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Preparation and antibacterial property of silver decorated carbon microspheres

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ABSTRACT

Carbon microspheres (CMSs) were prepared by glucose hydrothermal method. The effects of glucose concentration and reaction time on the size and morphology of CMSs were studied. CMSs with surface area of 642.5 m^2/g and pore size of 0.8 nm were exploited to design hybrid material of CMSs with Ag decoration by radio frequency plasma (RF plasma). A series of investigations using X-ray diffraction, UV–vis spectrometry, Fourier transform infrared spectrometry, X-ray photoelectron spectrometry, thermogravimetric analysis, scanning electron microscopy, energy dispersive X-ray spectroscopy, and transmission electron microscopy was carried out to characterize the Ag decorated CMSs. RF plasma was employed to reduce Ag^+ ions to metallic nano-particles with the particle size of 10–20 nm and form a clean metal-support (Ag-CMSs) interface. The mechanism for the structure formation of Ag decorated CMSs was discussed. Plasma produced Ag/CMSs showed antibacterial property and proved suitable for potential biological and environmental applications.

1. Introduction

Microbial pollution caused by microorganisms is one of the major problems related to human health and life quality. To solve this issue from the root, it is inevitable and indispensable to use antibacterial agents. Because of the increasing prevalence of antibiotic-resistant strains, great endeavours have been made to develop the effective, non-toxic, and durable antibacterial materials. Silver has been extensively investigated and well known as a bacteriostatic agent since the ancient times and has been used in many forms in the treatment of infectious diseases. In addition, silver has a broad-spectrum and long-term antibacterial activity and also exhibits low toxicity towards mammalian cells at a small concentration [1,2]. Recently, researchers have reported that Ag nanoparticles exhibited more efficient antibacterial performance compared with their bulk counterparts [3–5]. However, owing to their high surface energy and high reactivity, these silver nanoparticles easily aggregate into large ones. This behaviour contributes to the deterioration of the unique chemical properties of silver and results in the loss of the antibacterial activity.

Good dispersion of Ag nanoparticles is a prerequisite for a sufficient contact and interaction between Ag and microbial species. A great deal of attention has been paid to design and synthesize narrowly distributed Ag nanoparticles with high dispersity and stability. Among them, Ag nanoparticles dispersed on suitable substrates was a promising method. Oxides [6,7], zeolites [8,9] and carbon materials [10–13] have been used as the host supports for Ag nanoparticles. Above all, the carbon materials have been regarded as promising candidates for Ag supporting materials due to their fine chemical durability. The preparation, characterization, and antibacterial activities of carbon nanostructures associated with Ag nanoparticles have been studied. Carbon fibers [10], active carbons [11], carbon nanotubes [12] and graphene oxide [13] have been extensively studied as the supporting materials. Carbon microspheres (CMSs), derived from the fullerene, have unique physical and chemical properties and are ideal materials for Ag loading.

Many efforts have been made to synthesize CMSs and many methods have been developed, such as chemical vapor deposition [14], ultrasonic spray pyrolysis [15], solvothermal [16] and hydrothermal [17] methods. Among these approaches, hydrothermal synthesis of CMSs appears to be an especially facile and green route, since it does not involve organic solvents, surfactants or catalysts. CMSs also had relatively reactive surfaces of oxygen-containing groups inherited from glucose during hydrothermal process. While additional modification of CMSs fabricated by other

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methods was needed. The reactive surfaces of CMSs pave the way for a preparation of Ag decorated CMSs nanocomposites. To date, strategies, including chemical method and physical method have been developed to prepare the Ag/CMSs nanocomposites. In the general chemical method, silver precursors are usually adsorbed onto the CMSs and then reduced to metal nanoparticles by the application of the reducing agent such as sodium borohydride [18], and hydrazine hydrate [19]. In this approach, the processes of separation and purification are necessary to get rid of the impurities with the reducing agents. More green reduction methods have been proposed to explore and implement the way for design of Ag/CMSs nanocomposites. Li et al. deposited the silver particles onto the CMSs using sonication dispersion method [17].

In this work, a novel reduction method with radio frequency plasma (RF plasma) to obtain Ag/CMSs was carried out. Plasma reduction is a facile, green and environmental-friendly way for a preparation of Ag nanoparticles, because the reduction process by plasma is always conducted at low temperature so that it maximally avoids the agglomeration caused by the high temperature calcination [20–23]. In addition, this technology does not need an introduction of additional agents and a subsequent separation and purification, and is considered as an efficient way for Ag decoration on CMSs. CMSs were synthesized by hydrothermal method from glucose and the parameters closely related to the synthesis of CMSs were studied. The growth mechanism of CMSs was proposed. Then, Ag/CMSs composites with well-dispersed Ag nanoparticles were prepared by RF plasma reduction. The antibacterial activity of Ag/CMSs was investigated.

2. Experimental

2.1. Synthesis of CMSs

A glucose solution (0.2 mol/L, 30 mL) was sealed into six stainless-steel autoclaves (50 mL) separately, and each one was autoclaved at 180 °C for 12, 14, 16, 18, 20, 22 h, respectively. Similarly, 0.3, 0.4, or 0.5 mol/L glucose solutions (30 mL) were also employed to produce CMSs at 180 °C based on different reaction time (10, 12, 14, 16, 18, 20 h). The as-obtained solution was cooled down to the room temperature in the air. The black precipitate was collected and sequentially washed with water, pure ethanol and acetone, then dried at 80 °C for 6 h. CMSs were produced by annealing the as-obtained samples under N_2 atmosphere in a tubular furnace. The annealing temperature was raised at a heating rate of 20 °C/min to 600 °C and then was kept isothermal for 0.5 h.

2.2. Synthesis of Ag decorated CMSs by RF plasma

Incipient wetness impregnation was applied to load Ag precursor onto CMSs (6 w% Ag). CMSs were firstly impregnated with an aqueous solution of silver nitrate for about 12 h. The obtained sample was dried at 60 °C for 12 h. This sample was denoted as Ag^+/CMSs. Then the sample (0.1 g) was exposed to helium RF plasma for 1 h with plasma power of 100 W and helium pressure of 50 Pa. The RF plasma system was illustrated in Fig. 1. The sample after RF plasma treatment was denoted as Ag/CMSs.

2.3. Characterizations

X-ray diffraction (XRD) analysis was performed with a Rigaku D/MAX-2500 V/PV using Cu $K\alpha$ radiation (40 kV and 200 mA) at a scanning speed of 4°/min over the 2θ range of 10°–80°. The surface areas and porosity of the samples were characterized with N_2 sorption analysis. N_2 adsorption-desorption isotherms were measured at −196 °C using a Micromeritics Tristar 3000 analyzer. The Diffuse-reflectance UV–vis (DR UV–vis) spectra were recorded with a Shimadzu UV-2550 spectrophotometer. Fourier transform infriared (FT-IR) spectra were recorded using a Tensor 27 spectrometer (Bruker) with a resolution of 4 cm^{-1}. X-ray photoelectron spectrometer (XPS) analysis was conducted by a Perkin-Elmer PHI-1600 spectrometer with monochromatic Mg $K\alpha$ (1253.6 eV) radiation. Binding energies were calibrated using the C1s peak (284.6 eV) as a reference. Thermo-gravimetric analysis (TGA) of the CMSs hybrid material decorated with Ag was carried out using a Netzsch STA 449 F3 system with a heating rate of 10 °C/min (from 100 °C to 800 °C) under flowing air (25 mL/min). Scanning electron microscopy (SEM) images with energy dispersive X-ray spectra were recorded with Hitachi field emission scanning electron microscope (S4800). Transmission electron microscopy (TEM) observations were carried out using JEM100CXII operated at 100 kV.

2.4. Computational methods

Geometry optimization and frequency calculations were performed by using density functional theory (DFT) as implemented in

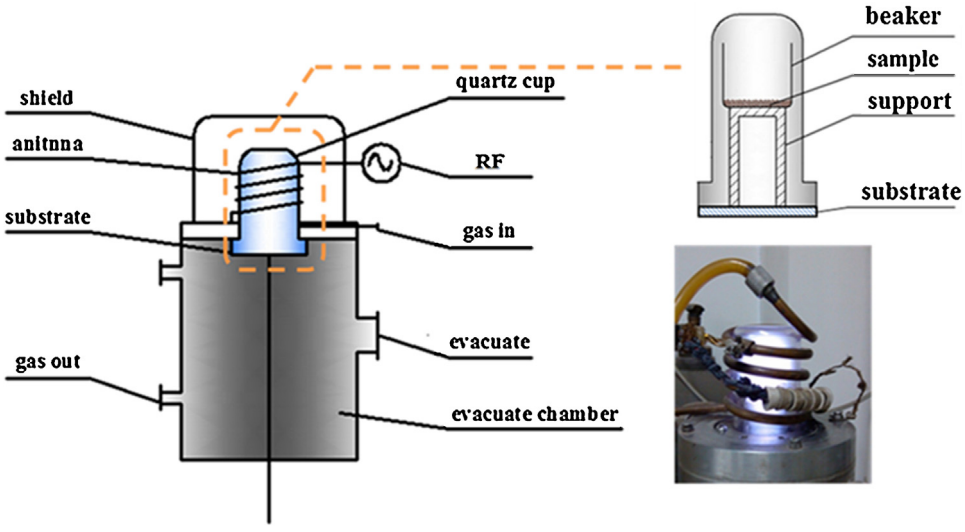

Fig. 1. The schematic diagram of RF plasma apparatus.

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