Direct Coating of Metal Nanoparticles with Silica by a Sol-Gel Method

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ABSTRACT
Nanometer-scale metal particles were directly coated with silica by a sol-gel method. The direct silica-coating did not require silane coupling agents that were often used in conventional silica-coating methods. For the silica-coated Au particles, the addition of tetraethylorthosilicate and water prior to ammonia was found to be critical to obtain a proper coating. The silica shell thickness was varied from 30 to 90 nm for TEOS concentrations of 0.0005 - 0.02 M at 10.9 M water and 0.4 M ammonia. For the silica-coated Ag particles, various amine catalysts were used for initialization of a sol-gel reaction of TEOS without need of a prior surface modification. Use of dimethylamine (DMA) as a catalyst was 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 silica-coated Au and Ag nanoparticles agreed with predictions by Mie theory.

KEYWORDS
core-shell, nanoparticle, silica-coating

INTRODUCTION
Nanometer-sized colloidal particles have special interest because they are in an intermediate state between atoms or molecules and bulk material and thereby they can be expected to exhibit unique properties different from those of bulk material (Brus, 1986; Ekimov et al., 1993). Traditionally the stabilization of colloids is performed through surface modification processes such as the adsorption of macromolecules forming a physical barrier against other approaching particles. The coating of the particles with inert silica shells has previously been used as a stabilizing technique (Liz-Marzán et al., 1996a, 1996b; Correa-Duarte et al., 1998; Ung et al., 1998). The role of the silica shell is two-fold, since it not only provides a greatly enhanced colloidal stability in water, but also can be used to control the distance between core particles within assemblies through shell thickness. From this point of view, extensive studies on metal-silica core-shell particles prepared by a liquid phase procedure have been made (Liz-Marzán et al., 1996b; Ung et al., 1998; Hall et al., 2000; Mulvaney et al., 2000). Those
methods have used three steps: (1) modification of the metal nanoparticle surface to make it vitreophilic by using silane coupling agents such as silicon alkoxides with an amino or thiol group as surface primers, (2) slow silica deposition in water from a sodium silicate solution, and (3) extensive growth of the silica shells through sol-gel reaction of silicon alkoxide in ethanol/ammonia mixtures (Liz-Marzán et al., 1996b). Those methods work well but require long procedures if thick shells are to be grown. Coupling agents can be used to activate the metal particle surface for sodium silicate. However, the coupling agents and sodium silicate can introduce impurities to the particles. Therefore, a simplified, more rapid variation of the method with no coupling agents between the metal core and the silica shell would be desirable.

Recently, the authors developed (Mine et al., 2003) a new technique for encapsulation of nanoparticles with silica shells in one single step, without 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 (Nagao et al., 2000; Mine and Konno, 2001). In this report, the new direct silica-coating technique is described that can be applied to gold and silver nanoparticles.

MATERIALS AND METHODS

Chemicals

Tetrachloroauric acid (HAuCl₄) (Sigma-Aldrich, 98%) and silver perchlorate (AgClO₄) (Kanto Chemical Co., Inc., 99%) were used as precursors of metal nanoparticles. Sodium borohydride (NaBH₄) (Wako Pure Chemicals Ltd., 99%) was used as reducing reagent for gold and silver. Trisodium citrate dihydrate (Na-cit) (Wako Pure Chemicals Ltd., 90%) was used as stabilizer for gold and silver nanoparticles, and also worked as reducing reagent for gold. Tetraethylorthosilicate (TEOS) (Wako Pure Chemicals Ltd., 95%) and ethanol (Wako Pure Chemicals Ltd., 99.5%) were used for silica-coating. Special grade reagents (Wako Pure Chemicals Ltd.) of ammonia (25% aqueous solution), methylvamine (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 MΩ cm) was used in all the preparations.

Preparation

Gold nanoparticles were prepared by reduction of the gold salt with Na-cit [24]. Freshly prepared 0.94 ml of 0.34 M Na-cit in H₂O was added to 200 ml of 0.24 mM HAuCl₄ in H₂O at a constant temperature of 80 °C under vigorous stirring. The color of the mixture turned wine red within a few minutes, which indicated the generation of gold nanoparticles. Typically, an average diameter of the nanoparticles was 15 nm. Aqueous ammonia solution was added to the gold colloid solution under vigorous stirring after TEOS/ethanol/water addition. Silica-coating was thus initiated by adding aqueous ammonia into the gold colloid. The concentrations of TEOS, water and ammonia were varied from 0 to 20 mM, from 10.9 to 20 M and from 0.2 to 1.5 M, respectively. The gold concentration was 0.043 mM in all the silica-coating experiments.
Silver nanoparticle colloids were prepared by reduction of AgClO₄ with NaBH₄. Freshly prepared 500 µl of 20 M AgClO₄ in H₂O was added to 100 ml of 0.3 M NaBH₄ and 1 M Na-cit in H₂O cooled with ice-water under vigorous stirring. The color of the mixture turned yellow within a few minutes, which indicated the generation of silver nanoparticles. Typically, the nanoparticles had an average size of 10 nm. To the silver colloid was added a solution of TEOS in ethanol. Thereafter, the silica-coating was initiated by rapidly injecting an aqueous amine solution into the silver/TEOS colloid. The concentrations of TEOS, water and amine were varied from 0 to 4 mM, from 11.1 to 20 M and from 0 to 2.0 M, respectively. To grow the silica shells, an additional volume of TEOS was added to the colloid prepared at a TEOS concentration of 4 mM, so that the total TEOS concentration increased to 6-15 mM. The silver concentration was 0.018 mM in all the silica-coating experiments.

Characterization

The gold-silica and 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 from difference between silver particle and composite particle sizes. UV-VIS extinction spectra were measured with a Hitachi UV-3010 spectrophotometer.

RESULTS AND DISCUSSION

Silica-coating of gold nanoparticles

Two series of experiments in which only the concentration of one reactant (either water or ammonia) was changed at a time were performed, so as to determine reaction conditions for uniform silica coating. The water concentration was varied between 10.9 and 20 M, while maintaining [ammonia] = 0.4 M; [TEOS] = 20 mM. At a water concentration of 10.9 M, most gold particles were coated with ca. 90-nm thick silica shells. At higher water concentrations, besides silica-coated gold particles, many gold core-free silica particles with various sizes were generated and their sizes decreased with water concentration. Because the dielectric constant of water/ethanol mixture increases with water concentration, silanol groups on the silica particle surface probably tend to ionize with increasing water concentration, and thus the electrostatic repulsion between generated particles also increased. Therefore, silica nuclei generated during the early stages of the sol-gel reaction probably grew as stable secondary silica particles rather than on the existing cores.

The ammonia concentration was varied between 0.2 and 1.5 M, while maintaining [water] = ca. 10.9 M; [TEOS] = 20 mM. At an ammonia concentration of 0.2 M, formation of gold core-free silica particles was observed. In contrast, at 0.4 and 0.8 M, the proportion of core-free silica particles formed was less than 30 percent of all the particles. Addition of ammonia increases the ionic strength of the solution and catalyzes the hydrolysis and condensation of the alkoxy silanes (Mine and Konno, 2001). Thus, the high ammonia concentration used in this work should reduce the double layer repulsion.
between particles. As a result, the formation of secondary silica particles should be greatly reduced. At 1.5 M, particles with gold particle aggregates were generated. At high ammonia concentrations, the gold cores probably aggregated before due to the increased ionic strength becoming coated with silica.

Figure 1 shows TEM images of Au@SiO₂ particles formed using various TEOS concentrations. Silica particles with multiple cores were not found for any of the experiments with various TEOS concentrations. However, some core-free silica particles were observed and their amount increased as the TEOS concentration decreased. This is probably related to a decrease in ionic strength of the solution and the resulting increase in electrostatic repulsion between the gold and silica nuclei. However, most of the gold cores were surrounded by silica shells. The thickness was varied from 29 to 88 nm as initial TEOS concentration increased from 0.5 to 20 mM. This means the shell thickness can be controlled within a certain threshold.

**Silica-coating of silver nanoparticles**

![Figure 1](image_url)

**Figure 1**. Silica-coated Au particles synthesized at TEOS concentrations of 0.0005 (a), 0.005 (b), 0.01 (c) and 0.02 M (d). Water and ammonia concentrations were 10.9 and 0.4 M, respectively. The mole ratio of HAuCl₄ : H₂O : NH₃ was 1 : 2.51x10⁵ : 9.23x10³.

As-prepared silver nanoparticles were dissolved into water in the presence of ammonia or methylamine because of formation of amine complex. On the other hand, dimethylamine did not provide dissolving of the silver nanoparticles. Therefore, dimethylamine was used as a catalyst for all subsequent experiments.

Silica-coating was performed varying only the concentration of one reactant (either water or DMA) at a time. The water concentration was varied between 11.1 and 20.0 M, while maintaining [DMA] = 0.8 M; [TEOS] = 1 mM. The main conclusion here was that, as the water concentration increases, dissociation of DMA and ionic strength increase in turn (Bogush et al., 1988), leading to both aggregation of silver nuclei and formation of smaller core-free silica particles. At a water concentration of 11.1 M, the silver nanoparticles were uniformly coated with silica and an amount of core-free silica was negligible. Thus, for [H₂O] = 11.1 M and [TEOS] = 1 mM, DMA concentration was varied from 0.2 to 2.0 M. It was observed that TEOS condensation was not completed for [DMA] < 0.4 M, while neither significant silver core aggregation nor formation of free silica was observed for [DMA] > 0.8 M.
Figure 2 shows TEM images of Ag@SiO\textsubscript{2} particles formed at various TEOS concentrations. At [TEOS] = 1.0-4.0 mM, most of the particles were quasi-perfect core-shells with just one silver core. Further addition of TEOS ([TEOS] = 6-15 mM) increased the shell thickness, though a large amount of core free particles were also generated. The thickness ranged from 28 to 76 nm as the TEOS concentration was increased from 1 up to 15 mM. Silica-coating experiments at TEOS concentrations below 1.0 mM were also performed. At TEOS concentrations below 0.5 mM, aggregation of the silver nanoparticles was observed, rather than formation of core-shell particles. At [TEOS] = 0.5 mM, Ag@SiO\textsubscript{2} core-shell particles were obtained with thin shells, but some of them contained multiple cores.

UV-VIS spectroscopy

Figure 3 shows extinction spectra of the citrate-protected gold sols and of Au@SiO\textsubscript{2} particles with different silica shell thickness. Ethanol was added to the gold sols to adjust water concentration of the dispersion medium to 10.9 M (1:4 (v/v) water/ethanol). Surface plasmon absorption bands were observed to red-shift from 520 nm to 530 nm when a thin silica shell was deposited. Above 40 nm shell thickness, the band blue-shifted back (Figure 3, inset).

Figure 4 shows extinction spectra of the citrate-protected silver sol and of Ag@SiO\textsubscript{2} particles with different silica shell thickness. Ethanol was added to the silver sol, so that the water concentration of the dispersion medium was adjusted to 11.0 M (1:4 (v/v) water/ethanol). 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 (\(\lambda_{\text{max}} = 399\) nm) (Figure 4, inset). 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.

The surface plasmon absorption band in the visible is very sensitive both to particle size and shape and to the properties of the surrounding medium (Liz-Marzán et al., 1996b), and its variation with various parameters has been extensively studied (Doremus, 1964 and 1965; Kreibig et al., 1986; Farbman et al., 1992; Underwood et al., 1994; Liz-Marzán et al. 1996b; Kobayashi et al., 2001). In particular, the effects of silica shells in various solvents have been predicted by Mie theory (Liz-Marzán et al., 1996b). According to the literature, red-shifts and blue-shifts are due to a local increase of refractive
index and to scattering from large silica shell. The experimental peak positions were in qualitative agreement with the predictions. A larger difference between the experimental peak positions and the predictions was observed for the Ag@SiO₂ particles, though the reason for the difference is still unclear.

CONCLUSIONS

Direct coating of gold and silver nanoparticles with silica by a seeded growth technique has been demonstrated. With an increase in TEOS concentration, the silica shell thickness increased. Concentration effects can probably be explained by differences in ionic strength of the solution. The obtained gold-silica and silver-silica particles exhibited a change in surface plasmon absorption depending on the silica thickness, which agreed qualitatively with theoretical predictions of conventional absorption and scattering theory.

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