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Synthesis of copper nanoparticle-coated poly(styrene-*co*-sulfonic acid) hybrid materials and its antibacterial properties

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ABSTRACT

Sphere-shaped and monodispersed copper nanoparticle-coated poly(styrene-*co*-sulfonic acid) (Cu/PS) hybrid nanomaterials had been successfully synthesized by a green and facile synthesis method, in which chlorosulfonic acid and glucose were used as a sulfonating agent of polymer beads and a reducing agent. SEM and X.RD measurements revealed that the Cu/PS hybrid materials were successfully acquired. Moreover, the size and shape of Cu nanoparticles of the Cu/PS hybrid materials (*i.e.*, Cu/PS-1, Cu/PS-2 and Cu/PS-3 hybrid materials) depended on the sulfonating agent and reducing agent concentrations. The results revealed that the Cu nanoparticles and PS spheres of the Cu/PS-3 hybrid materials had the average diameters of ca. 10 and 120 nm, respectively. Moreover, the Cu/PS-3 displayed excellent antibacterial properties such as relatively low minimal inhibitory concentrations (MICs) against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*).

1. Introduction

In recent years, hybrid materials which were fabricated by using organic or inorganic as cores have been receiving significant attentions [1,2] because they exhibit a wide range of applications such as surface-enhanced Raman scattering (SERS) [3], catalysis [4], semiconductor community [5] and bioanalysis [6]. The antimicrobial potential of nanoparticles (Ag and Cu, *etc.*) is a subject of great interest to chemists and biologists in recent years [7]. And the usefulness of Cu as an antibacterial agent has been known for a long time, which is an effective agent with lower cost and lower toxicity antibacterial treatment. If Cu is immobilized on the hosts, the release time of Cu ions would be delayed for a long time so that Cu-supported materials will be of great potential for this application [8,9]. At present, many antibacterial agents were mainly based on organic materials [10]. The polystyrene is an effective template for the preparation of hybrid materials because of ease in surface functionalization and flexibility in size variations. And synthesis of metal/polymer hybrid materials is an ongoing challenge in materials preparation.

The most common methods for preparation metal/polymer hybrid nanomaterials are electroless plating [9], microwave absorbing coating [10] and in-situ deposition [11]. In the past, Cu/polymer hybrid nanomaterials had been synthesized using various methods including supercritical carbon dioxide, involving chemical agents like sodium borohydride and hydrazine hydrate [12]. All these chemicals pose potential environmental and biological risks. Utilization of nontoxic chemicals, environmentally benign solvents and renewable materials are some of the key issues that merit important consideration in a green synthesis strategy. There were reports on the synthesis of Cu nanparticles using environment-friendly glucose as the reducing agent [13,14].

In this work, we reported a green and facile synthesis method for the fabrication of Cu/PS hybrid materials by using chlorosulfonic acid and glucose as sulfonating agent and reducing agent, respectively. With gentle heating, this system is a mild, renewable, inexpensive and nontoxic reducing agent. The chemical structure, morphology and antimicrobial activities of Cu/PS-3 hybrid materials were investigated.

2. Experimental

Styrene and sodium lauryl sulfate (SDS) were purchased from Aldrich-Sigma. Other chemical reagents were obtained from Guangdong Chemical Reagent Company. All reagents were analytical grade and used without further purification. All aqueous solutions were purified by using the PINE-TREE system (> 18.2 M Ω cm, 25 °C).

Sulfonated PS (–SO_3H grafted PS) were prepared through a modified method [15,16]. In a typical experiment, 1.0 g PS beads

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were dispersed in 35 mL dichloromethane and stirred for 2 h. Then 3.5 mL chlorosulfonic acid was added and kept stirring for 1 h. Finally, the sulfonated PS beads were acquired through drying in vacuum.

In a typical procedure for the preparation of Cu/PS-1 hybrid materials, a 500 mL beaker containing aqueous solution including 0.5 g of PS and 100 mL water was prepared. Then 30 mL of 0.05 mol/L $Cu(NO_3)_2 \cdot 3H_2O$ was added to the above solution. After complete dissolution, 25 mL of 0.1 mol/L glucose was added and kept stirring. Finally, the product was obtained by heating the mixture at 40 °C for 20 h. Also, Cu/PS-2 and Cu/PS-3 hybrid materials were also synthesized through using 0.5 g of as-sulfonated PS and 25 mL of 0.1 mol/L $NaBH_4$ or 0.1 mol/L glucose, respectively. Finally, the products were obtained by centrifuging at 8000 rpm for 15 min, washing several times with absolute ethanol and dried in vacuum at 60 °C for 12 h.

The morphologies of the samples were performed on a scanning electron microscopy (SEM, LEO1530 VP) at an accelerating voltage of 20 kV. The crystallinities of the samples were determined with a MSAL-XD2 X-ray diffractometer (XRD). The high-resolution transmission electron microscopy (HRTEM) images were taken on a JEM-2010 instrument. The particles size distribution of samples was calculated by using the zeta particle sizing instrument (Malvern Zetasizer IV, UK). The elemental depth profiles were determined by an ESCALAB 250 X-ray photoelectron spectroscopy (XPS). The topographic image of *Escherichia coli* was examined with an AutoProbe CP Research atomic force microscope (AFM).

3. Results and discussion

Fig. 1 shows SEM images of PS and Cu/PS-X hybrid materials produced thus. The PS spheres (Fig. 1a) possessed uniform sizes (the average diameter of ca. 120 nm) and shape and exhibited smooth surface. The Cu/PS-1 hybrid materials, fabricated by using glucose and without using sulfonating agent, have few Cu nanoparticles deposited on the PS beads (Fig. 1b). The Cu/PS-2 hybrid materials, prepared through using sodium borohydride and sulfonating agent, had only a few Cu nanoparticles (Fig. 1c). The Cu/PS-3 hybrid materials produced through using sulfonating agent and glucose as reducing agent had larger Cu nanoparticles of the average of about 10 nm (Fig. 1d). And spherical profile of the core–shell structured Cu/PS-3 hybrid materials has been expected, some Cu nanoparticles were visible to make the coating layer even and uniform.

Fig. 2a shows XRD patterns of PS and Cu/PS-3 hybrid materials. The broad XRD reflection peak at 20.5° could be assigned to diffraction of amorphous structures of the PS spheres. The data for the Cu/PS-3 hybrid materials peaks at 38.15°, 44.35°, 64.45°, 77.40° and 81.54° corresponded to the (111), (200), (220), (311) and (222) crystalline planes of Cu crystal, respectively, which corresponded to the typical peaks of the face centered cubic Cu (JCPDS: 03-1005).

Fig. 2b displays HRTEM image of the Cu/PS-3 hybrid materials. The distance between the adjacent fringes in the particle's shell was 0.196 nm, which fitted well with the distance between the (111) crystalline planes of the Cu nanoparticles. The point pattern of the corresponding selected area electron diffraction (SAED) (Fig. 2c) further confirmed the single-crystalline nature of the Cu. The size distribution of the Cu/PS hybrid materials is shown in Fig. 2d, indicating that the hybrid materials had a narrower size distribution. The formation of Cu/PS hybrid materials is schematically represented in Fig. 2e, which schematically displays an overall procedure for synthesis of hybrid materials.

Fig. 3a shows XPS spectrum of the Cu/PS-3 hybrid materials. The content of Cu nanoparticles on the surface of PS could be estimated to be about 4.3%. In order to investigate the chemical state of Cu, XPS spectrum of the Cu2p is recorded (Fig. 3b). Indexed to the standard spectra, the peaks at 935.60 and 955.60 eV could be attributed to Cu2p3/2 and Cu2p1/2 of Cu, indicating that the nanocomposites contained Cu nanoparticles. In addition, the aromatic p-electrons of PS also interacted with the atoms of metal surface layer, which greatly increased the stability of the nanoparticles in the hybrid materials [17].

The antibacterial property of the Cu/PS-3 hybrid materials was determined by using *E. coli* (ATCC 25922) and *Staphylococcus aureus* (ATCC 25923) bacterial strain as the test bacterials. The

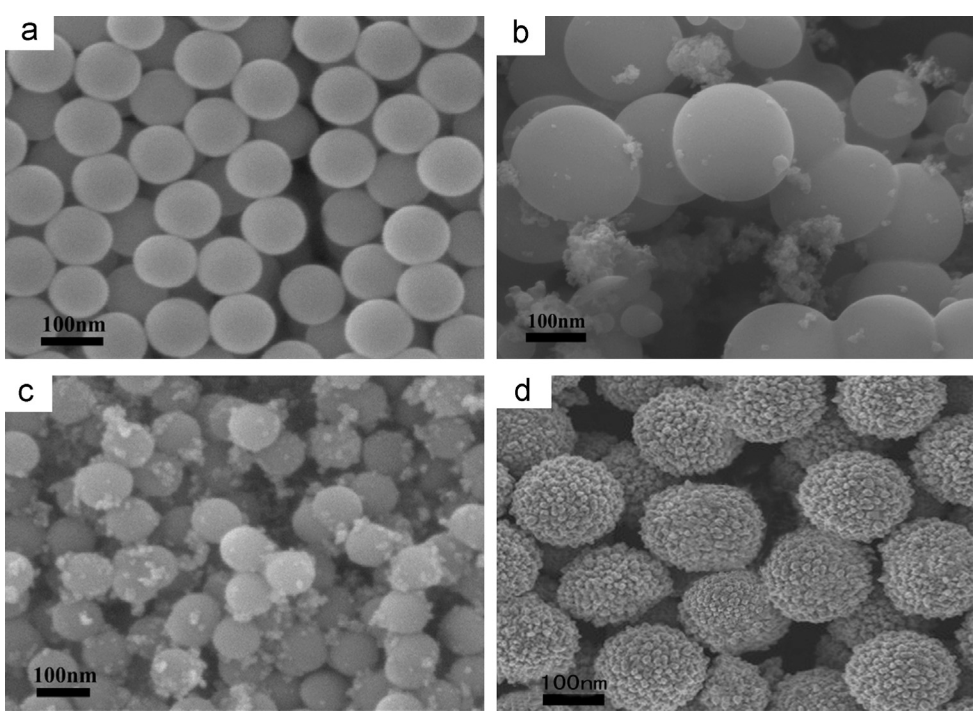

Fig. 1. SEM images of (a) PS, (b) Cu/PS-1, (c) Ag/PS-2 and (d) Cu/PS-3.