Controlled Preparation of PS@Au/Ag Nanoshells with Chitosan Polyelectrolyte

Xinbing Jiang, Shujiang Ding, Guang Yang and Ben Q. Li

Abstract—**This paper discusses the effect of two crucial processing parameters (seed size and amount of ion solution) on the controlled seed-and-grow preparation of polystyrene@gold/silver nanoshells with chitosan (CHI) as a surface modifier. Experiments involved synthesizing PS nanospheres and functionalizing them with CHI. Au seeds were then attached onto the CHI-functionalized PS spheres and metal was subsequently deposited onto the PS spheres from metal ion solutions to form PS@metal nanoshells. It is found that Au seed size can have a profound effect on the seed coverage of PS surface and the quality (morphology and optical properties) of nanoshells. Use of smaller-sized seed sizes gives a better seed coverage and good quality nanoshells. Appropriate volumetric amount of K-gold/silver nitrate solution is required for obtaining a complete nanshell with desired shell thickness. These findings are confirmed by the TEM characterization and the UV-vis spectra of light absorption.**

Keywords— polystyrene, gold, silver, nanoshell, chitosan.

I. INTRODUCTION

THERE has been considerable interest in noble metal nanoshells, which are composite nanoparticles made of a dielectric core covered by a metal shell with a thickness of a few to a few tens nanometers. These nanostructured composite particles possess a useful optical property of frequency-tunable localized surface plasmon resonance (LSPR) that originates from the resonant optical excitation of the collective oscillation of conduction electrons in the metal [1-4]. By varying the relative geometric dimensions of the dielectric core and the metal shell, the resonance of a nanoshell may be tuned over hundreds of nanometers in wavelength from the visible into the infrared region. Because of this unique frequency-tunable feature, metal nanoshells have found applications ranging from photonics and electronics to biomedical technology. The higher refractive index of polystyrene (PS) yields a narrower plasmon resonance absorption peak for gold nanoshells on polystyrene (PS@Au), in comparison with nanoshells on silica cores [5]. A narrower resonance peak is often desired for better sensitivity in biomedical image and optical communications.

There are many methods to fabricate core@shell nanostructure, for example, ion sputtering [6], self-assembly [7], and “seed and growth” [8]. The most popular approach is perhaps the “seed and grow” method. By this approach, the surface of the dielectric core particle is functionalized, whereupon tiny gold seed nanoparticles are attached. This is then followed by reducing the metal from its ion solutions onto these ‘seed’ particles to form a complete metal shell around the dielectric core.

In this paper, experiments were conducted to determine the effect of Au seed size and the K-gold/silver nitrate solution on the quality of PS@Au (core@shell) and PS@Ag nanoshells fabricated using the seed-and-grow method. Understanding of these parametric effects is crucial in designing and optimizing processing conditions for controlled preparation of these nanostructures with adequate properties desired for specific applications.

II. EXPERIMENTAL

2.1 Preparation of carboxylic-modified polystyrene spheres

Carboxylic-modified polystyrene latex particles (PS) were made by the process of emulsifier-free emulsion polymerization [9]. In a reaction vessel containing 100 ml of deionized water and 2.5 ml of 0.75 M ammonium hydroxide solution, 3 ml of styrene and 0.03 ml of divinyl benzene were injected. The temperature was then raised to 70°C for the decomposition of initiator potassium persulfate ($K_2S_2O_8$). Prior to adding the initiator, nitrogen gas was introduced in the reactor for 30 min in order to purge oxygen out. This was followed by adding 1.25 ml of 0.17 M acrylic acid solution and then 6.25 ml of 37 mM $K_2S_2O_8$ solution (separate agents). The reaction was left to reflux for 8h. Nitrogen purge and stirring at a rate of 400 rpm were maintained throughout the polymerization. Fig. 1 shows the TEM image of PS spheres so obtained.

2.2 Synthesis of gold seeds

The preparation of gold seeds typically involves a reduction of gold salts in the presence of surfactants and stabilizers. In this study, three types of gold seeds were prepared by reducing chloroauric acid, with the reducing agents: (1) sodium citrate, or (2) sodium borohydride or (3) tetrakis(hydroxymethyl)phosphonium chloride (THPC). These seeds are labeled as cirate-gold, borohydride-gold and THPC-gold, respectively. The preparation of cirate-gold

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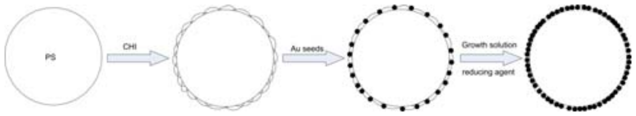
followed the Weiser's method [10]. In brief, 10 ml of $HAuCl_4$ (5 mM) solution was added to a flask containing 85 ml of boiling HPLC water, and the mixture was allowed to back to a boil. Then, a freshly prepared sodium citrate solution (5 ml, 0.03 M) was added to the mixture. Several minutes later, cirate-gold was obtained when the color of the solution changed from colorless to deep wine-red. Borohydride-gold was synthesized by the following method described by Murphy et al. [11]. 20 ml aqueous solution containing 0.25 mM of $HAuCl_4$ and 0.25 mM of sodium citrate was prepared in a conical flask in an ice water bath. And then, 1 ml of freshly prepared 0.08 M sodium borohydride solution was added to the mixture and stir intensively. Borohydride-gold formed when the color of the resulting solution is shallow wine-red. For the formation of THPC-gold seeds, the method described by Pham et al. [12] was adopted. 0.5 ml of freshly prepared 1 M sodium hydroxide and 1 ml of THPC solution (prepared by adding 60 µl of 80% THPC in water to 5 ml of HPLC water) were added to a flask that contained 45 ml of HPLC water. The mixture was stirred for a few minutes and then 10 ml of 5 mM $HAuCl_4$ was added. The color of the resulting solution became dark brown, indicating the formation of THPC-gold.



Scheme 1 Schematic of steps for preparing PS@Au/Ag nanoshells

2.3 Functionalization of the surface carboxylic-modified polystyrene with CHI

Nanoshells were prepared following the procedures illustrated in Scheme 1. First, the surface of PS nanoparticles obtained as described in Section 2.1 was functionalized with chitosan polyelectrolyte (CHI) [13]. This started with dispersion of 0.1 g PS spheres in 30 ml 0.2 M acetate buffer with pH of solution kept at 2.6. A solution mixture of 1ml of 0.1% chitosan and 1% acetic acid to the colloid under stirring and then stirring was continued for 15 minutes. After that, the excess CHI polymer in the supernatant was rinsed by HPLC water after centrifugation at 10,000 rpm for 10 minutes. Repeat this action three times.

2.4 Link of gold seeds to the CHI-modified PS

Next, gold seeds prepared as described in 2.2 were attached onto the surface of CHI–modified PS particles. This was done by mixing 2 ml PS particles functionalized by CHI with an appropriate amount of one of the three different types of gold seeds.

2.5 Growth of gold shell

The last step was the growth of gold shell by reducing gold ions from gold hydroxide solution. For that, the growth solution, that is, the gold hydroxide (or K-gold) solution, must be prepared in advanced [14]. The preparation is outlined as follows. In a reaction flask, 0.05 g potassium carbonate was dissolved in 185 ml HPLC water. Then the solution was stirred for 10 min and afterwards, 15 ml of 5mM $HAuCl_4$ were added to the solution. The color of the mixture changed from initially light yellow to colorless, which indicated the formation of gold hydroxide. The resulting solutions should be aged for more than 24h in dark before use. The PS particles coated by gold seeds were mixed with K-gold solution and stirred gently. Then, formaldehyde, as a reducing agent, was added into the mixture. The color of the mixture solution turned from colorless to blue green, which indicated the gold shells were formed.

2.6 Growth of silver shell

Silver nanoshells were made following the method reported by Jackson *et al*. [15] to deposit silver onto the gold-decorated silica microspheres, which is an modification of the Zsigmondy method [16]. Briefly, the gold-coated polystyrene spheres were mixed with a fresh 0.15 mM solution of silver nitrate ($AgNO_3$) and stirred vigorously. Then, 50 µl formaldehyde, as a reducing agent, was added to the former solution. This step was followed by adding 20-50 µl of 28-30% ammonium hydroxide to increase the pH value of mixture which facilitates the reduction of Ag^+ to Ag^0. The volume radio of the gold-coated PS to the silver nitrate solution controls the amount of silver available for deposition on the polystyrene surface.

2.7 Material and Optical Characterization

The nanoparticles (PS, seeded PS and nanoshells) are characterized by transmission electron microscope (TEM, JEOL-2100) operated at 200 kV and the optical properties of the nanoshells are measured by a photospectrometer (Shimadzu 3100PC UV–vis-NIR spectrophotometer).

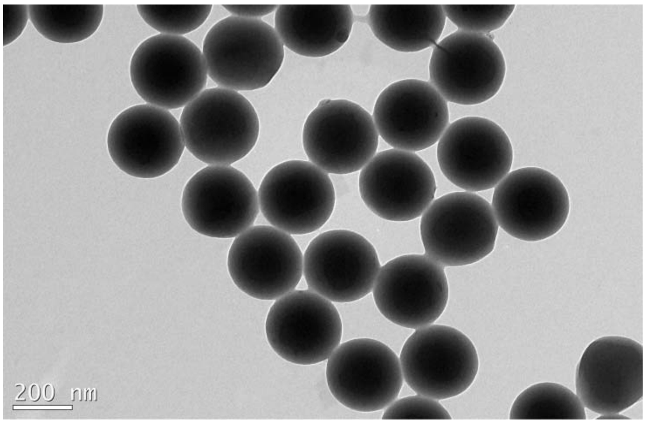


Fig. 1 TEM image of PS particles.

III. RESULTS AND DISCUSSION

3.1 Size effect of gold seeds on seeding and shell growth

Experiments were conducted to determine the size of gold seeds on the linkage of gold seeds onto CHI-modified PS spheres and on the subsequent growth of complete nanoshells. Seeds of the three different gold particles, prepared as described in 2.2, were used, with the THPC-gold being 3~5 nm in diameter, the citrate-gold ~20 nm, and the borohydride-gold ~10 nm. In all these three experiments, the volumes of gold seeds are enough to cover the surfaces of PS particles (CHI modified). The surface coverage of PS with these gold seeds is shown by TEM images given in Fig. 2.

From Fig. 2(a), it is evident that only a small amount of citrate-gold seeds (~20nm) is anchored onto the PS surface, the surface coverage being ~10%. In comparison, the borohydride-gold yields a larger coverage (~50%) as observed in Fig. 2 (b), but the coverage is non-uniform. The largest surface coverage (~70%) with a uniform seed distribution was obtained with THPC-gold, as shown in Fig. 2 (c). These experiments suggest that the smaller size of gold seeds yields a higher quality surface coverage, that is, a larger surface coverage with a more uniform distribution, if other parameters are kept at the same. This is also confirmed by repeated experiments.

After attaching gold seeds on the surface of CHI-PS, the shell growth was executed by reducing the gold ions onto the nucleate points from the K-gold solution with a reducing agent, which there is formaldehyde. To assess the seed size effect of final shell growth, the volume radio of seed-covered PS spheres to the K-gold solution was fixed, and the amount of formaldehyde (reducing agent) was kept at constant. Fig. 3 displays the TEM images of the nanoshells grown on corresponding seed-covered PS spheres in Fig. 2. Apparently, reduction of gold ions occurs on all these three types of seed-covered PS spheres, but the quality of the shell is rather different. As illustrated in Fig. 3(a), nanoshells grown on citrate-gold-seeded PS spheres are rather incomplete, characterized by a sparodic coverage of gold reduced from the K-gold solution. Somewhat more complete shells, compared with Fig. 3(a), are observed on the borohydride-gold-seeded PS spheres, as shown in Fig.3 (b). However, the growth left many residue gold nanoparticles formed in the solution. The most complete and uniform nanoshells are formed on the THPC-gold-seeded PS spheres, without any residue gold nanoparticles left in solution. This suggests that the smaller gold seeds lead to a better surface coverage of the CHI-modified PS spheres, and to the subsequent growth of nanoshells of better quality (i.e. completed and uniform shell).

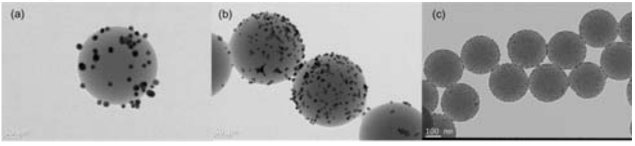


Fig. 2 TEM images of carboxylated polystyrene spheres coated with (a) citrate-gold, (b) borohydride-gold, and (c) THPC-gold

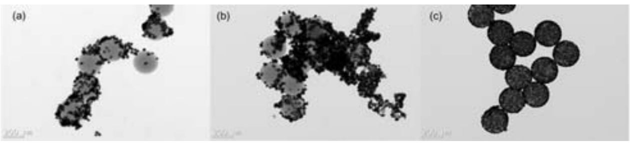


Fig.3 TEM images of nanoshells grown on PS spheres covered by the seeds of (a) citrate-gold, (b) borohydride-gold, and (c) THPC-gold

3.2 Effect of the volume of K-gold solution on gold shell formation

To obtain a complete gold shell, the volume of K-gold solution is critical for the final step of gold shell growth. Experiments were conducted to study the effect of K-gold solutions. The volume of seeded PS and the amount of formaldehyde reducing agent are fixed, to just consider only the effect of K-gold solution's volume. THPC-gold was chose to functionalize the CHI-modified PS. Fig.4 compares the TEM images of nanoshells grown with various volumes of K-gold solution. In Fig.4 (a) ,it is evident that gold ions are reduced by formaldehyde, but the gold ions aren't enough to form a complete shell. Compared with Fig.4 (a), more complete shell was obtained in Fig.4 (b), but some void still existed on the surface. A thin nanoshell was observed in Fig.4 (c). When more K-gold solution was used, a whole complete and thick shell could be acquired in Fig.4 (d). The UV-Vis spectra of light absorption are shown in Fig. 5 for these four cases. These results show the classical behavior of light scattering by nanoparticles. In the case of 4ml K-gold solution, light scattering is primarily due to the individual gold nanoparticles with relatively weak interference from each. As the volume of K-gold increases, the coverage of shell improves and the adsorption of spectra has a clear red shift. When the volume of K-gold solution is 10ml, just as the Fig.4 (c) show, a complete shell was obtained, and the UV-Vis spectra of nanoshell has a red shift to 859 nm. As the volume of K-gold added to 14ml, it is observed that the thickness of the shell increased and the UV-Vis spectra of nanoshells has a blue shift to 749 nm. This phenomenon inosculates with the scattering theory of nanoshells.

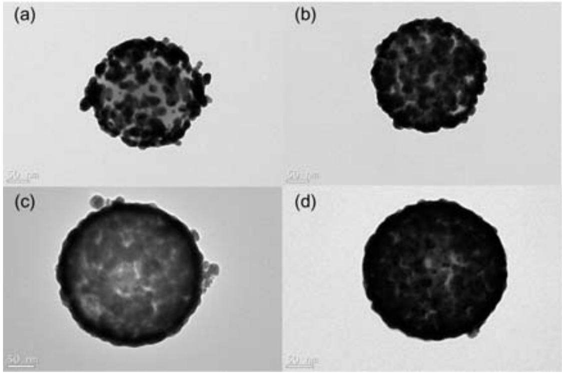


Fig.4 TEM images of gold nanoshell which the volumes of K-gold solution are (a) 4ml; (b) 7ml; (c) 10ml; (d) 14ml respectively. The volumes of THPC-gold coated PS and formaldehyde reducing agent are 0.5ml and 40μl.

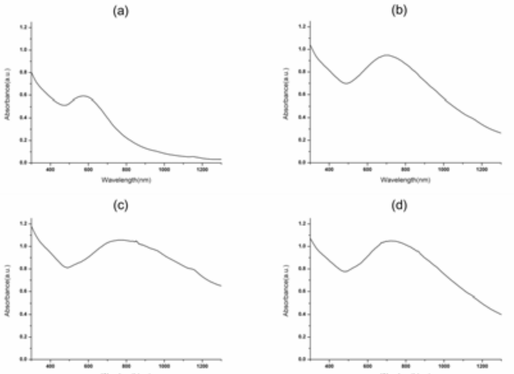


Fig.5 UV-Vis spectra of gold nanoshells which the volumes of K-gold solution are (a) 4ml; (b) 7ml; (c) 10ml; (d) 14ml respectively. The volumes of THPC-gold coated PS and formaldehyde reducing agent are 0.5ml and 40μl.

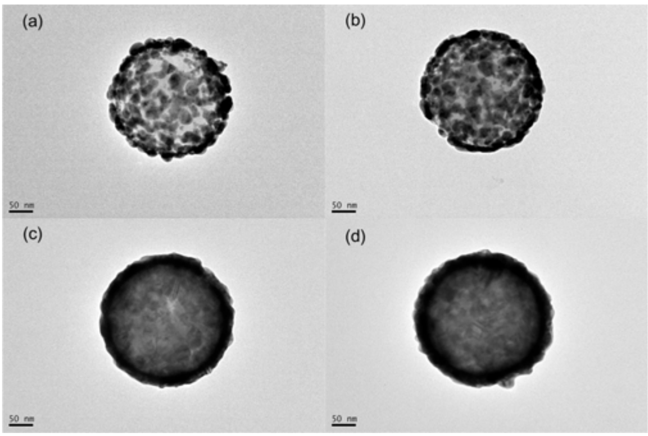


Fig.6 TEM images of silver nanoshell which the volumes of silver nitrate ($AgNO_3$) solution are (a) 10ml; (b) 12ml; (c) 20ml; (d) 40ml respectively. The volumes of THPC-gold coated PS and formaldehyde reducing agent are 0.25ml and 50μl.

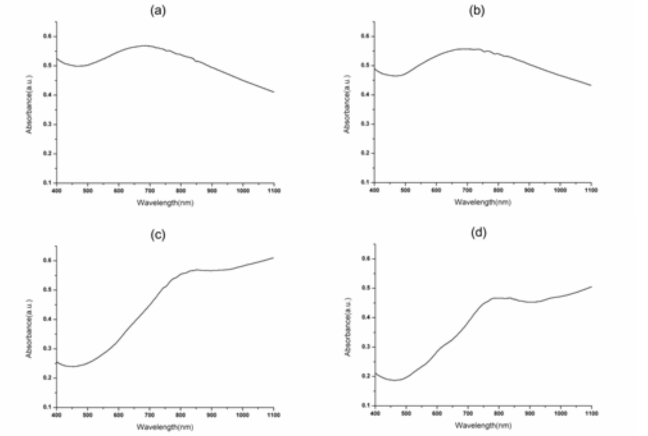


Fig.7 UV-Vis spectra of silver nanoshells which the volumes of silver nitrate ($AgNO_3$) solution are (a) 10ml; (b) 12ml; (c) 20ml; (d) 40ml respectively. The volumes of THPC-gold coated PS and formaldehyde reducing agent are 0.25ml and 50μl.

3.3 Morphology and UV-Vis absorbance spectra of silver nanoshells

PS@Ag core@shell particles can also be synthesized following the same procedure as shown in Scheme 1. In fact, the procedures are almost identical except that the last step involves the growth of the silver shell on a gold-seed-covered PS template (or sphere). Thus, the tests conducted above, the volumetric amount of the Ag-ion solution is the remaining parameter that determines the quality of the Ag nanoshells. In place of K-gold solution, the $AgNO_3$ solution was used, from which Ag is reduced onto the PS template. The preparation of $AgNO_3$ solution was discussed in Section 2.6. TEM images of PS@Ag nanoshells are shown in Fig. 6, which demonstrate the effect of the volumetric amount of silver nitrate solution on the growth of silver nanoshell. These experiments used the volumes of 0.25ml THPC-gold-seeded PS and 50μl formaldehyde. Fig. 6(a) and (b) show that an incomplete Ag shell was formed, mainly because there was not enough Ag^+ present in the solution to be reduced to Ag^0. A complete shell was growth on the PS sphere when more silver ions exist in solution, as shown in Fig. 6(c). As for the Ps@Au case, an overdose of silver nitrate solution produces a thicker Ag shell as displayed in Fig. 6(d). Fig. 7 shows the corresponding UV-Vis spectra of PS-silver nanoshells shown in Fig. 6. Apparently, deposition of silver onto the gold-seeded PS spheres causes a red shift of UV-Vis absorbance spectra before the formation of a complete shell. Once a continuous shell has formed, a further increase in the amount of silver ions leads to the formation of a thicker shell, which produces a blue shift of the UV-Vis spectra. This is consistent with the reported studies [17].

IV. CONCLUSION

This paper has presented an experimental study of the effect of two crucial processing parameters (i.e. size of Au seeds and the volumetric amount of metal ion solutions) on the quality (i.e. morphology, shell completeness and optical properties) of PS@Au and PS@Ag (core@shell) nanostructures prepared by the seed-and-grow method. Nanosized PS spheres were prepared in the laboratory and functionalized with CHI polyelectrolyte. Gold seeds were then linked to the functionalized PS spheres and the PS@metal nanoshell structures were formed by the subsequent reduction of metal onto the Au-seeded PS spheres from metal ion solutions. Results show that gold seed sizes are important in controlled preparation of the nanoshells of good quality. A better seed coverage and good quality nanoshells are produced with Au seeds of smaller size. Also, an appropriate volumetric amount of K-gold/silver nitrate solution is pre-requisite for obtaining a complete nanshell with desired shell thickness. These findings are confirmed by the TEM images of Au seed coverage and metal shell morphology and by the UV-vis spectra of light absorption.

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