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Preparation and characterization of functional fabrics from bamboo charcoal/silver and titanium dioxide/silver composite powders and evaluation of their antibacterial efficacy

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ABSTRACT

Bamboo charcoal supporting silver (BC/Ag) and titanium dioxide supporting silver (TiO_2/Ag) were prepared by activation and chemical reduction. The BC/Ag and TiO_2/Ag composites were characterized by silver particle size and distribution and antibacterial properties. The pore and surface properties were studied in terms of BET volumetric measurement with nitrogen adsorption, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The antibacterial effects of the BC/Ag and TiO_2/Ag composite powders were assessed from the minimum inhibitory concentrations (MICs) and minimum bactericidal concentrations (MBCs), and an excellent antibacterial performance was discovered. Moreover, these composite powders were deposited via immersion coating onto fabrics (nonwoven and carbon fibers) to improve the antibacterial efficacy and to act as a biologically-protective material. The antibacterial activities of the fabrics supported by BC/Ag and TiO_2/Ag were studied in zone of inhibition and plate counting tests against Gram-positive *Staphylococcus aureus* ME/GM/TC Resistant, *Bacillus subtilis*, *Candida albicans*, Gram-negative *Pseudomonas aeruginosae* (CTZ&EM&GM) Res. Clin. Isol., *Escherichia coli* Juhl, and *Klebsiella pneumoniae*. The results showed that fabric-BC/Ag and fabric-TiO_2/Ag possess a strong antibacterial activity and an inhibitory effect on the growth of these bacteria and are therefore believed to have great potential for use as antibacterial fabrics.

1. Introduction

In recent years, there has been increasing interest in the antibacterial finishing of fibers and fabrics for practical applications [1,2]. Most textile materials currently used in hospitals and hotels are conducive to cross-infection or the transmission of diseases caused by microorganisms. The manufacture of dressings for medical and hygienic use has become an important area in the textile industry. In general, antimicrobial properties can be imparted to textile materials by chemically or physically incorporating functional agents onto fibers or fabrics. Wound infections are mainly caused by Gram-positive *Staphylococcus aureus* (*S. aureus*), *Bacillus subtilis* (*B. subtilis*), Gram-negative *Pseudomonas aeruginosae* (*P. aeruginosae*), and *Escherichia coli* (*E. coli*) [3].

Bamboo charcoal has a number of advantageous characteristics, such as a high electric conductivity and self-lubricity, and can be used as a friction material and an electromagnetic shield material [4]. Among such materials, bamboo is recognized as one of the most popular bioresources, and its adsorption characteristics have been the subject of many studies [5,6]. The photocatalytic activity of titanium dioxide results in thin coatings of the material exhibiting self-cleaning and disinfecting properties under exposure to UV radiation. These properties make this material a candidate for applications such as medical devices, food preparation surfaces, air conditioning filters, and sanitary ware surfaces.

Silver ions have long been known to possess strong inhibitory and bactericidal effects as well as a broad spectrum of antibacterial activities [7,8], and therefore silver has been commercially used to take advantage of its antibacterial properties [9]. If silver is immobilized on porous hosts, the release time of silver ions can be delayed for a long time, and so silver-supported materials are of great potential for antibacterial applications [10]. At present, antibacterial agents are mainly based on organic materials [11,12], which are often not suitable for use under conditions where chemical durability is required. However, silver-supported inorganic materials can be used to overcome this constraint well, and materials such as zeolites, calcium phosphate,

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silica, bamboo charcoal, titania and carbon fiber have been developed as inorganic supports for antibacterial silver-containing materials [13–18]. Nanocrystalline silver dressings have been demonstrated *in vitro* as effective antifungal agents, antibacterial agents, and antibacterial agents for antibiotic-resistant bacteria [19].

Bamboo charcoal supporting silver (BC/Ag) and titanium dioxide supporting silver (TiO_2/Ag) composite materials are of special interest because of their unusual antibacterial properties, and are expected to be suitable for use as water purifiers or biologically-protective materials. The objectives of the present work were to prepare antibacterial BC/Ag and TiO_2/Ag using a chemical reduction method and to examine the surface structures and chemistry before and after the supporting of silver. The emergence of multi-drug-resistant strains of bacteria represents a particular challenge in the field of wound management; moreover, studies of biomaterial for application in cases of resistant bacteria are very limited. The antibacterial activities against Gram-positive *S. aureus* ME/GM/TC Resistant (*S. aureus* Resistant), *B. subtilis*, *Candida albicans* (*C. albicans*), Gram-negative *P. aeruginosa* (CTZ&EM&GM) Res. Clin. Isol. (*P. aeruginosa* Resistant), *E. coli* Juhl, and *Klebsiella pneumoniae* (*K. pneumoniae*) of fabric-BC/Ag and NF-TiO_2/Ag were examined in this investigation. The aim of the current study was to investigate whether nanocrystalline silver possesses the physical properties necessary to act as a barrier to the transmission of *S. aureus* Resistant and *P. aeruginosa* Resistant in the laboratory setting. The antibacterial effects of BC/Ag and TiO_2/Ag composite powders were evaluated by determination of the minimum inhibitory concentrations (MICs) and minimum bactericidal concentrations (MBCs) by the broth dilution method. In order to explore the antibacterial effects of fabric-BC/Ag and fabric-TiO_2/Ag, measurement of the zone of inhibition and the plate counting method were employed.

2. Materials and methods

2.1. Preparation of BC/Ag and TiO_2/Ag composite powders

The BC and TiO_2 powders (particle size < 10 μm) were activated with surfactant sodium alginate under stirring for 1 h. The activated BC and TiO_2 powders (2 g) were then immersed separately into 100 ml of biamminesilver nitrate ($[Ag(NH_3)_2]NO_3$) solution, which was formed by adding 25 wt.% aqueous ammonia into $AgNO_3$ solution at room temperature. This will favor an increase in the negative surface charge of BC in the basic $[Ag(NH_3)_2]NO_3$ solution and interaction of the NH_3 ligands of the $[Ag(NH_3)_2]^+$ complexes with the surface of BC via hydrogen bonding [10]. The weight ratio between BC, TiO_2 and $AgNO_3$ was approximately equal to 1:1. After stirring for 1 h, dilute aqueous solutions of hydrazine monohydrate were introduced into the BC–$[Ag(NH_3)_2]NO_3$ and TiO_2–$[Ag(NH_3)_2]NO_3$ solutions in appropriate quantities (molar ratio 1:1 with respect to silver nitrate) using a syringe. Stirring was continued under an inert atmosphere at room temperature for another 4 h. The BC/Ag and TiO_2/Ag composite powders were subsequently separated and washed with deionized water and ethanol, then dried in a vacuum at 60 °C overnight. The samples were designated, for example, BC/Ag, which denotes BC reacted with $AgNO_3$ in a weight ratio of 1:1. Preparation of BC/Ag and TiO_2/Ag composite powders followed F.C. Yang et. al.'s manufacture method [17].

2.2. Manufacture of fabrics with BC/Ag and TiO_2/Ag

The typical esterification procedure was as follows: 3-g (10 × 10 cm) samples of blank nonwoven fiber (NF-Blank, Kang Na Hsiung Enterprise Co., Ltd.) and blank carbon fiber (CF-Blank, Taiwan Carbon Technology Co., Ltd.) were placed in 250-ml round-bottom flasks equipped with a stirrer, and then 100 ml distilled water, 5 ml polyvinyl alcohol (PVA) and 0.2 g BC/Ag and TiO_2/Ag composite powders were added. The reactions were carried out at 25 °C and the resulting samples dried in vacuum at 100 °C overnight. The samples were designated as follows: NF-BC/Ag, denoting NF-Blank reacted with BC/Ag:H_2O in a weight ratio of 2:100; NF-TiO_2/Ag, denoting NF-Blank reacted with TiO_2/Ag:H_2O in a weight ratio of 2:100; and CF-BC/Ag, denoting CF-Blank reacted with BC/Ag:H_2O in a weight ratio of 2:100.

2.3. Characterization

Phase identification of composites was performed using X-ray diffraction (XRD; Siemens D5000) with Cu Kα radiation. Average grain sizes (D) of Ag were determined from the XRD peaks using Scherrer's formula. The morphology of composites was observed using a scanning electron microscope (SEM, Hitachi S-800) equipped with an energy-dispersive X-ray (EDX, Hitachi S-300) microanalysis system. The Brunauer–Emmett–Teller (BET) specific surface areas (S_{BET}) of the BC/Ag and TiO_2/Ag composites were determined using a NOVA 1000e automatic physical absorber with highly purified nitrogen gas at 77 K. The concentration of silver ions released from BC/Ag and TiO_2/Ag to the aqueous medium was measured using an atomic absorption spectrophotometer (Pantech, GBC-932AA) [20].

2.4. Test of antibacterial properties

S. aureus Resistant (ATCC33592), *B. subtilis* (ATCC 43223), *C. albicans* (ATCC 44858), *P. aeruginosa* Resistant, *E. coli* Juhl and *K. pneumoniae* (ATCC 10031) were used as reference strains for antibacterial testing, and were obtained from the American Type Culture Collection (Rockville, MD, USA).

The antibacterial effects of composites were evaluated by determination of MICs and MBCs using the broth dilution method. Tubes containing 3 ml Muller–Hinton broth with 3-fold dilutions of the BC/Ag and TiO_2/Ag composite powders ranging from 3 mg/L to 10 g/L were inoculated with 10^7 CFU/ml of bacteria. The inoculated tubes were then incubated at 37 °C for 24 h. After incubation, tubes were examined without shaking for visible turbidity; the MIC was determined as the lowest dilution of composites that produced no visible turbidity [21]. The test was performed three times for each strain, and results agreeing on two or more occasions were adopted as the MIC of the strain. The number of grown colonies on this subculture after the incubation period was counted and compared with the number of CFU/ml in the original inoculum. The lowest concentration of BC/Ag and TiO_2/Ag composites that allowed less than 0.1% of the original inoculum to survive was taken as the MBC [22].

The antibacterial spectra of fabric-BC/Ag and NF-TiO_2/Ag were evaluated by zone of inhibition testing [23]. Sections (2 × 2 cm^2) of test-substance-coated and uncoated fabric were placed on agar plate surfaces upon which 10^6–10^7 CFU/plate of individual test strains had been spread. The fabrics were wetted with an additional 0.1 ml of sterile pure water before testing. The agar plates were incubated for a total of 72 h at 37 °C, and were observed at 24, 48 and 72 h. Inhibition zones was measured with calipers, and photographs were taken. The antimicrobial activities were determined in the clear zone area for each fabric; the growth condition of individual microbes in the touch area for each fabric was also observed as another parameter for evaluating antimicrobial activity.

The plate counting method was used to further investigate the antibacterial effect of the fabric [10]. Sterile water agar (0.6% agar with 0.6% NaCl in distilled water) was poured onto a sterile Petri dish to form water agar plates. Test-compound-coated fabrics and vehicles (nonwoven fabrics) were placed on the surface of water agar plates in order to maintain moisture, and 0.1 ml of prepared 10^5–10^6 CFU/ml of individual test strains was spread on the fabric samples. At each time point of 0, 1, 2, 4 and 24 h incubation with the *S. aureus* Resistant strain, and after 4 h of incubation with the other 5 strains, a fabric sample was transferred to a sterile test tube containing 4 ml PBS with a few glass beads and whirled in a vortex for 1 min, followed by 5 min