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Silver nanoparticles-loaded activated carbon fibers using chitosan as binding agent: Preparation, mechanism, and their antibacterial activity

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ABSTRACT

The effective and strong adherence of silver nanoparticles (AgNPs) to the substrate surface is pivotal to the practical application of those AgNPs-modified materials. In this work, AgNPs were synthesized through a green and facile hydrothermal method. Chitosan was introduced as the binding agent for the effective loading of AgNPs on activated carbon fibers (ACF) surface to fabricate the antibacterial material. Apart from conventional instrumental characterizations, i. e., scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), zeta potential and Brunauer-Emmett-Teller (BET) surface area measurement, molecular dynamics simulation method was also applied to explore the loading mechanism of AgNPs on the ACF surface. The AgNPs-loaded ACF material showed outstanding antibacterial activity for *S. aureus* and *E. coli*. The combination of experimental and theoretical calculation results proved chitosan to be a promising binding agent for the fabrication of AgNPs-loaded ACF material with excellent antibacterial activity.

1. Introduction

The rapid development of nanotechnology enables the controllable synthesis of metal silver to nano-scale [1–3]. Silver nanoparticles (AgNPs), as a broad spectrum antimicrobial agent, have been used extensively in therapeutic applications such as catheters [4,5], surgical devieces [6] and wound dressings [7–9]. However, the antibacterial efficiency of AgNPs depends on both colloidal stability and particle size [10]. Additionally, the practical application of AgNPs in colloidal form are often confronted with the problem of aggregation and loss of antibacterial activity [11–13]. Therefore, the stability of AgNPs is an important issue for their practical application as antibacterial material [14,15].

An effective way to prevent AgNPs from aggregation is to deposite AgNPs on specific surface to fabricate AgNPs-loaded materials. Apart from the better stability, these kinds of materials are easy to be recycled and reused compared with the colloidal form of AgNPs. The common supporting materials (substrates) are SiO_2, zeolite and carbon materials [16–18]. Activated carbon fiber is an ideal supporting material for AgNPs loading because of the huge specific surface area, proper micropores and excellent adsorption capacity, which have been widely used in water treatment field [19,20].

The strong adherence of AgNPs to the supporting surface is critical for the practical feasibility of the AgNPs-loaded materials. Binding agent is needed to guarantee the effective connection of AgNPs and supporting surface. For instance, butane tetracarboxylic acid was applied as the cross-linking agent to bind AgNPs on the surface of cotton [21]. As a natural polysaccharide, chitosan is rich in amino groups, which results in high percentage of nitrogen (6.89%) [22]. Chitosan has wide applications in medical science, food industry, cosmetic industry, agriculture and environmental field [23–25].

In this paper, we introduced chitosan as the binding agent for the first time to prepare AgNPs-loaded ACF. Chitosan is a natural polysaccharide, which has advantages over synthetic ones when used for water purification. In the research method, we combined the two aspects of experimental result and theoretical calculation together. Specifically, molecular dynamics simulation method was applied except for the conventional instrumental characterizations of scanning electron microscope (SEM), energy dispersive spectrum (EDS), X-ray diffraction (XRD), Fourier Transform Infrared Spectrum (FT-IR), zeta potential and Brunauer-Emmett-Teller (BET)

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surface area. Instrumental characterizations were carried out to observe the morphology, crystalline structure, chemical bonds, surface charge and specific surface area of the material. Besides, molecular dynamics simulation method was also applied to explore the loading mechanism of AgNPs on ACF surface. This combination of experimental result and theoretial calculation may provide a new way for the material science researchers in mechanism studying. The AgNPs-loaded ACF material was also tested for antibacterial activity to evaluate its use potential.

2. Experimental section

2.1. Materials and reagents

All the chemical reagents of sodium hydroxide (NaOH), hydrogen chloride (HCl) were purchased from Shanghai Chemical Reagent Co. Ltd (Shanghai, China). Silver nitrate ($AgNO_3$) was primary reagent. Maltose was biochemical reagent purchased from Beijing AOBOX biological technology Co. Ltd (Beijing, China). All the chemicals were used as received without further purification. All the ultrapure water used in this study was produced by EPED system (Nanjing, China). ACF cloth was purchased from Nantong Yongtong Environmental Protection Science and Technology Co., Ltd (Nantong, China).

2.2. Synthesis of silver nanoparticles

Silver nanoparticles used in this study were prepared by hydrothermal method similarly as described by Tang et. al [26]. Typically, 15 mL of $AgNO_3$ aqueous solution (0.02 M) and 15 mL of maltose aqueous solution (0.02 M) were added to 30 mL of deionized water with magnetic stirring. Then the mixture was adjusted to pH value of about 11 by NaOH (1 M) and transferred into a Teflon-lined stainless steel autoclave (100 mL volume) and maintained at 160 °C for 15 min in an electronic oven. After the autoclave cooled down naturally, the precipitate at the bottom of the reactor was sufficiently washed with water and then dried at 60 °C for further usage.

2.3. Preparation of the AgNPs-loaded ACF

To carry out attachment of chitosan onto ACF, pre-weighed quantity of ACF were put in acetic acid solution (0.4%, v/v) containing 0.2% (wt) chitosan, 0.2% (wt) crosslinker citric acid, and 0.15% (wt) sodium dihydrogen phosphate and esterification was carried out at 180 °C for 10 min. Then chitosan-grafted ACF was placed at 60 °C in an oven until the ACF were completely dry. A dry pre-weighed piece of chitosan-grafted ACF was put in AgNPs suspension prepared by dissolving 20 mg of AgNPs in 100 mL of ultrapure water for next 24 h. Then the ACF were washed in deionized water and dried at 60 °C in an oven for further characterization and use.

2.4. Characterization of the AgNPs-loaded ACF

The morphologies of the samples were observed by a JSM-6390A scanning electron microscope (SEM, JEOL, Japan) with an EDS system. The crystalline structures of all the samples were examined by X-ray diffraction meter (XRD, X'pert PRO with Cu Kα radiation). FT-IR spectra of the as-prepared materials was collected by using a FT-IR spectrophotometer (Vertex 70, Germany) in the range of 4000–400 cm^{-1} at a resolution of 2 cm^{-1}. Zeta potential of the samples (dispersed sample powders in deionized water) were measured by Malvern zetasizer NanoZS 90 (Malvern, England). BET surface area of ACF before and after AgNPs loading were measured by a pore size and specific surface area analyzer (BET, Builder, SSA-4300). The loading amount of AgNPs on ACF surface as well as Ag^+ ions concentration released in the disinfection process was checked by the Inductively Coupled Plasma (ICP) measurement in ICPE-9000 system (Shimadzu, Japan).

2.5. Coarse-grained molecular dynamics simulation

Coarse-grained molecular dynamics simulation was carried out to explore the interactions between the chitosan, AgNPs and ACF surface, aiming at revealing the loading mechanism of AgNPs on ACF surface. All simulations were conducted in reduced LJ units. The masses of chitosan monomer, silver nanoparticle and counterion were set to *1.0* to reduce the equilibrium time. Furthermore, implicit solvent model was used. A flat surface consists of uniformly distributed wall particles was used to mimic the carbon surface. Single chitosan chain was coarse-grained as a "bead-spring" model. Unit positive charge was carried by each chitosan monomer. AgNPs were represented by face-centered cubic lattice structural particles with a fixed radius of 8σ. To simulate the negative charge property of AgNPs, unit negative charges were randomly distributed on the nanoparticle surface. The distance between negative charges and nanoparticle center was greater than or equal to 7.92σ. In this study, the number of monomers in single chitosan chain was set to *100*. The number of silver nanoparticles was to be *8*. The sizes of simulation box was $L_x = L_y = 50\sigma$, $L_z = 100\sigma$.

2.6. Antibacterial activity of the AgNPs-loaded ACF

Antibacterial property of the as-prepared chitosan-grafted ACF and AgNPs-loaded ACF materials were tested by the disk-diffusion method [27]. The water disinfection experiment was carried out in a circulated system (Fig. S1) using the AgNPs-loaded ACF material as the filter. Typical gram-positive and gram-negative bacteria of *Staphylococcus aureus* (*S. aureus)* and *Escherichia coli* (*E. coli*) were selected as the model bacterial with initial bacterial concentration of 7×10^5 cfu mL^{-1}. The antibacterial efficiency was determined by comparing the inflow and effluent bacterial concentration via plate counting method [28].

3. Results and discussion

3.1. Preparation and characterization of AgNPs-loaded ACF

3.1.1. SEM observation

The surface morphologies of the differently treated ACF were observed by SEM images. The as-obtained ACF surface is smooth and clean as shown in Fig. 1(a), while numberable particles were found on the smooth ACF surface after the ACF was impregnated in AgNPs suspension (Fig. 1(b)). When the ACF was immersed in chitosan acetic acid solution (0.4%, v/v, containing 0.2% chitosan, 0.2% citric acid, and 0.15% sodium dihydrogen phosphate), followed by impregnation in AgNPs suspension for 24 h, there exists plentiful particles on the ACF surface (Fig. 1(c), (d)). As can be seen, the AgNPs loaded on ACF surface present piles of 1–5 particles. Since no additional dispersant or stabilizer was used, the AgNPs tend to accumulate in the water suspension because of their huge specific surface area and surface energy. We can also see from the SEM image (Fig. 1(c)) that the AgNPs distributed all around the ACF surface, which will be beneficial to the antibacterial process. SEM images of the three samples show apparently that the chitosan-treated process increased the particle number on ACF surface.

3.1.2. EDS analysis

EDS measurement was carried out to confirm the elemental composition of the particles on the ACF surface, the results are