm × 3.0 cm) was immersed in the colloidal solution, stirred at 25 °C for 30 min, padded to give a wet pick up of 80 ± 2% (by squeezing rollers), cured at 180 °C for 5 min, rinsed with distilled water (50 mL × 3 times), dried at 100 °C to obtain sample Cotton-1. The sample of Cotton-2 was prepared via a similar process but a 2 wt % CMC solution was used (Table S1).

2.3. Characterizations

Transmission electron microscopy (TEM; TF20, FEI, America) was used to study the size distribution of Ag NPs. The size distribution of the Ag NPs in the colloidal solution was statistically calculated by measuring 100 bright points in the TEM images using ImageJ software. The size distribution of the Ag NPs on fiber surface was statistically calculated by measuring 300 bright points in the SEM images. Other instruments such as FE-SEM, EDS, ATR, XRD, XPS, and ICP-MS were same to our previous reports (Xu, Gu et al., 2017; Xu, Xie, 2017; Xu, Ke, Cai et al., 2018; Xu, Ke, Shen et al., 2018). Antibacterial test and cytotoxicity analysis were described in the "Supporting Information". Other tests, such as laundering durability, water absorptivity, water vapor permeability and tensile strength tests were same to the previous work (Xu, Gu et al., 2017; Xu et al., 2016; Xu, Xie et al., 2017).

3. Results and discussion

3.1. Characterization of the Ag NPs/CMC colloidal solution and the modified cotton fabrics

Scheme 1 describes the one-pot modification process of the cotton fabric. A colloidal solution of Ag NPs stabilized by CMC was first prepared. As shown in Fig. 1, the TEM images show that the Ag NPs have spherical shapes. It is thought that the CMC chains would adsorb onto