In situ decoration of Ag nanoparticles on chitosan spheres with enhanced photo-catalytic activity

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Abstract. In this study, Ag-decorated chitosan (Ag-chitosan) spheres were synthesized through in situ decoration of Ag nanoparticles (NPs) on the surface of chitosan spheres via a hydrothermal route. Chitosan spheres were synthesized through emulsification of chitosan solution in the paraffin oil followed by cross-linked with glutaraldehyde. They were then soaked in the solution of AgNO₃ and subject to a hydrothermal treatment at 120°C to produce Ag-chitosan spheres. SEM observation showed that the Ag-chitosan spheres were spherical in shape with the diameter of 5-20 µm. An EDS spectrum showed that the Ag-chitosan spheres were rich in C, O, and Ag elements. After incubation in the solution of 4-nitrophonol and NaBH₄, Ag-chitosan spheres showed good photo-catalytic activity for reduction of 4-nitrophonol.

1. Introduction
Ag nanoparticles (NPs) are one type of the representative noble metal nanoparticles and have received considerable attention because of easy preparation route, controllable size and morphology, strong anti-bacterial property and excellent photo-catalytic activity[1-2]. They have been extensively utilized as the anti-bacterial components in the biomaterials for inhibition of the growth of bacteria[1] and photo-catalyst for decomposition of organic pollutants in the wastewater[2]. However, their practical application is still limited by their serious agglomeration.

Immobilization of Ag NPs on the material substrates has been considered as one of the most promising methods to reduce their agglomeration and improve their stability. Numerous types of materials have been developed for immobilization of Ag NPs, including inorganic materials[3] and polymeric materials. Compared with inorganic materials, the polymeric materials[4] are much more interesting because many functional groups are involved in the polymers and have a strong affinity to Ag NPs.

Chitosan is one of the natural polysaccharides and shows excellent biocompatibility, biodegradability and anti-bacterial property[5-7]. It has been extensively utilized as biomaterials for a variety of applications such as drug delivery system[5], bone regeneration[6] and food packaging[7]. Especially, the amino groups of chitosan well complex with Ag ions to produce chitosan-Ag composites, including chitosan-decorated Ag NPs[8], chitosan-Ag NP composite films[9] and chitosan-Ag NP hydrogels[10]. However, most of the above researchers focused on the anti-bacterial property of chitosan-Ag composites. The photo-catalytic activity of chitosan-Ag composites has been little addressed.

In this study, a simple method was developed to synthesize Ag-decorated chitosan (Ag-chitosan) spheres through in situ reduction of chitosan spheres in the solution of AgNO₃ via the hydrothermal
treatment. Microstructure and photo-catalytic activity of the resultant Ag-chitosan spheres were investigated. 4-nitrophenol was used as model chemical to evaluate the photo-catalytic activity of the Ag-chitosan spheres.

2. Experimental

2.1. Synthesis of chitosan spheres

Chitosan spheres were synthesized through emulsification of chitosan solution in the paraffin oil via an emulsion technique (figure 1). Briefly, appropriate amount of chitosan powder was dissolved in the acetic acid (1%, v/v) solution to obtain chitosan solution (2%, w/v). 7 mL of chitosan solution was then added to 50 mL of paraffin containing 2 mL of Span-80 and kept stirring at room temperature for 1 h. 2 mL of glutaraldehyde solution (5%, v/v) was then added to the emulsion and kept stirring for another 1 h to produce chitosan spheres. The resultant spheres were collected by centrifugation at 5,000 rpm for 5 min, washed with petroleum ether, isopropanol and water, and finally freeze-dried.

2.2. Synthesis of Ag-chitosan spheres

Ag-chitosan spheres were synthesized through hydrothermal treatment of chitosan spheres in the solution of AgNO$_3$ (figure 1). Briefly, the freeze-dried chitosan spheres (30 mg) were soaked in 20 mL of AgNO$_3$ (1 mg/mL) which was held in a 100-mL Teflon-lined autoclave and hydrothermally treated at 120°C for 4 h. The resultant samples were then collected by centrifugation at 5,000 rpm for 5 min, washed with water and finally freeze-dried.

2.3. Characterizations

Microstructure of chitosan spheres and Ag-chitosan spheres was observed with a scanning electron microscope (SEM, JEOL, Japan), equipped with the energy diffractive spectrophotometer (EDS). Infrared spectra of them were measured with a Fourier transformed infrared spectroscopy (FT-IR, Bruker, Nicolet 710) with a KBr pellet method.

2.4. Photo-catalytic activity

4-nitrophenol (4-NP) was utilized as model chemical to investigate the photo-catalytic activity of the as-synthesized samples. Briefly, a mixture of 4-NP and NaBH$_4$ was obtained by mixing 0.8 mL of 4-nitrophenol (0.25 mmol/L) and 0.8 mL of NaBH$_4$ (0.1 mol/L) in a 4 mL-quartz cuvette. Chitosan spheres (15 mg) and Ag-chitosan spheres (15 mg) were separately added to the above mixture. The photo-catalytic activity of both types of samples was monitored with an Ultraviolet-visible (UV–vis) machine (UV-8000S, Shanghai Metash, China). The absorption of the mixture was collected at the intervals of 2 min.

3. Results and discussion

In our previous study[11], gold nanorod-doped gelatin/hydroxyapatite composite spheres were successfully synthesized through emulsification of gold nanorod/gelatin/hydroxyapatite mixture in the plant oil and presented spherical morphology. In the present study, the similar emulsion technique was also applied for synthesis of chitosan spheres. Size and morphology of the as-synthesized chitosan spheres were shown in figure 2. It was clearly observed that the as-synthesized chitosan spheres were
spherical in shape and had the diameter of 5-20 µm (figure 2a). For immobilization of Ag NPs, the chitosan spheres were subject to a hydrothermal treatment in the solution of AgNO₃. After hydrothermal treatment, the resultant Ag-chitosan spheres were also spherical in shape and had the similar diameter of 5-20 µm (figure 2b). A SEM image further confirmed that the Ag-chitosan spheres presented spherical morphology with the diameter of 5-20 µm (figure 2c). A high magnification image (figure 2c, inset) showed that much smaller Ag NPs were clearly observed on the surface of Ag-chitosan spheres. Moreover, a significant difference in color was found between both types of spheres. Chitosan spheres were yellow due to the cross-linking of glutaraldehyde (figure 2a, inset). After hydrothermal treatment in the solution of AgNO₃, Ag-chitosan spheres were deeply dark (figure 2b, inset). This difference in color further indicated that Ag NPs were successfully immobilized on the chitosan spheres. To confirm this speculation, an EDS spectrum of Ag-chitosan spheres was conducted. As shown in figure 2d, the elements C, O, and Ag were found in the Ag-chitosan spheres. The presence of those elements indicated that the Ag-chitosan spheres were derived from chitosan and AgNO₃. This confirms the successful synthesis of Ag-chitosan spheres.

Figure 2. Optical microscopy images of (a) chitosan spheres and (b) Ag-chitosan spheres, (c) SEM image and (d) EDS spectrum of Ag-chitosan spheres.
Figure 3 shows FT-IR spectra of (a) chitosan spheres and (b) Ag-chitosan spheres. In the case of chitosan spheres, the peaks at 2850 and 2930 cm\(^{-1}\) were assigned to \(-\text{CH}_2-\) bonds. The peaks at 1650 cm\(^{-1}\), 1560 cm\(^{-1}\), 1390 cm\(^{-1}\) were assigned to the amide I (C=O), amide II (N-H), and amide III (C-N), respectively. The peak at 1110 cm\(^{-1}\) was attributed to C-O bonds. After Ag decoration, Ag-chitosan spheres had the similar spectrum to chitosan spheres, indicating that the as-synthesized Ag-chitosan spheres were derived from chitosan. This is consistent with the result in figure 2d. Biao et al. synthesized chitosan-stabilized Ag NPs through hydrothermal treatment of the mixture of chitosan and AgNO\(_3\) and pointed out that the amino groups in the chitosan might serve as active site to reduce Ag ions to Ag NPs[8]. Therefore, the presence of amino groups in the chitosan spheres might play a similar role for the formation of Ag-chitosan spheres.

4-NP is one of the typical organic pollutants in the wastewater and has been utilized as model chemical to examine the photo-catalytic activity of different types of noble metal NPs[12-13]. In the present study, it was also used as model chemical to examine the photo-catalytic activity of Ag-chitosan spheres. Figure 4 shows UV spectra of the mixture of 4-NP and NaBH\(_4\) after exposed to chitosan spheres and Ag-chitosan spheres. In the case of chitosan spheres, only a sharp peak at 400 nm was observed and normally assigned to 4-nitrophnolate ions[12]. With increasing the reaction time, no significant difference in intensity of peak at 400 nm was observed, indicating that chitosan spheres had no photo-catalytic activity. In the case of Ag-chitosan spheres, the intensity of peak at 400 nm was significant decreased with increasing the reaction time from 0 to 10 min. This indicated that the Ag-chitosan spheres presented photo-catalytic activity for reduction of 4-NP. Also, a small peak around 295 nm assigned to 4-aminophenol (4-AP) was observed and its intensity was increased with increasing the reaction time from 0 to 10 min. This indicated that 4-NP was successfully converted to 4-AP due to the photo-catalytic activity of Ag-chitosan spheres.
4. Conclusions
In summary, Ag-decorated chitosan spheres were successfully synthesized through in situ immobilization of Ag nanoparticles on chitosan spheres. They were spherical in shape and had the diameter of 5-20 µm. They presented the excellent photo-catalytic activity for reduction of 4-NP to 4-AP.

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