Preparation of Silica Core-Gold Shell Structural Materials via Layer by Layer Method

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Abstract. The silica core-gold shell structural material was prepared using mono-dispersed silica microsphere as template and gold nanoparticles from HAuCl4 solution. Gold nanoparticles were assembled on the silica surface modified by aminopropyl triethoxysilane (APTES) via a convenient layer-by-layer method. The evolution of gold coverage over the surface of silica microspheres are demonstrated via transmission electron microscopy (TEM) and scanning electron microscopy (SEM). TEM and SEM images show that the gold nano-particles could be deposited on the surface of silica spheres, and the total gold nanoparticle got increase with the deposited layer number. And ultraviolet-visible adsorption spectrum was introduced to characterize the successful incorporation of gold nanoparticles on the microspheres. The layer-by-layer method could provide a simple way to control the ratio of gold on the silica surface.

Keywords: gold, silica microspheres, core-shell, step-by-step

1. Introduction

The design and controlled fabrication of core-shell nanomaterials and nanostructure are important in many research areas, including the developments of novel catalysis, the potential applications as chemical sensors, and some advanced photonic researches such as surface-enhance Raman scattering (SERS), photonic crystal, and nanoengineering of optical resonance. In particular, the fabrication and study of metallic nanoshells with dielectric cores have attracted wide interests because of their good optical and chemical properties for biomedical imaging and therapeutic applications. [1-3] Several strategies have been reported to prepare metallic nanoshells, including layer-by-layer (LBL) self-assembly of nano-particles on suitable colloid particles, [4] precipitation/chemical conversion, [5] and electroless deposition. [6] Interestingly, some novel functions can be realized after coating with metals, such as the photonic band gap, which can be tuned as desired by controlling some parameters. [7]

Recently, nano-scale silica complexes such as magnetic silica microspheres, fluorescent particles with quantum dots and metal-silica core-shell compounds gradually become the focus of biochemical researches due to their special optical properties and promising potentials for wide applications. [8-10] Silica-gold core-shell compounds (Au@SiO2) have got rapid development in biomedical fields such as the drug releasing, the cancer treating, biological sensing and imaging. [11, 12] Among all the methods that can synthesize a contiguous gold shell over silica microspheres, the deposition-precipitation (DP) approach is an inexpensive and easy method to prepare the core-shell materials. [13] Phonthammachai et al. [14] have reported that the homogeneous gold shells could be obtained by optimizing these key parameters including pH value, reaction time and reaction temperature. Here, we develop a multideposition method to prepare the silica core-gold shell materials using mono-dispersed silica microsphere as template and gold nanoparticles from the reduction of the HAuCl4 solution. In this work, Our main idea is to use the mono-dispersed silica microsphere as a template to prepare a metallo-dielectric silica-gold core-shell structural particles. The original pure silica spheres as the supporting core to improve the mechanics stability of silica-gold core-shell materials. Moreover, transparent silica sphere and very fine gold particles layer can allow the partial light to
propagate through the silica core – gold shell. Using the multideposition method, the gold nanoparticles could be directly deposited on the surface of silica spheres.

2. Experimental Sections

2.1. Preparation of Monodispersed Silica Microspheres

Monodispered SiO₂ microspheres with an average diameter of approximate 200 nm were prepared by hydrolysis of tetraethylorthosilicate (TEOS) in ethanol medium with the presence of deionized water and ammonium hydroxide, a reformulation of the method reported by Stöber et al. (1968). In general, we added TEOS:EtOH (1:3 volume rate) to one beaker with vigorously stirring for 5 minutes. Then the mixture was added into a flask with EtOH: deionized water: ammonium hydrxide (9: 4: 0.5 volume rate) already under stirring. About 2 minutes later, white particles began to emerge, making the solution change from transparent to a little turbid. Under vigorously stirring for 2 hours, the solution was then totally a white turbid suspension. We took away a little suspension, wash three times using centrifugation and ultrasonical re-dispersion with deionized water.

2.2. Gold Nanoparticles Growing Over SiO₂ Microspheres as Seeds

After natural precipitation of the SiO₂ suspension, we removed the upper liquid. Then, 5ml of a pre-prepared solution of 60 mM aminopropyl triethoxysilane (APTES) in an EtOH: deionized water (3:1 volume ratio) was added into the solution under vigorously stirring at 95℃ for 1 hour. Then, 10 ml of 50 mM HAuCl₄ solution and 5ml of 0.1M NaOH solution was added to the APTES grafted silica spheres to adjust the pH value to 7.2, and the solution was under stirring for 15 minutes to incorporate gold seed into the spheres. After that, we could see the white SiO₂ particles show a golden color, demonstrating the gold nanoparticles were successfully incorporated on the silica spheres. The solution was centrifugated and washed for 3 times with deionized water, and then re-dispersed ultrasonically into the deionized water.

2.3. Formation of Au@SiO₂ Core-shell Structure

After the mixture was cooled down to room temperature, pre-prepared potassium -gold solution (K-gold, which is made by adding 50 mM HAuCl₄ into 1 mM K₂CO₃ solution) was added to the suspension with the presence of 0.1 M 0℃ NaBH₄ solution to reduce the gold anion, which would attach to the gold crystal already incorporated into the spheres to form a gold shell. When the NaBH₄ solution was added into the suspension, the color of the solution immediately changed into dark purple, indicating the reducing HAuCl₄ into gold anion. After stirring for 3 hours, the solution was centrifugated at 7800 rpm and washed with deionized water for 3 times before ultrasonically re-dispersed in the deionized water. Then we add K-gold solution and 0.1M 0℃NaBH₄ into the solution to induce the gold shell formation for the second time. The gold-shell-formation reactions need to be repeated for 4 times to obtain a contiguous and coherent gold shell.

3. Results and Discussion

Fig.1 is consisted of a sequence of TEM images taking after each step of the reaction, which show intuitively and explicitly the gradual growth and formation of the gold shells over silica microspheres. From the Fig.1(a), we can see that the surface of the monodispersed silica spheres is relatively smooth. After introducing the APTES fictionalizations to the microspheres, the amino groups have been grafted on the silica surface. Then, gold nano nuclei were successfully incorporated on the silica surface via amino groups to form gold seeds for the subsequent reactions, decorating complete gold increasing the amount of gold crystals incorporated into the surface of the silica microspheres (Fig.1(b)). After growing the second layer of gold nano particles, the amount of gold nanoparticles adhered on the silica surface is clearly increased, and the surface of the silica sphere is much rougher than the pure silica sphere (Fig.1(c)), indicating more and more gold nanoparticles adhered on the silica spheres. Moreover, after growing the third (Fig.1(d))and the fourth layer(Fig.1(e)) of gold nanoparticles, it is clearly seen that more and more gold nanoparticles have been attached to the surface of silica spheres, especially, we can see that the final product present a contiguous and uniform gold shell.
Fig. 1: TEM images of the evolution of gold crystals growing on APTES-grafted silica spheres, (a) bare silica microspheres; (b) gold seeds synthesized from APTES-grafted silica microspheres; (c) gold shells after synthesis for the first time; (d) gold shell after synthesis for the second time; (e) gold shell after synthesis for the third time.

The formation of gold shells is also demonstrated via SEM images (Fig. 2). Fig. 2a shows the gold seeds on the silica spheres, from which we can see the nano crystals on the surface of the micro spheres were limited and sparsely located. But after growing the second layer of gold nanoparticles, a remarkable increase of the gold nanoparticles on the surface of the silica spheres has been clearly observed (Fig. 2b). Consistence with the TEM images, after growing the third layer of gold nanoparticles, one can see some isolated white particles, like some islands standing on the surface of silica sphere, indicating some gold nuclei have been changed to form bigger gold particles. From the the Fig 2(c), the surface of the each silica spheres were coated with lots of gold particles, indicating Au nanoparticles from Au+ could first form a relatively uniform gold super thin layer on the silica microspheres, and more and more Au nuclei would be assembled and collected to grow bigger particles on the surface of each sphere with the increasing the treatment number.
The UV absorption spectrum of Au@SiO$_2$ shows a peak around 575 nm (Fig. 3). As is well known, the original chloroauric acid solution before adding NaBH$_4$ clearly presents a peak at 306 nm of [AuCl$_4$]$^-$ ions, which due to the ligand-to-metal charge-transfer transition. However, with adding of NaBH$_4$, the color of the solution becomes brown and finally wine red. The peak at 306 nm in the UV-vis spectrum disappears, while a new peak around 575 nm emerges, suggesting that all Au ions were reduced to gold particles. The broad peak about 575 nm indicates a relative big particle size distribution, as was evident in the TEM examination.

4. Conclusions

The silica core – gold shell structural materials were obtained by using monodispersed gold-seeded APTES-grafted silica microspheres via a step-by-step deposition-precipitation (DP) method. Through TEM images, SEM images and UV-vis absorption spectrum, the evolution of the gold shells growing over the surface of silica microspheres was explicitly characterized. The prepared silica core – gold shell structural materials might find potential applications in enhancement of Raman scattering, plasmon excitation, and photonic bandgap materials in the visible spectrum. In particular, this method might prove valuable in enhancing the thermal stability of other types of assembled nanostructures and nanoscale materials.

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6. References


