〔特集〕 光機能材料の新展開
Paper

Synthesis of Gold-Silica Core-Shell Nanoparticles with Tunable Shell Thickness

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ABSTRACT

A synthesis procedure of gold-silica core-shell nanoparticles has been developed in this work. We have investigated the effects of the amounts of poly(vinylpyrrolidone) (PVP), water, and tetraethoxysilane (TEOS) in the starting materials on the shell thickness. The results reveal that the modification of the surface of gold nanoparticles with PVP plays a critical role in the formation of smooth coating with silica. The shell thickness can be well controlled by changing the amounts of water and TEOS, typically ranging from 2 to 25 nm. We have examined optical extinction properties experimentally and numerically; our experimental results are consistent with the calculations.

KEY WORDS

Gold nanoparticles, Core-shell nanoparticles, Localized surface plasmon resonance

1 Introduction

Metal nanoparticles could potentially lead to extensive applications in various areas such as nanolasers¹⁾, solar cells²⁾, sensors³⁻⁵⁾, and magneto-optics⁶⁾ primarily owing to localized surface plasmon resonance (LSPR). LSPR gives enhanced local electric field in the vicinity of the surface of a metal nanoparticle, which can modify many optical processes. In studies on the modification of spontaneous emissions, both fluorescence enhancement and quenching have been observed for fluorophores in the vicinity of metallic nanostructures^{7,8)}. The enhancement factor is largely dependent on the distance between the fluorophore and the metal, because the radiative and nonradiative transitions of fluorophores vary with their spatial separation⁷⁾. As a result, it is usual that the maximum enhancement is obtained not on the metallic surface but in the region a few to tens of nanometers away from the surface⁸⁾. Therefore, to attain the maximum enhancement, a shell-isolation technique has been widely adopted by inserting a dielectric spacer between a fluorophore and the metal nanostructure⁹⁻¹⁴⁾.

Among various dielectric shells, silica (SiO₂) is the most practical and studied material. The SiO₂ shell can provide a chemically inert environment for the metal core while keeping the high optical transparency¹⁵⁾. The general SiO₂ coating technique is based on the Stöber method in a system

containing metal core nanoparticles¹⁶⁾. Namely, a silane precursor is added to the solutions of metal nanoparticles in a mixture of ethanol, water, and catalyst (e.g., ammonia) to cause nucleation of SiO₂ on the surface of the particles. Subsequently, hydrolysis and polycondensation of the silane precursor result in the formation of SiO₂ shell with controlled thickness. Since gold (Au) and silver (Ag) nanoparticles are not suitable for direct SiO₂ coating due to their low chemical affinity to SiO₂, Mulvaney *et al.* reported a three step procedure for coating Au nanoparticles with SiO₂ using a silane coupling agent, aminopropyltrimethoxysilane, as the surface primer¹⁷⁾. This method is effective but time-consuming and not easily controlled. Alternatively, using a nonionic and amphiphilic polymer, poly(vinylpyrrolidone) (PVP), instead of a silane coupling agent as the surface primer, Graf *et al.* developed a simpler and faster method to coat Au and Ag nanoparticles with SiO₂¹⁸⁾. A thin shell thickness, less than several tens of nanometers, is usually required for many potential applications, because the enhancement of the electric field occurs only in the vicinity of the surface. Although several research groups have prepared Au-SiO₂ core-shell (Au@SiO₂) nanoparticles with SiO₂ thickness less than several tens of nanometers, the shell tends to be rough and inhomogeneous and the fine tuning is difficult as the thickness becomes smaller^{17,19-21)}.

In this work, we improve the method of Graf *et al.* to give

a fast, easy, and adoptable method to coat Au nanoparticles with SiO₂ thickness below 25 nm. We have systematically examined the effects of the amounts of PVP, water, and tetrathoxysilane (TEOS) on the shell thickness. Furthermore, we have examined optical extinction properties of the Au@SiO₂ nanoparticles experimentally and numerically. The experimental results agree with the calculations, confirming the uniform growth of the shell.

2 Experimental

2.1 Materials

For the preparation of Au nanoparticles, HAuCl₄ (Kishida), trisodium citrate (Wako) and distilled water were used as the starting materials. For the preparation of Au@SiO₂ nanoparticles, the as-prepared Au nanoparticles, TEOS (95 %, Nacalaitesque), PVP (average molar masses of 10 kg/mol, Sigma-Aldrich), ethanol (99 %, Nacalaitesque), and ammonia aqueous solution (28 wt%, Wako) were used as the starting materials.

2.2 Synthesis

Au nanoparticles having an average diameter of 13.5 nm were synthesized according to the standard sodium citrate procedure²²⁾. First, 4 ml of aqueous HAuCl₄ solution (10 mg/ml) was added to 96 ml water in reflux at 100 °C under vigorous stirring. After 10 min, 10 ml of aqueous sodium citrate solution (10 mg/ml) was added into the above solution. The reaction lasted 12 min, and then the colloidal solution was cooled down to room temperature for subsequent purpose.

The outline of the SiO₂ coating procedure is shown in Fig. 1. In this study, we performed SiO₂ coating by altering the amounts of PVP, H₂O, and TEOS. The composition of the starting solutions is summarized in Table 1. The first step was the functionalization of the surface of Au nanoparticles with PVP by mixing varied amounts of aqueous PVP solution (25.6 mg/ml, 0.5 ml ≤ x ≤ 0.15 ml)

with 7.0 ml of Au colloidal solution under vigorous stirring for 24 h at room temperature. The mixture was washed once with acetone by centrifugation (6,000 rpm) for 30 min and then redispersed in 1.816 ml of ethanol for the purpose of SiO₂ coating. An aqueous ammonia solution (0.084 ml) and a varied amount of water (0.00 ml ≤ y ≤ 0.15 ml) were added into the Au-PVP/ethanol solution under vigorous stirring. Then, a TEOS/ethanol solution (10 vol%, 0.5 ml ≤ z ≤ 0.15 ml) was added under vigorous stirring. When the amount of TEOS/ethanol solution was more than 0.080 ml, the TEOS/ethanol solution was added stepwise by 0.040 ml at each step with an interval of 1 h. After the TEOS/ethanol solution was added completely, the solution was stirred further for 12 h at room temperature to grow SiO₂ shell. The Au@SiO₂ nanoparticles were separated by centrifugation for 30 min three times (acetone, 6,000 rpm). The resultant Au@SiO₂ nanoparticles were redispersed in water for storage.

2.3 Sample characterizations

The morphology of the nanoparticles was characterized with transmission electron microscope (JEM 2100F, operation voltage: 200 keV). The optical extinction spectra were measured by a JASCO V-570 UV-VIS-NIR spectrophotometer.

2.4 Numerical simulations

Optical extinction properties were simulated by a discrete dipole approximation (DDA) method in DDSCAT. DDSCAT is a Fortran code for calculating scattering and absorption of light based on DDA^{23,24)}. In the simulation, we supposed that the refractive index of the surrounding medium of the particle was 1.36. A linearly polarized light was incident on the particle. The diameter of Au core is 13.5 nm, and the shell thickness was set to be 0, 4.2, 14.5, and 25.0 nm. The refractive index of Au was taken from the literature²⁵⁾ and the refractive index of SiO₂ was set to be 1.45.

Fig. 1 Schematic of preparation of Au@SiO₂ nanoparticles. The surface of the Au nanoparticles is modified with PVP followed by the Stöber process for the formation of SiO₂ shell.

Table 1 Composition of the starting solution for fabricating Au@SiO₂ nanoparticles.

Sample number	Amount of aqueous PVP solution, x (ml) ^a	Average number of PVP molecules at Au surface (nm ⁻²)	Amount of H ₂ O, y (ml)	Amount of TEOS/ethanol solution, z (ml) ^b	Ethanol solution of Au nanoparticles (ml) ^c	Aqueous ammonia solution (ml) ^d
1	0.50	110	0.10	0.080	7.0	0.082
2	1.07	240	0.10	0.080	7.0	0.082
3	1.24	280	0.10	0.080	7.0	0.082
4	1.50	340	0.10	0.080	7.0	0.082
5	1.24	280	0.00	0.080	7.0	0.082
6	1.24	280	0.05	0.080	7.0	0.082
7	1.24	280	0.10	0.080	7.0	0.082
8	1.24	280	0.15	0.080	7.0	0.082
9	1.24	280	0.10	0.040	7.0	0.082
10	1.24	280	0.10	0.080	7.0	0.082
11	1.24	280	0.10	0.160	7.0	0.082
12	1.24	280	0.10	0.240	7.0	0.082

^a The concentration of PVP is 25.6 mg/ml.^b The concentration of TEOS is 10 vol%.^c The number density of the particles is 8.74×10^{11} particles/ml.^d The concentration of ammonia is 28 wt%.

Fig. 2 TEM images of the samples with a varied amount of PVP: (a) 0.5 ml, (Sample 1), (b) 1.07 ml, (Sample 2), (c) 1.24 ml, (Sample 3), (d) 1.50 ml, (Sample 4). Scale bars = 100 nm.

3 Results and Discussion

3.1 Influence of the starting composition on the shell morphology

3.1.1 Influence of PVP

The role of PVP is to stabilize the Au nanoparticles during the SiO₂ shell growth and to provide the Au surface with the affinity to SiO₂. We fix the amounts of the other materials and examine the influence of PVP. The amount of aqueous PVP solution (x) is changed as shown in Table 1 and the corresponding TEM images are in Fig. 2. All samples have the similar thickness of the SiO₂ shell, but uniformity of the shell varies with the samples. When $x < 1.24$ ml,

multiple cores exist in one particle (see Fig. 2a). This is because the surface of Au nanoparticles was not effectively modified with PVP so that attached PVP molecules do not sufficiently shield the large attractive force based on van der Waals force between these particles¹⁸⁾. The amount of PVP is enough when $x = 1.24$ ml which gives rise to a smooth shell compared to the other samples. When $x = 1.24$ ml, there are approximately 280 nm^{-2} PVP molecules on the Au surface. This is about five times more than that used in the previous paper by Graf *et al.*¹⁸⁾.

3.1.2 Influence of water

We fix the amount of aqueous PVP solution as 1.24 ml

and examine the effects of the amount of water. The amount of water (y) is changed as shown in Table 1 and the corresponding TEM images are shown in Fig. 3. The results show that the more y is, the thicker the shell is until its amount reaches 0.10 ml. This is because water accelerates the hydrolysis and condensation of TEOS. It is noted that the shell grows even though $y = 0$ ml because the system contains water from aqueous ammonia solution. However, when $y = 0.15$ ml, the shell is thinner than that at $y = 0.1$ ml because the reaction is so fast that Au-free SiO_2 nanoparticles are formed by the homogeneous nucleation of SiO_2 in the solution.

3.1.3 The influence of TEOS

Lastly, we examine the influence of the amount of TEOS/ethanol solution under the conditions that the amount of aqueous PVP solution is 1.24 ml and the amount of water is 0.1 ml. The amount of TEOS/ethanol solution (z) is changed as shown in Table 1 and the corresponding TEM images are shown in Fig. 4. The shell becomes thicker with an increase of the amount of z . This is because the amount of shell precursor, i.e., TEOS, is increased. The monotonous increase in shell thickness suggests the absence of homogeneous nucleation of SiO_2 , which produces Au-free SiO_2 nanoparticles.

3.1.4 Fine control of shell thickness by the amount of TEOS

The above results suggest that the fine control of the shell thickness is possible by tuning the amounts of water (y) and TEOS/ethanol solution (z) in the starting solution that contains a sufficient amount of PVP. Especially the variation is monotonous with z under the conditions we have adopted as shown in Fig. 5 (a). The shell thickness increases from 8.5 to 21.2 nm when z increases from 0.04 to 0.24 ml. Fig. 5 (b) shows that the shell volume per particle increases in roughly proportion to the amount of TEOS. The shell volume is about 1/8 of the value when all the TEOS is converted to SiO_2 . This discrepancy indicates that the reactions are not completed in 12 h so that it would be possible to tune the shell thickness by the reaction time.

3.2 Extinction properties of Au and Au@ SiO_2 nanoparticles

In order to examine the optical quality of the core-shell nanoparticles prepared, we picked up several samples and measured optical extinction spectra. Fig. 6 (a) is the extinction spectra of Au nanoparticles and Au@ SiO_2 nanoparticles dispersed in water. As the shell thickness is varied from 0 to 25 nm, the extinction peak is slightly red-shifted from 519 to 524 nm. This is because the refractive index around Au nanoparticles is changed due to the

Fig. 3 TEM images of the samples with varied amount of water: (a) 0.00 ml, (Sample 5), (b) 0.05 ml, (Sample 6), (c) 0.10 ml, (Sample 7), (d) 0.15 ml, (Sample 8). Scale bars = 100 nm.

Fig. 4 TEM images of the samples with varied amount of 10 vol% TEOS/ethanol solution: (a) 0.040 ml, (Sample 9), (b) 0.080 ml, (Sample 10), (c) 0.160 ml, (Sample 11), (d) 0.240 ml, (Sample 12). Scale bars = 100 nm.

Fig. 5 Variation of the shell thickness (a) and of the shell volume per particle (b) with the amount of TEOS. Note that the concentration of TEOS is 10 vol% in ethanol.

Fig. 6 (a) Measured extinction spectra of Au nanoparticles and Au@SiO₂ nanoparticles. (b) The extinction cross section of Au and Au@SiO₂ nanoparticles calculated by DDSCAT. (c) The variation of the peak wavelength and corresponding extinction cross section extracted from the experimental and calculated spectra.

presence of SiO₂ coating. It should be noticed that the thicker the shell is, the larger the extinction cross section is. This is mainly because the geometrical cross section is increased with the shell thickness. The results are compared to the simulation results based on DDA. The simulated spectra are shown in Fig. 6 (b), and Fig. 6 (c) shows the peak wavelength and corresponding cross section extracted from the simulated and experimental spectra. Although the values of cross section derived from the simulation are not exactly the same as those obtained experimentally, we can reproduce the red-shift of the peak with an increase of shell thickness without using any adjustable fitting parameters. The experimental spectra are broader compared to the simulated spectra, because of the size distribution of Au nanoparticles prepared experimentally.

4 Conclusions

We have developed a method to tune the shell thickness of Au@SiO₂ nanoparticles. The typical shell thickness is below 25 nm, which is useful for plasmonic applications.

With the optimal amount of PVP absorbing onto the surface, the Au nanoparticles become stable in both water and ethanol. By changing the amounts of water and TEOS in the solution, we can control the surface smoothness and thickness of the SiO₂ shell. The extinction cross section of the Au@SiO₂ nanoparticles is well reproduced by the simulation.

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