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Hyperbranched Polyphenylene Sulfide as Stabilizer to Prepare Colloidal Silver Nanoparticles

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Hyperbranched polyphenylene sulfide (HPPS) was used as a promising stabilizer to prepare stable colloidal silver nanoparticles in solution. Silver nano composites with small particle sizes were obtained and the average particle size could be controlled from 5 to 13 nm by adjusting the mass ratio of HPPS/Ag. The antibacterial activity of the HPPS/Ag nano composites was also investigated against common bacteria (such as *Escherichia coli* and *Staphylococcus aureus*). The resulting silver nanoparticles were able to efficiently inhibit the growth and multiplication of these bacteria.

Keywords: Hyperbranched polyphenylene sulfide, Stabilizer, Silver-nanoparticle, Antimicrobial.

INTRODUCTION

During recent years, the polymer/silver[1,2] nanocomposites have received much attention due to their various potential applications in catalysts, electronics, chemical sensors, *etc.*[3-6]. Due to the high surface energy, they tend to aggregate and aggregation limits their use in above-mentioned applications. Thus the most prominent challenge in dealing with nanoscale particles is to prevent their aggregation in the media. Generally, the metal cations are complexed with a certain polymer, to form the stable colloidal polymer/metal nanocomposites. Here the polymers acted as stabilizers, templates, or protecting agents. For example, silver nano decahedrons were fabricated under the assistance of linear polymer[6]. Silver was successfully encapsulated within dendrimers[7]. In this case, the polymer matrix serves as a suitable scaffold for immobilizing the nanoparticles and preventing them from aggregation. All of these polymers possessed some strong electron-donating centers, such as sulfur group or nitrogen group, to facilitate the complex with the metal ions. But linear polymer as the scaffold for metallic nanoparticles often resulted in the coagulation of metallic nanoparticles and dendrimers is not simple to synthesized[8,9]. In order to solve these problems, we designed and synthesized a new kind of stabilizer, the hyperbranched polyphenylene sulfide (HPPS), to protect colloid silver nanoparticles. The advantages of this method come from the structure and property benefits of the used hyperbranched polymer HPPS. This work was started using 2,4-dichlorobenzenethiol, to generate the hyperbranched polyphenylene sulfide by self-condensation reaction. As a stabilizer, HPPS contains plenty of S atoms, which allows the formation of strong Ag-S bond. Meanwhile the one-step synthesis allows hyperbranched polyphenylene sulfide to be more readily available and prepared on a large scale for potential applications as compared with dendrimers.

It is generally recognized that the materials containing silver nanoparticles exhibit some effective antibacterial properties[10-12]. Hence the antibacterial properties of the HPPS/Ag nanocomposites were also studied. As expected, they showed highly antibacterial activity against several bacteria.

EXPERIMENTAL

$AgNO_3$ was purchased from Aladdin reagent co and used as received. Hyperbranched polyphenylene sulfide ($M_n = 9578$, $M_w/M_n = 1.14$) was synthesized according to the literature. Ultrapure water processed by the Milli-Q plus system was used to prepare all the aqueous solutions. Tetra-*n*-octylammonium bromide and $NaHB_4$ was purchased from Aladdin reagent co. *Escherichia coli* and *Staphylococcus aureus* were cultivated in a incubator. The sterilized beef broth was prepared in a incubator.

Preparation of silver nanoparticles: The preparation was performed based on the S/Ag mass ratio calculated by the total S value of HPPS and the concentration of aqueous solution of $AgNO_3$. A typical procedure is as follows: 0. 1 mL of aqueous solution of $AgNO_3$ (10 mmol/L) was dropped into 5 mL of chloroform solution of HPPS (20 g/L) under vigorous stirring within 5 min. Next, 10 mL of tetra-*n*-octylammonium bromide chloroform solution (5 mmol/L) was droped into the above mixture. Then it was kept stirring at room temperature for 2 h in the dark. In addition, 10 mL of $NaBH_4$ aqueous solution was mixed into the above mixture. Last it was kept stirring at room temperature for 2.5 h in the dark. In this progress, the milky solution gradually changed into the yellow-brown collid, indicating that silver cations (Ag^+) were reduced into elemental silver (Ag^0). By adjusting the ratio of HPPS/Ag (HPPS/Ag = 185, 37, 18.5 and 1.85, respectively), a series of colloidal silver nanoparticles were obtained. The method based on NaCl was conducted to confirm no remaining Ag^+ in the resulting colloidal solution[10].

Antibacterial experiment: An antibacterial test was performed by the inhibition zone method[15]. The inhibition ratio based on the bacterial optical density (OD) was presented as the antibacterial efficiency. Typically, 10 mL of sterilized beef broth was added into a sterile dish. The cultured *Escherichia coli* in the stationary phase was inoculated into the sterile dish containing beef broth the solution. Four circular filter papers at the same size were placed in the sterile dish. The HPPS/Ag colloid in a certain silver concentration was dropped onto the circular filter paper. The mixture was incubated 2 h at 37 °C in a incubator. The antibacterial abilities of the above stable colloidal HPPS/Ag nanocomposites were tested at different HPPS/Ag mass ratios (1.85, 18.5 and 37), corresponding to 2, 3 and 4. The antibacterial ability of pure HPPS (1) was also tested as a contrast.

For Fourier transform infrared (FTIR) measurement, the colloidal silver solution was centrifuged and the resulting precipitates were dried in the vacuum oven for characterization. The formation of stable HPPS/Ag nanocomposites was further monitored by the UV-visible absorption band of silver nanoparticles. Ultraviolet spectrum were recorded on a PuXi Company in Beijing 20/2.0 UV-visible spectrometer. Transmission electron microscopy was used to measure the particle size and morphology of the silver nanoparticles in the colloids.

RESULTS AND DISCUSSION

When $NaBH_4$ solution was added to the chloroform solution of HPPS and the aqueous solutions of $AgNO_3$, Ag^+ was shifted to the organic phase by tetra-*n*-octylammonium bromide and complexed with HPPS[13]. Then Ag^+ was reduced into Ag to form colloid silver nanoparticles. The process was conducted at room temperature, under normal pressure, so it is a straight forward route. The obtained silver nanoparticles have small particle sizes. Hyperbranched polyphenylene sulfide shows strong interactions with the reduced silver nanoparticles. Fig. 1 displays the FTIR spectra of HPPS and the HPPS/Ag nanocomposites. If silver nanoparticles are present, the infrared absorption peak[14] will appeared at 770-720 cm^{-1}. As can be seen in Fig. 1, there is a clear infrared absorption peaks at 753.15cm^{-1}in FTIR spectra of HPPS/Ag nanocomposites. There is a clear UV absorption peaks about 420 nm. As shown in Fig. 2, only one characteristic peak at 320 nm was observed for the pure HPPS. However, a new strong absorption band appeared at 420 nm after $NaBH_4$ solution was added to the mixed solution of HPPS and $AgNO_3$ and stirred for 2h. This can be attributed to the surface plasmon absorption of silver colloids. As for the HPPS/Ag colloid, it was very stable without any precipition for several months. A representative TEM micrograph of the colloidal HPPS/Ag nanocomposites is shown in Fig. 3. The silver nanoparticles are spherical and uniform particle size and the average particle size is about 9.55 nm.

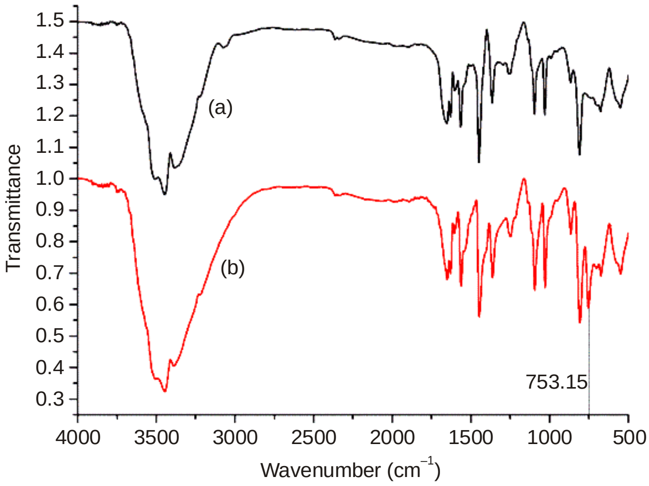

Fig. 1. FTIR spectra of neat HPPS (a) and HPPS/Ag (b) nanocomposites. The mass radio (HPPS/Ag) = 18.5

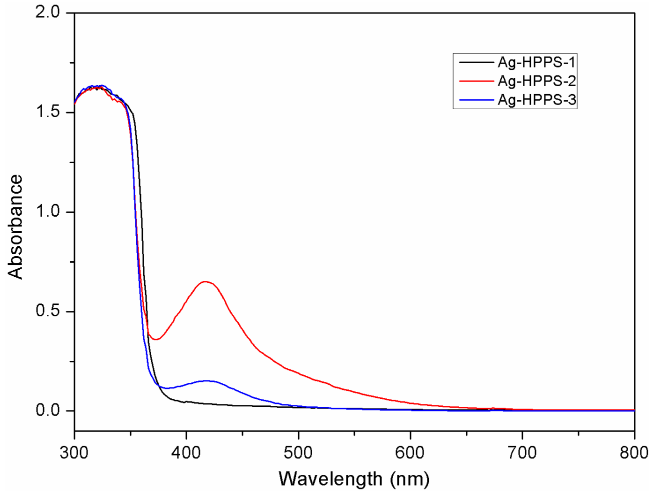

Fig. 2. UV-visible absorption spectra of colloid silver nanoparticles stabilized by HPPS among a series of colloid silver nanoparticles. Ag-HPPS-1 is neat without Ag. Ag-HPPS-2: The mass radio (HPPS/Ag)=18.5

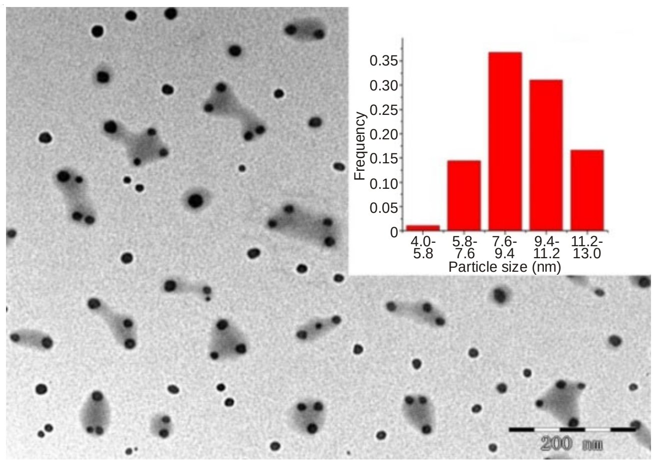

Fig. 3. (a) TEM image of HPPS/Ag nanocomposites. The mass radio (HPPS/Ag) = 18.5. Inset: Corresponding size distribution histogram from the TEM

It is generally recognized that silver nanoparticles have a high affinity to react with the sulfur- and phosphorus-containing compounds in the bacterial cells. Therefore, they can attach to the surfaces of the bacterial cells and binding membrane protein, resulting in its inactivation, leading to bacterial death[15,16]. Besides, the HPPS macromolecules are able to capture the surrounding negatively charged bacteria through the strong ionic interaction, which can effectively decrease the distance between the silver nanoparticles and bacteria[16-19].

Conclusion

In conclusion, a series of stable colloid silver nanoparticles were prepared by utilizing hyperbranched polyphenylene sulfide as stabilizer through a facile process; the nanoparticles were able to effectively inhibit the growth and multiplication of several bacteria. Hyperbranched polyphenylene sulfide possesses a highly branched structure, so it has excellent solubility in chloroform and can effectively avoid chain entanglements in comparison with the linear polymers. These features make it a nice template to obtain monodispersed silver nanoparticles.

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