Deposition of Gold Nanoparticles on Polystyrene Spheres by Electroless Metal Plating Technique

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Abstract. A previous method proposed for gold deposition on silica spheres (Kobayashi et al., 2005) was extended to uniform deposition of Au nanoparticles on submicron-sized polystyrene spheres. This method consisted of surface-modification and electroless Au plating. The chemical agents examined for the surface-modification were sodium persulfate, 3-aminopropyltrimethoxysilane, polyelectrolytes and polyvinylpyrrolidone. The electroless Au plating included three steps: (1) the adsorption of Sn^{2+} ions took place on surface of silica particles, (2) Ag^{+} ions added were reduced and simultaneously adsorbed to the surface, while Sn^{2+} oxidized to Sn^{4+}, and (3) Au^{+} ions added were reduced and deposited on the Ag surface. TEM observation revealed that Au nanoparticles with sizes of 8-25 nm were uniformly deposited on the polystyrene spheres that were modified with polyvinylpyrrolidone. The Au nanoparticle deposition was confirmed by UV-VIS absorption spectroscopy.

1. Introduction

Nanometer-sized particles have special interest because they can be expected to exhibit unique properties different from those of bulk material. Among various materials of nanoparticles, metals are attracting a great deal of attention due to their special optical and electronic properties that depend on particle size, particle shape and environment around the particles.

Assembly of nanoparticles has attracted much attention in the field of materials science. Properties of such assembly materials can be modulated not only through the nature of the nanoparticles but also through structure of the assembly materials. Recently, there have been some reports on deposition of metal nanoparticles on submicron particles for the stabilization. Frequently, the deposition techniques involve simple mixing the nanoparticle colloid and the suspension of submicron spheres [1,2]. The nanoparticles are deposited on the spheres through interactions such as complexation with amino groups on the silica surface. In this technique, however, aggregation of the nanoparticles during the deposition can not be negligible and it is necessary to remove excess nanoparticles from the suspension.

In our previous work, Au nanoparticles were successfully deposited on silica spheres by electroless plating that is a common procedure to deposit metals on surfaces [3]. The Au electroless plating consists of three steps: the first is a modification of the surface of the silica spheres with Sn^{3+} ions (Sn^{3+}-sensitization), the second is a redox reaction in which the Sn^{3+} ions get oxidized to Sn^{4+} and at the same time Ag^{+} ions get reduced into metallic Ag (Ag-activation), which adheres to the silica surface in the form of nanometer-sized Ag particles, and the third is a reduction of Au^{+} ions into...
metallic Au on the Ag particles pre-deposited on the silica spheres, so that the metallic Ag sites work effectively for electroless Au plating because of galvanical displacement of the metallic Ag by Au. This method takes an advantage over the simple mixing method, because the reduction of Au⁺ takes place only on the Ag sites so that the aggregation of nanoparticles during the deposition can be avoided.

The purpose of the present work is to extend the electroless Au plating technique to deposition of Au nanoparticles on polystyrene (PS) spheres. In the electroless Au plating technique, affinity between aqueous Sn²⁺ solution and substrate surface in Sn²⁺-sensitization is an important factor for uniform metal deposition. Since surface of the PS spheres is hydrophobic compared to silica surface, surface modification of the PS spheres will be necessary for efficient Sn²⁺-sensitization. Various chemical agents for surface modification were examined in this work.

2. Experimental Details

2.1. Methods

2.1.1. Synthesis of PS spheres. Colloid of PS particles were prepared in a soap-free polymerization at an initiator potassium persulfate (KPS) concentration of 0.8 mM and a styrene concentration of 55 mM at 60°C for 6 h under stirring at 300 rpm. The PS particles prepared were highly monodisperse and had an average size of 340 nm. The PS particles were washed three times with centrifugation at 20000 rpm for 30 min, removal of supernatant and addition of the water. Finally, the PS concentration was adjusted to 0.2 wt% with the last water addition.

2.1.2. Surface modification

2.1.2.1 Na₂S₂O₈. With a method reported by Dutschke et al. [4], PS surface was hydroxylated by an aqueous Na₂S₂O₈ solution. The 0.2 wt% PS colloid (10 ml) was added to 0.2-2 wt% Na₂S₂O₈ aqueous solution (10 ml) at 60°C under stirring.

2.1.2.2 APS. Oldenburg et al. used 3-aminopropyltrimethoxysilane (APS) for depositing metal nanoparticles on surface of silica spheres [2]. APS has a terminal amino group that is cationic at neutral pH. The PS surface is anionic, arising from the anionic initiator (KPS) that was used for the preparation of PS spheres. Accordingly, the amino group of the APS should interact with the PS surface electrostatically, and then the PS surface becomes hydrophilic because of a terminal alkoxide group of APS. In the present work, the 0.2 wt% PS colloid (10 ml) was added to 0.14-14 mM APS aqueous solution (10 ml) at room temperature under stirring.

2.1.2.3 Polyelectrolyte. According to Caruso et al., Latex particles are coated with a variety of polyelectrolytes by a layer-by-layer method, and consequently surface charge of the Latex particles can be changed with the polyelectrolytes used [5]. The present work examined this surface modification technique. The 0.2 wt% PS colloid (10 ml) was added to 10 ml of 0.2 wt% aqueous solution of cationic polyelectrolyte (poly(allylamine hydrochloride) (PAH) or poly(diallyldimethylammonium chloride) (PDADMAC)) at room temperature under stirring. After 1 h, the colloid was three times washed by centrifuging at 20000 rpm for 30 min, removing supernatant and adding water. The PS concentration was adjusted to 0.2 wt% with addition of water (PAH/PS or PDADMAC/PS). The PAH/PS or PDADMAC/PS colloid (10 ml) was added to 10 ml of 0.2 wt% aqueous solution of anionic polyelectrolyte (poly(sodium 4-styrenesulfonate) (PSS)) at room temperature under stirring (PSS/PAH/PS or PSS/PDADMAC/PS).

2.1.2.4 PVP. In our previous work [6], polyvinylpyrrolidone (PVP) improves an affinity between silica nuclei and PS surface in silica-coating of fluorescent microsphere (PS spheres including fluorescent dye molecules). In the present work, the surface modification with PVP was also performed. The 0.2 wt% PS colloid (10 ml) was added to 0.1-10 g/l PVP aqueous solution (10 ml) at room temperature under stirring.
2.1.2.5 Adjustment of PSt concentration. The surface modifications mentioned above were all continued for 1 h. The prepared colloid was three times washed by centrifuging at 20000 rpm for 30 min, removing supernatant and adding water. The PSt concentration was adjusted to 0.02 wt% with addition of water.

2.1.3. Electroless Au-plating. The electroless metal plating technique that included three steps was employed for Au deposition on the silica spheres according to Menon and Martin [7]. The first step was performed for surface sensitization of the PSt spheres. Sn solution that contained tin chloride (0.0005 g), trifluoroacetic acid (0.0005 ml) and water (10 ml) was added to the surface-modified PSt colloid (10 ml). After 1 h, the colloid was twice washed centrifuging at 20000 rpm for 30 min, removing supernatant and adding water. The PSt concentration was adjusted to 0.02 wt% with addition of water (PSt@Sn²⁺). The second step was performed for surface activation. Ag solution that contained silver nitrate (0.0006 g), aqueous ammonia (several drops) and water (10 ml) was added to the PSt@Sn²⁺ colloid (10 ml). After 1 h, the colloid was washed again with centrifugation and redispersion in the water. The PSt concentration was adjusted to 0.02 wt% with addition of water (PSt@Ag). The third step was Au plating. Au solution that contained the Oromerse Part B (0.025 ml), formaldehyde solution (0.055 g), sodium bicarbonate (0.0021 g), sodium sulfite (0.016 g), sulfuric acid (several drops) and water (10 ml) was added to the PSt@Ag colloid (10 ml), and stood for 24 h. Then, the colloid was washed with the above-mentioned procedure (PSt@Au).

2.2. Characterization
Various composite particles were characterized by transmission electron microscopy (TEM), electrophoretic light scattering (ELS) and ultraviolet (UV)–visible (VIS) absorption spectroscopy. Samples for TEM were prepared by dropping and evaporating the particle suspensions onto a collodion-coated copper grid. ELS was performed to measure the electric surface potential of the surface-modified PSt spheres. Before measurement, the colloid of the PSt spheres was diluted in water and then introduced into a thermostated scattering cell at 25 °C.

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3. Results and discussion

3.1. PSt spheres without surface modification
Fig. 1 shows TEM image of PSt@Au particles prepared with the use of PSt spheres without surface modification. Though some Au nanoparticles with a size of ca. 10 nm were deposited on the PSt spheres, many aggregates of Au nanoparticles were also attached on the spheres. Formaldehyde contained in the Au solution reduced Au⁺ not on the surface of the spheres but in the solution, which led to generation of Au nanoparticles in the solution. Probably, the Au nanoparticles generated in the solution formed the aggregates, and then the aggregates were deposited on the spheres. This result indicated that Sn²⁺ did not have a strong affinity for the PSt surfaces.

![Figure 1. TEM image of PSt@Au spheres.](image)

3.2. PSt spheres surface-modified with Na₂S₂O₈
At a Na₂S₂O₈ concentration of 0.1 wt%, many aggregates composed of Au nanoparticle with a size of ca. 10 nm were obtained both on and apart from the spheres. Even at a Na₂S₂O₈ concentration as high
as 1.0 wt%, Au nanoparticles were not successfully deposited on the spheres. Probably, the surface-modification with Na₂S₂O₈ did not increase the amount of Sn²⁺ deposited on the PST surface.

3.3. PST spheres surface-modified with APS
At APS concentrations of 0.14 and 1.4 mM, many aggregates composed of Au nanoparticle with a size of ca. 10 nm were produced apart from the PST spheres. At an APS concentration of 14 mM, though aggregates of Au nanoparticles were also obtained between the PST spheres, Au nanoparticles with sizes of 10-33 nm were deposited on the PST surfaces, which indicated that APS provided efficient surface sensitization of the PST, compared to Na₂S₂O₈.

3.4. PST spheres surface-modified with polyelectrolytes
The unmodified PST spheres had a negative ζ-potential of -30.1 mV, since the KPS used as initiator is anionic. After the modification with PAH and PDADMAC, the ζ-potentials turned to positive charges of 3.6 and 39.6 mV, respectively. After the modification with PSS, the PSS/PAH/PST and the PSS/PDADMAC/PST spheres had negative charges of -29.1 and -31.1 mV, respectively. These results indicated that the PST spheres were efficiently coated with the polyelectrolytes.

For the PSS/PAH/PST and the PSS/PDADMAC/PST spheres, many aggregates of Au nanoparticles were produced apart from the PST spheres. In contrast, for the PAH/PST and the PDADMAC/PST spheres, Au particles were deposited on the PST surface. Au particle sizes on the PAH/PST and the PDADMAC/PST spheres that were 10-50 and 25-60 nm, respectively, were large compared to that of APS/PST and that previously reported for the Au-plated silica spheres [3]. Probably, deposition of Au nanoparticles did not take place on the PST surface, and Au nanoparticles was generated in the solution Au particles. The Au nanoparticles should have negative charge in neutral and higher pH, since anions such as SO₃²⁻, CO₃²⁻ and SO₄²⁻ derived from the Au solution were probably adsorbed on Au surface. The Au nanoparticles were electrostatically attached on the sphere surface, and then grown to the large Au nanoparticles. Accordingly, the surface-modification with polyelectrolytes did not suit for uniform deposition of Au nanoparticles on PST spheres.

3.5. PST spheres surface-modified with PVP
Fig. 2 shows TEM images of the PST@Au spheres prepared with PST spheres surface-modified at various PVP concentrations. At PVP concentrations of 0.1 and 1 g/l (Figs. 2 (a) and (b)), not only Au nanoparticles but also their aggregates were deposited on the surfaces of PST spheres. At a PVP concentration as high as 10 g/l (Fig. 2 (c)), no aggregates were observed on the PST@Au spheres, and the spheres composed a myriad of Au nanoparticles with sizes of 8-25 nm uniformly distributed on the PST surfaces. It can be considered that PVP improved an affinity between the Sn²⁺ and the PST surfaces.

Fig. 3 shows UV–VIS absorption spectra of the PST@Au spheres prepared with PST spheres surface-modified at various PVP concentrations. All the spheres revealed monotonously tailed spectra due to scattering of the PST spheres. Absorption bands observed at 520 nm were attributed to surface plasmon resonance of Au nanoparticles [1]. Peak intensity of the surface plasmon resonance peak increased with an increase in the PVP concentration. This meant that many Au nanoparticles were deposited at the high PVP concentration, which corresponded to the TEM observation (Fig. 2).

At the PVP concentration of 1 g/l, tailing in a wavelength range of 600-800 nm was distinguishing compared to that of the 10 g/l. Probably, this resulted from the generation of the aggregates.
In the previous work for the SiO$_2$@Ag with Ag sizes of 13.3-60 nm [8], a red shift of the Ag plasmon peak with respect to the usual surface plasmon peak position of Ag nanoparticles was observed, which was mainly attributed to the interaction between neighboring Ag particles. For all the PVP/PSt spheres used, no difference in the Au surface plasmon resonance peak positions was observed, which indicated that the nanoparticles were deposited on the spheres independently from other nanoparticles.

4. Conclusions
Deposition of Au nanoparticles on the surfaces of submicron-sized polystyrene spheres was performed applying electroless metal plating technique for submicron-sized polystyrene spheres surface-modified with various chemical agents such as Na$_2$S$_2$O$_8$, APS, polyelectrolytes and PVP. Au nanoparticles with sizes of 8-25 nm were uniformly deposited on the surfaces of polystyrene spheres modified with PVP. As PVP concentration in the surface-modification increased, the amount of Au deposited on polystyrene surface increased, and the deposition of Au nanoparticles was more uniform. Accordingly, PVP was suitable for the surface-modification of PSt spheres.

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