

Silica coating of silver nanoparticles using a modified Stöber method

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Abstract

Silver nanoparticles prepared through a borohydride-reduction method were directly coated with silica by means of a seeded polymerization technique based on the Stöber method. Various amine catalysts were used for initialization of a sol–gel reaction of TEOS with no need for a prior surface modification. Use of dimethylamine (DMA) as a catalyst was found to be necessary to obtain a proper coating. The silica shell thickness was varied from 28 to 76 nm for TEOS concentrations of 1–15 mM at 11.1 M water and 0.8 M DMA. The optical spectra of the core–shell silver–silica composite particles show a qualitative agreement with predictions by Mie theory.

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1. Introduction

Extensive studies have been performed on the homogeneous coating of metal nanoparticles with silica shells (core–shell particles) [1–10]. The silica shells not only enhance the colloidal stability but also control the distance between core particles within assemblies through shell thickness [11]. Liz-Marzán, Mulvaney, and co-workers have extensively studied metal–silica core–shell particles prepared by a liquid phase procedure in which the use of a surface primer (a silane coupling agent) was necessary to provide the surface with silanol anchor groups [1,2,6,7]. Extensive growth of the silica shells was performed through the sol–gel processing of silicon alkoxides in ethanol–ammonia mixtures [1]. Other authors have demonstrated that coating of “vitro-phobic” materials such as gold or silver with silica shells can be accomplished without using silane coupling agents. Xia and co-workers, for instance, prepared silica-coated gold nanospheres [12] and silver nanowires [13] through hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in

ethanol. Similarly, Hardikar and Matijevic [4] performed the coating of 60-nm silver particles stabilized with Daxad 19. More recently, Graf et al. [14] used poly(vinylpyrrolidone) as a stabilizer to transfer gold and other nanoparticles into ethanol and perform a direct coating with TEOS. In all three cases, the role of the surface stabilizer is probably the key to direct coating, but this has not been carefully disclosed. We have recently developed [15] a new technique for the encapsulation of citrate-stabilized gold nanoparticles with silica shells in one single step, and with no need of coupling molecules. The method is based on previous results on the preparation of monodispersed silica particles by the sol–gel method using small silica particles as seeds [16,17]. Fine control of the concentrations of water, ammonia (catalyst), and silicon alkoxide allowed the preparation of gold–silica core–shell particles with various shell thicknesses.

Silver nanoparticles also show a plasmon resonance in the visible, and find even wider applications than gold, since the silver plasmon band is narrower, its extinction coefficient is ca. 5 times larger than that for gold, and the position of the band is typically 400 nm for Ag, and it is well apart from the band-to-band transition energy, which is not the case for Au [18]. All these features are of relevance in fields

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such as SERS or nonlinear optical response. However, the coating of silver nanoparticles with thick shells poses an additional difficulty that is related to the chemical instability of such particles in the presence of ammonia, which are readily oxidized and form complex ions that are soluble and colorless [2,13]. One approach to overcome this difficulty has been the use of AgAu alloy nanoparticles, which allowed extensive silica coating when the gold content was higher than 25% [19]. Accordingly, a good technique for the synthesis of silica-coated nanoparticles is still missing.

In the present paper, we applied the direct silica-coating technique based on the seeded condensation of alkoxy-silanes for the encapsulation of silver nanoparticles with thick shells. In order to prevent the dissolution of the silver cores, various amines were tested as catalysts for the hydrolysis and condensation of TEOS (Stöber method) [20]. Additionally, the concentrations of TEOS, ethanol, water, and amine were tuned to optimize the morphology of the final coated particles.

2. Materials and method

2.1. Chemicals

Silver perchlorate (AgClO_4) (Kanto Chemical Co., Inc., 99%), sodium borohydride (NaBH_4) (Wako Pure Chemicals Ltd., 99%), and trisodium citrate dihydrate (Na-cit) (Wako Pure Chemicals Ltd., 90%) were used as silver precursor, reducing reagent, and stabilizer for preparation of silver nanoparticles, respectively. Special grade reagents (Wako Pure Chemicals Ltd.) of tetraethylorthosilicate (TEOS) (95%) and ethanol (99.5%) were used for silica coating and ammonia (25% aqueous solution), methylamine (MA) (40%), and dimethylamine (DMA) (50%) were used as catalysts for a sol–gel reaction of TEOS. All chemicals were used as received. Ultrapure deionized water (resistivity higher than $18 \text{ M}\Omega \text{ cm}$) was used in all the preparations.

2.2. Preparation of materials

2.2.1. Preparation of silver nanoparticles

Silver nanoparticle colloids were prepared by reduction of AgClO_4 with NaBH_4 . Freshly prepared $500 \mu\text{l}$ of 20 M AgClO_4 in H_2O was added to 100 ml of 0.3 M NaBH_4 and 1 M Na-cit in H_2O cooled with ice water under vigorous stirring. The color of the mixture turned yellow within a few minutes, which indicated the presence of silver nanoparticles [2]. Typically, spherical silver nanoparticles with an average size of 10 nm were observed in TEM (see Fig. 1a).

2.2.2. Silica coating of silver nanoparticles

The seeded polymerization technique with a sol–gel reaction [15] was used for silica coating of the silver nanoparticles. To the silver colloid was added a solution of TEOS in ethanol. Thereafter, the silica coating was initiated by

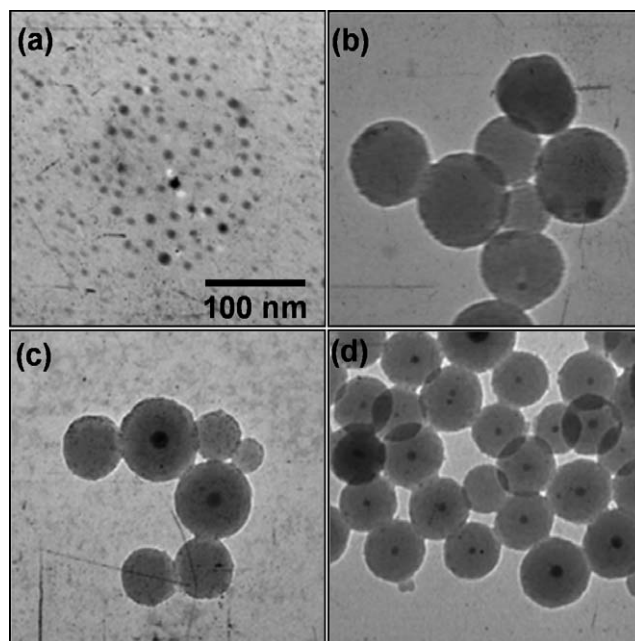


Fig. 1. TEM images of Ag nanoparticles (a) and Ag@SiO₂ prepared by TEOS hydrolysis using ammonia (b), methylamine (c), and dimethylamine (d) as catalysts. Concentrations of water, amine, and TEOS were 11.1 M , 0.8 M , and 1 mM , respectively.

rapidly injecting an aqueous amine solution into the silver/TEOS colloid. The concentrations of TEOS and water were varied from 0 to 4 mM and from 11.1 to 20 M with respect to the total solution volume, respectively. In order to grow the silica shells, an additional volume of TEOS was added to the colloid so that the total TEOS concentration increased by 4 mM , leading to total TEOS concentrations of 6 – 15 mM . The silver concentration was 0.018 mM in all the silica-coating experiments.

2.3. Characterization

The silica-coated silver–silica composite particles were characterized by transmission electron microscopy (TEM) and ultraviolet (UV)–visible (vis) spectroscopy. TEM was performed with a Zeiss LEO 912 OMEGA microscope operating at 100 kV . Samples for TEM were prepared by dropping and evaporating the nanoparticle suspensions onto a collodion-coated copper grid. Silica shell thickness was estimated as the difference between silver particle and composite particle sizes. UV–vis extinction spectra were measured with a Hitachi UV-3010 spectrophotometer.

3. Results and discussion

3.1. Silver nanoparticles

The initial choice of amines was based on the chemical stability of Ag colloid in the presence of the amines. Fig. 2

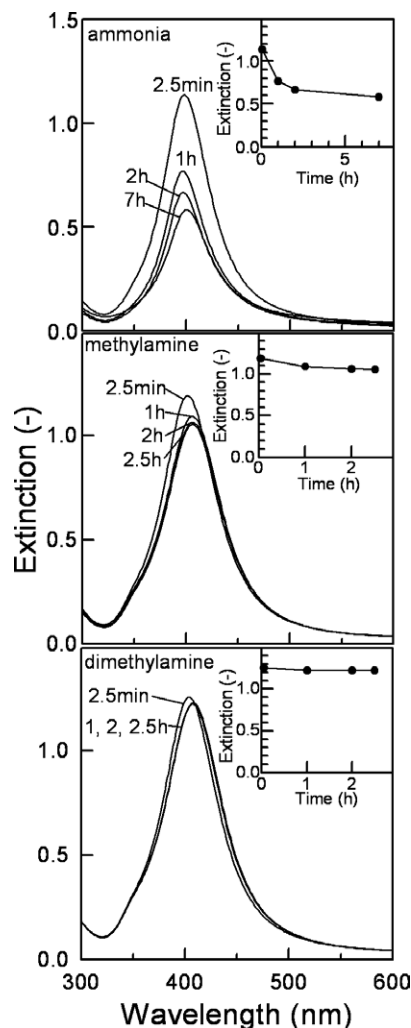


Fig. 2. UV-vis extinction spectra of Ag nanoparticles in water at various times after amine addition. Concentrations of Ag and amine were 0.1 M and 0.3 mM, respectively. The insets show extinction versus time.

shows UV-vis extinction spectra of Ag nanoparticles at various times after addition of the different amines. The presence of peaks centered around 400 nm corresponds to the surface plasmon resonance of silver nanoparticles in the 10-nm size range. As expected [2], addition of ammonia promotes relatively rapid damping of the surface plasmon band with time, such that after 7 h, the intensity at the maximum was decreased to ca. half of the initial value. This is due to aerial oxidation of Ag in the presence of NH_3 and dissolution in water as $\text{Ag}(\text{NH}_3)_2^+$ complex ions, which do not absorb in the visible [2]. Addition of MA also led to a decrease in the extinction intensity at the maximum, but the magnitude of the damping was only of around 13% and saturated after 2 h, while the maximum was red-shifted. This suggests that the optical effect is related to adsorption of the amines on the surface (rather than oxidation of Ag^0 to Ag^+), possibly leading to a reduction in surface charge, which has been shown to have the same effect [21,22]. In the case of DMA addition, the damping and red-shift are very limited and completed

within a short time. Steric effects may be of importance here since DMA is bulkier than MA. Thus, DMA was considered the option of choice as a catalyst for the Stöber process.

3.2. Silica-coated silver nanoparticles

3.2.1. Effect of amines

Fig. 1 shows typical TEM images of the starting silver nanoparticles (Fig. 1a) and silica-coated silver ($\text{Ag}@\text{SiO}_2$) particles prepared using various amines. Darker and lighter parts of particles correspond to silver and silica, respectively, since the electron density of silver is significantly higher. The results shown in Fig. 1 agree with the spectra plotted in Fig. 2. Thus, using ammonia as a sol-gel catalyst (Fig. 1b), core-free silica particles with sizes of 50–95 nm were observed. This is a confirmation that silver nanoparticles reacted with ammonia, leading to formation of $\text{Ag}(\text{NH}_3)_2^+$ complex ions and dissolution into the water/ethanol solvent. Oppositely, using MA (Fig. 1c) and DMA (Fig. 1d), well-defined silver-silica core-shell nanoparticles coexist with a population of smaller, core-free silica spheres, which arise from secondary nucleation during the Stöber process [23]. According to the TEM observation, the ratio of core-shell to core-free particles is significantly higher for DMA than for MA. It can be seen in Fig. 1d that most particles contain a single silver core with a size of ca. 10 nm (in agreement with the initial Ag nanoparticle size). Given the efficiency of DMA for the formation of high-quality core-shells, together with the very limited effect on the Ag plasmon band, it was used as a catalyst for all subsequent experiments.

3.2.2. Silica-coating optimization

Two series of experiments were performed where only the concentration of one reactant (either water or DMA) was changed at a time, so as to optimize reaction conditions for homogeneous silica coating, while avoiding the formation of free silica nuclei. The water concentration was varied between 11.1 and 20.0 M, while maintaining $[\text{DMA}] = 0.8 \text{ M}$; $[\text{TEOS}] = 1 \text{ mM}$. The main conclusion here was that, as the water concentration raises, dissociation of DMA, and ionic strength increase in turn [24], leading to both aggregation of silver nuclei and formation of smaller core-free silica particles (see the supplemental material). A water concentration of 11.1 M corresponds to particles shown in Fig. 1d, which are uniformly coated and with a negligible amount of core-free silica.

Thus, with $[\text{H}_2\text{O}] = 11.1 \text{ M}$ and $[\text{TEOS}] = 1 \text{ mM}$, experiments with varying DMA concentrations between 0.2 and 2.0 M were carried out. It was observed (see the supplemental material) that, while at $[\text{DMA}] < 0.4 \text{ M}$, TEOS condensation was not complete, for $[\text{DMA}] > 0.8 \text{ M}$, there is significant silver core aggregation and formation of free silica. This is clearly related to the influence of DMA concentration on the rate of hydrolysis of TEOS and condensation into SiO_2 .

3.2.3. Control of silica shell thickness

For many applications of core–shell particles, such as photonic crystals [25], it is of paramount importance to precisely control the thickness of the shell. In the system we are considering, the simplest approach to vary shell thickness is to use different amounts of TEOS, which is used as silica precursor. Although this can be performed stepwise after the deposition of an initial shell, we investigated the effect of adding various amounts of TEOS in one single step. Fig. 3 shows TEM images of Ag@SiO₂ particles formed

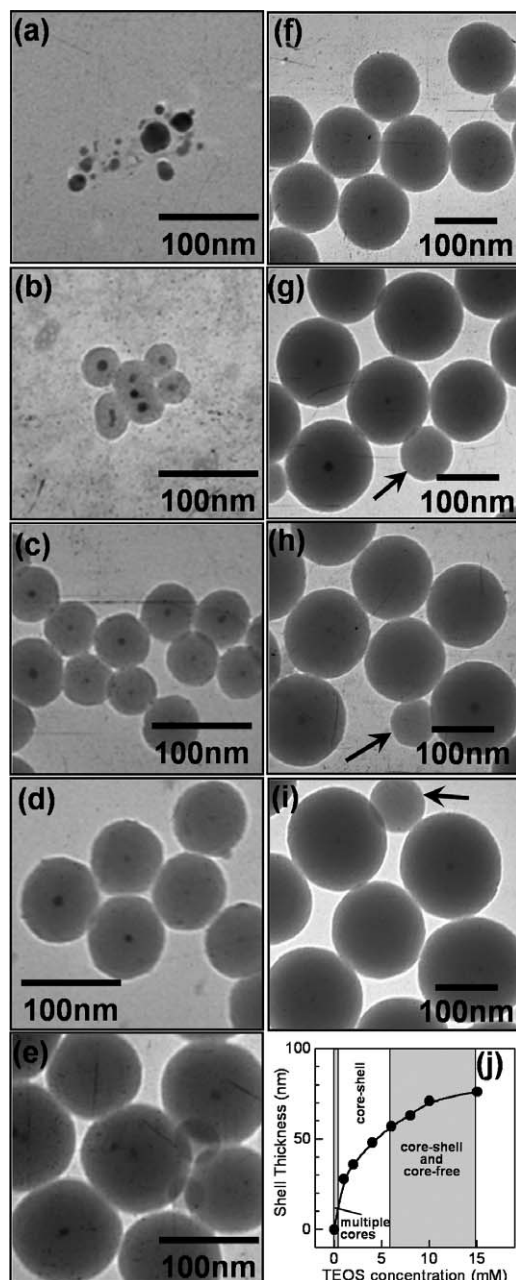


Fig. 3. TEM images of Ag@SiO₂ prepared using total TEOS concentrations of 0.1 (a), 0.5 (b), 1.0 (c), 2.0 (d), 4.0 (e), 6.0 (f), 8.0 (g), 10 (h), and 15.0 mM (i). The concentrations of water and DMA were 11.1 and 0.8 M, respectively. Arrows stand for core-free silica particles. (j) Plot of silica-shell thickness as a function of TEOS concentration.

using various TEOS concentrations. At TEOS concentrations below 0.5 mM, aggregation of the silver nanoparticles is observed, rather than formation of core–shell particles. Above 0.5 mM, no uncoated silver nanoparticles were observed. At [TEOS] = 0.5 mM, Ag@SiO₂ core–shell particles are obtained with rather thin shells, but some of them contain multiple cores. At [TEOS] = 1.0–4.0 mM, most of the particles are quasi-perfect core–shells with just one silver core and increasing shell thickness. Further addition of TEOS ([TEOS] = 6–15 mM) can increase the shell thickness, though a large amount of core free particles with sizes of 80–90 nm were also generated, in which the proportion of core-free silica particles formed was around 10% of all the particles. A plot of the silica shell thickness as a function of TEOS concentration is shown in the same figure, with values ranging from 28 to 76 nm as the TEOS concentration was increased from 1 up to 15 mM. This means that the shell thickness can be controlled within a broad range.

3.3. UV-vis spectroscopy

Fig. 4 shows extinction spectra of the citrate-protected silver sol and of Ag@SiO₂ particles with different silica shell thickness. Ethanol was added to the silver sol, so that the water concentration of the dispersion medium was 11.0 M (1:4 (v/v) water/ethanol), as used for the samples in Fig. 3. For the silica shell thicknesses of 28–48 nm, a single plasmon band was measured, with maxima located around 408.5 nm, i.e., red-shifted with respect to the uncoated nanoparticles ($\lambda_{\max} = 399$ nm) (Fig. 4, inset). This is due to the increase in the local refractive index around the particles. For the shell thicknesses of 57–76 nm, a blue-shift of the plasmon band to around 400 nm and a weakening in the apparent intensity of the plasmon band were observed, which indicated that the sufficiently large silica shell promoted significant scattering at shorter wavelengths. The surface plasmon absorption

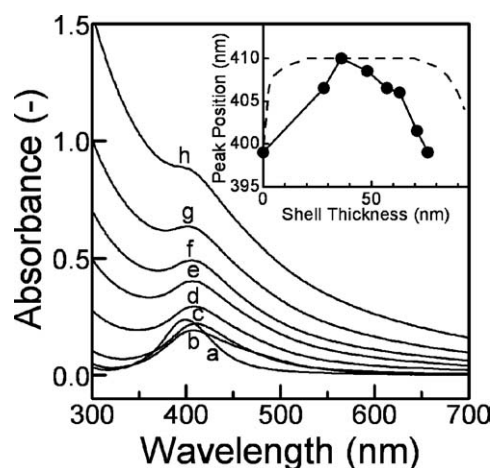


Fig. 4. UV-vis extinction spectra of citrate-Ag (a) and Ag@SiO₂ particles with shell thicknesses of 28 (b), 36 (c), 48 (d), 57 (e), 63 (f), 71 (g), and 76 nm (h). The inset shows the surface plasmon peak position (closed circles) and predictions by Mie theory (dashed line).

band in the visible is very sensitive to both particle size and shape and to the properties of the surrounding medium [1] and its variation with various parameters has been extensively studied [1,7,26–29]. In particular, the effects of silica shells with various thicknesses, and in various solvents, have been predicted by Mie theory [1]. According to the literature, shifts of the surface plasmon absorption are due to a local increase of refractive index and to scattering from large silica shells. Extinction spectra of colloidal suspensions can be predicted by Mie theory. The dashed line in the inset of Fig. 4 shows the position of the maxima predicted through calculations using Mie theory, in which extinction of the core-free silica particles was neglected [30]. The experimental peak positions were in qualitative agreement with the calculations.

4. Summary

Coating of silver nanoparticles with thick silica shells is possible, without affecting the integrity of the cores, when dimethylamine (rather than ammonia) is used as a catalyst in a standard Stöber process. The synthesis of Ag@SiO₂ can be accomplished through a simple, one-step procedure, where a TEOS solution in ethanol/water is added to a citrate-stabilized silver colloid. The silica shell thickness can be conveniently controlled through TEOS concentration, which allows a simple test of the influence of silica shell thickness on the optical properties of the colloid.

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Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi: 10.1016/j.jcis.2004.08.184.

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