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Fabrication of silver nanoparticle sponge leather with durable antibacterial property

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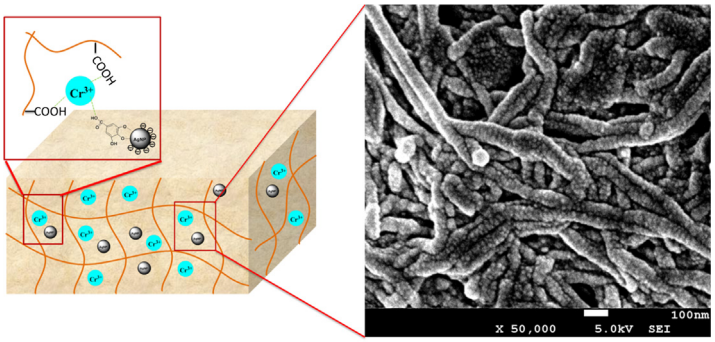
GRAPHICAL ABSTRACT



"AgNPs Sponge" leather with durable antibacterial property

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ABSTRACT

Leather product with durable antibacterial property is of great interest both from industry and consumer's point of view. To fabricate such functional leather, gallic acid modified silver nanoparticles (GA@AgNPs) were first *in situ* synthesized with a core–shell structure and an average size of 15.3 nm. Due to its hydrophilic gallic acid surface, the GA@AgNPs possessed excellent stability and dispersibility in wide pH range from 3 to 12 and also showed effective antibacterial activity with a minimum inhibitory concentration (MIC) of around 10 μg mL^{-1}. Then, such GA@AgNPs were used as retanning agent to be successfully filled into leather matrix during the leather manufacturing process. Moreover, taking the advantage of its high surface density of carboxyl groups, these GA@AgNPs could be further chemically cross-linked onto collagen fibers by chrome tanning agent. After retanning, the resultant leather was given a "AgNPs sponge" feature with high payload of silver nanoparticles against laundry, exhibiting high and durable antibacterial activity.

1. Introduction

Leather is a durable and flexible material produced by tanning the collagen fiber network of animal hides and skins [1]. In leather manufacture, chrome tanning is the most popular tanning method based on chemical cross-linking of the collagen fibers by forming complexation between Cr^{3+} and carboxyl groups on the collagen

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fibers, giving the leather matrix known as wet-blue leather with enhanced hydrothermal stability and mechanical strength [2]. After chrome tanning, retanning process is usually needed by using acrylic resin e.g. poly(acrylic acid) (PAA) with multi carboxyl groups to fill into leather matrix and form complexation with Cr^{3+} for improving utilization of chrome tanning agent and leather fullness [3]. Then, the resultant leather are suitable for making various goods. Because of its breathable, soft and comfortable nature, leather goods, such as shoes, clothing and bags have been widely used in daily life [4]. Especially, the excellent moisture permeability of leather goods can absorb sweat from the sweat glands of skin, which bring comfort to users [5]. But in the meantime, the absorbed sweat containing proteins may provide nutrient sources for the growth of bacteria on the leather surface [6]. Besides, the collagen fibrous network of leather can also offer other ideal conditions such as moisture, temperature and oxygen for bacterial growth and rapid colonization, resulting in the formation of a biofilm which can lead to unpleasant odor, discoloration, reduced mechanical strength and even risks of skin infection [7,8]. Therefore, the antibacterial property of leather product has been a major issue to be addressed, both at industrial level and from the consumer's point of view.

To solve this problem, considerable efforts have been directed toward constructing various antibacterial coatings on leather surface [9–13]. For example, chitosan has been applied as antimicrobial coating material for leather surface based on its contact-active disruption of microbe cell membrane [12,14–18]. Recently, our group have prepared a PEGylated chitosan (PEG-g-CS) coating on leather, which exhibited more efficiently antibacterial activity than that of single chitosan coating due to the synergistic effect between bacterial resistance of PEG and contact-killing of chitosan [13]. Despite the high antibacterial efficiency of these polymer coating, one important defect of these coatings in application is that they can be easily damaged and even fell off from leather surface by abrasion during wearing and laundry, causing loss of antibacterial activity [19]. Therefore, incorporating biocides into leather matrix with sustained release behavior will be an ideal strategy for leather products with durable antibacterial property. Though chemical biocides were commonly used in leather industry, they were mainly play the role in preventing biodeterioration of hides rather than to endow antibacterial property to the final products [6,20]. What's more, some of these biocides have been restricted due to human health and environmental issues [8]. Thus, the development of eco-friendly and effectively antimicrobial bactericide that can be applied in leather tanning process will be great interesting.

Silver nanoparticles (AgNPs) are well known for their strong and broad-spectrum of bacterial and fungal strains through the sustained release of Ag^+ ions, damaging the microbial cell membrane as well as disrupting the function of bacterial enzymes and nuclei acid groups in protein and DNA [21–28]. In addition, AgNPs are less toxic to human as compared to other metals and have been widely selected as suitable antibacterial finishing agent for textile fibers [26,29,30–34]. Inspired by these AgNPs-based antibacterial finishing, durable antibacterial leather is supposed to be fabricated via filling AgNPs into leather matrix and subsequently immobilized on collagen fibers during leather tanning process. However, due to the complicated and versatile pH environments of the whole tanning process, the application of AgNPs in leather manufacture is still a challenge that requires high stability and dispersibility of AgNPs. In this work, gallic acid stabilized silver nanoparticles (GA@AgNPs) were *in situ* synthesized by chemical reduction of $AgNO_3$, with excellent stability and dispersibility. Due to the high carboxyl group density on its surface, these GA@AgNPs were used as retanning agent instead of traditional acrylic resin to filled into the leather matrix. Simultaneously, these GA@AgNPs could be chemically immobilized onto collagen fibers through the cross-linking of carboxyl groups between GA and collagen fiber by chrome tanning agent, resulting a "AgNPs sponge" leather with high payload of silver nanoparticles (Scheme 1). Based on the sustained release behavior of Ag^+, the resultant leather or its products possessed durable and even long-term antibacterial activity against laundry and mechanical abrasion. To the best of our knowledge, this is the first report about durable antibacterial leather with "AgNPs sponge" feature.

2. Materials and methods

2.1. Materials

Gallic acid (GA, 99%) was purchased from AiBi Chemical Reagents Corporation (Shanghai, China). Silver Nitrate ($AgNO_3$, 99.8%) was purchased from Tianhua Technological Incorporated Company (Chengdu, China). Basic Chromium Sulfate [$Cr(OH)SO_4$] containing 25% Cr_2O_3 was purchased from Tianjin Mingyang Chemical Co., Ltd. (Tianjin, China). Sodium borohydride ($NaBH_4$, >96%) and other Chemical materials are purchased from Jinshan Chemical Reagents Corporation (Chengdu, China). Silver standard solution with the silver concentration of 1000 μg mL^{-1} was purchased from Jinan Zhongbiao Technology Co. Ltd. (Jinan, China). Pickled pelt was made by treating sheep skin follow the process of degreasing, unhairing, liming, deliming, bating and picking in our own lab.

2.2. Synthesis of gallic acid modified silver nanoparticles (GA@AgNPs)

10 mL $AgNO_3$ (5 mM) was first completely mixed with 10 mL gallic acid solution at the concentration of 0.5, 2.5, 3 and 5 mM, respectively. Then the above mixture was added dropwise into 30 mL $NaBH_4$ solution with a concentration of 10 mM for reacting 2 h at dark. The obtained GA@AgNPs were further purified by centrifugation at 15,000 rpm for 20 min and re-dispersed into water with a concentration of 50 μg mL^{-1}.

2.3. The colloidal stability of GA@AgNPs

To determine the stability of GA@AgNPs with respect to pH, a series of GA@AgNPs solutions with the pH value from 1 to 13 were prepared. Then, the UV–vis spectra, size distribution and zeta-potential of these nanoparticle solutions were measured, respectively. To determine the stability of GA@AgNPs with respect to storage time, the UV–vis spectra, size distribution and zeta-potential of GA@AgNPs solutions storage at 1, 30 and 120 days under room temperature were measured, respectively.

2.4. Antibacterial assay for GA@AgNPs

The antibacterial activity of GA@AgNPs was conducted by the minimum inhibitory concentration (MIC) test, with *Escherichia coli* (*E. coli*, ATCC25922) and *Staphylococcus aureus* (*S. aureus*, ATCC6538) as model bacteria. GA@AgNPs in sterile water with an initial concentration of 50 μg mL^{-1} were prepared and diluted to 30, 20, 10, and 5 μg mL^{-1} by using sterile water, respectively. Then, 1 mL GA@AgNPs solution was added into tubes with 5 mL LB medium at bacteria concentration of 5×10^6 cfu mL^{-1}. For the blank samples, 1 mL sterile water was added into the control tube with 5 mL LB medium at bacteria concentration of 5×10 fu mL^{-1}. The tubes were incubated at 37 °C with shaking at 200 rpm for 24 h in a shaking bath. After incubation, 20 μL solution was withdrawn from tubes and spread on Luria-Bertani agar in petri dish. The petri dishes were incubated for 24 h at 37 °C, and counted for colony-