

# Synthesis of Nanosized Gold–Silica Core–Shell Particles

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Gold colloids have been homogeneously coated with silica using the silane coupling agent (3-aminopropyl)-trimethoxysilane as a primer to render the gold surface vitreophilic. After the formation of a thin silica layer in aqueous solution, the particles can be transferred into ethanol for further growth using the Stöber method. The thickness of the silica layer can be completely controlled, and (after surface modification) the particles can be transferred into practically any solvent. Varying the silica shell thickness and the refractive index of the solvent allows control over the optical properties of the dispersions. The optical spectra of the coated particles are in good agreement with calculations using Mie's theory for core–shell particles.

## Introduction

The preparation of ultrafine metal particles can be facilitated greatly by careful choice of the ligands or stabilizers used to prevent particle coalescence. For example, in aqueous solution, polymeric stabilizers are very efficacious dispersants,<sup>1</sup> whereas, in organic media, long chain surfactants or chemically specific ligands are most commonly used.<sup>2</sup> Alternatively, stabilization can be achieved through compartmentalization in micelles and microemulsions,<sup>3</sup> while immobilization in glasses<sup>4</sup> or sol-gels<sup>5</sup> is the preferred technique when redox reactions of the particles with the matrix need to be avoided. More recently, LB films have been used as particle stabilizers,<sup>6</sup> and electrodeposition<sup>7</sup> of surfactant stabilized metal particles has been used to create ordered 2D crystals. These various techniques not only permit the synthesis of pure metal particles; they also allow the preparation of ultrafine alloys, mixed metal particles, and coated

particles<sup>8</sup> as well as particles with nonspherical geometries (e.g. rods or platelets).<sup>9</sup>

However, many of the stabilizers employed affect the solid state properties of the particles.<sup>1a,†</sup> To circumvent this problem it is necessary to find a stabilizer which not only prevents particle coalescence but also is chemically inert and optically transparent. These conditions are met by silica, a coating material used in a wide range of industrial colloid products ranging from paints<sup>10</sup> and magnetic fluids,<sup>11</sup> to high-quality paper coatings.<sup>12,13</sup> To date, silica coating has not been applied to stabilize nanosized metal particles or to modulate their optical properties.

The silica-coating procedures reported in the literature<sup>14–17</sup> generally involve surfaces with a significant chemical or electrostatic affinity for silica. However gold metal has very little affinity for silica because, unlike most other metals, it does not form a passivating oxide film in solution. Furthermore, there are usually adsorbed carboxylic acids or other organic anions present on the surface to stabilize the particles against coagulation. These stabilizers also render the gold surface vitreophobic.

Previous attempts to overcome this vitreophobic character involved the heterocoagulation of gold colloids on silica colloids dispersed in water, followed by extensive

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growth in ethanol.<sup>18</sup> This resulted in a mixture of labeled and unlabeled silica particles, with a rather low concentration of the labeled ones. The approach presented here is fundamentally different and involves modifying the particle surface to make it vitreophilic. The simplest way to do this is using silane coupling agents as surface primers.<sup>19</sup> Virtually all the studies on silane coupling agents focus on the adsorption of the silanol groups onto different surfaces to generate functionalized surfaces, while here we use them to form a hydrated silica monolayer bonded to the metal substrate. A brief report on the preparation of silica-coated gold has appeared,<sup>20</sup> we discuss here in detail the preparation and optical properties of silica-coated gold particles.

### Experimental Section

(3-Aminopropyl)trimethoxysilane (APS), tetraethoxysilane (TES), 3-(trimethoxysilyl)propyl methacrylate (TPM), and sodium silicate solution ( $\text{Na}_2\text{O}(\text{SiO}_2)_{3-5}$ , 27 wt %  $\text{SiO}_2$ ) were purchased from Aldrich.  $\text{HAuCl}_4$  (Sigma), trisodium citrate dihydrate (Normapur), and  $\text{NH}_4\text{OH}$  (Rhône-Poulenc, 28%) were used as received. Technical grade ethanol and Milli-Q water were used in all the preparations.

Transmission electron microscopy (TEM) was carried out with a Philips CM10 microscope, and particle size distributions were measured from several TEM negatives of each sample. UV-visible spectra were measured with a Hitachi 150-20 spectrophotometer. Refractive indices of solvents were measured at 589.3 nm using an Abbe refractometer.

**Particle synthesis.** The procedure comprises several independent steps, which means that it can be interrupted at any stage of the preparation, depending on the aim for which the particles are being prepared. The standard preparation is as follows:

A gold sol (500 mL,  $5 \times 10^{-4}$  M  $\text{HAuCl}_4$ ) is prepared according to the standard sodium citrate reduction method.<sup>21</sup> This method produces a stable, deep-red dispersion of gold particles with an average diameter of around 15 nm and 10% polydispersity. A freshly prepared aqueous solution of APS (2.5 mL, 1 mM) is added to 500 mL of the gold sol under vigorous magnetic stirring. The mixture of APS and gold dispersion is allowed to stand for 15 min to ensure complete complexation of the amine groups with the gold surface. A solution of active silica is prepared by lowering the pH of a 0.54 wt % sodium silicate solution to 10–11 by progressive addition of cation exchange resin (Dualite C225-Na 14-52 mesh, from BDH Chemicals, converted into the acid form by repeated washing with HCl and water). Twenty milliliters of active silica is then added to 500 mL of the surface-modified gold sol, again under vigorous magnetic stirring. The resulting dispersion (pH  $\approx$  8.5) is then allowed to stand for at least one day, so that the active silica polymerizes onto the gold particle surface. The silica shell thickness is about 2–4 nm after 24 h.

The particles can then be transferred into ethanol if further growth or chemical modification of the silica layer is intended. At this point, thicker shells can be grown via the Stöber method. To 500 mL of the sol in 1:4 water/ethanol containing particles with a silica shell 4 nm thick is added 0.3 mL of TES and 2 mL of ammonia. The solution is allowed to stand for 12 h under mild magnetic stirring, and additions are repeated until the desired shell thickness is attained. The amount of TES to be added can be calculated from the initial and final particle sizes, by means of the following formula,

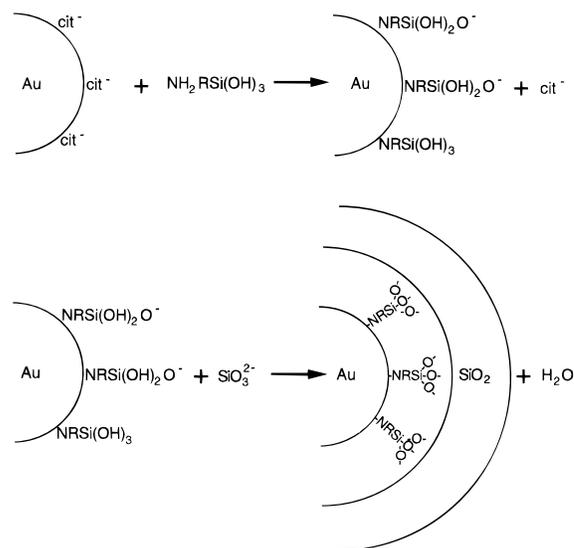
$$V_{\text{TES}} = \frac{\bar{V}_{\text{TES}} \bar{V}_{\text{Au}} [\text{Au}] 10^3 \left[ \left( \frac{R_{\text{tot}}}{R_{\text{Au}}} \right)^3 - 1 \right]}{\bar{V}_{\text{SiO}_2}} \quad (1)$$

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**Figure 1.** Sketch of the surface reactions involved in the formation of a thin silica shell on citrate-stabilized gold particles.

where  $\bar{V}$  refers to molar volume,  $R_{\text{tot}}$  is the final radius, and  $R_{\text{Au}}$  is the radius of the starting colloid.

If the particles are to be dispersed in low-polarity solvents, they can be coated with a second silane coupling agent, such as TPM.<sup>22</sup> The coating is performed by addition of excess TPM to the alcisol (in our case 0.5 mL of TPM to 500 mL of alcisol, which contains about 0.5 g/L  $\text{SiO}_2$ ), stirring at room temperature for 45 min, slowly distilling 100 mL of the solvent for 1 h, and final cleaning of the excess TPM by repeated centrifugation at 3000 rpm and redispersion in pure ethanol. The TPM-coated particles are stable in organic solvents with low polarity, such as ethanol and toluene, as well as in ethanol/toluene mixtures.

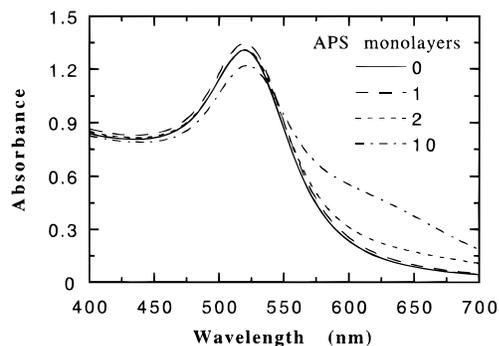
### Results and Discussion

In section I we consider the preparation and characterization of the coated particles, and in section II the optical properties of the coated particles are compared with the predictions of modified Mie theory.

**I. Synthesis.** A variety of thioalkane derivatives may be used to stabilize gold colloids,<sup>7</sup> but aminoalkanes also complex strongly with gold metal.<sup>23</sup> The method reported here involves the primer (3-aminopropyl)trimethoxysilane (APS). One monolayer of APS is allowed to adsorb onto the gold colloid surface. During this process, the previously adsorbed (negatively charged) citrate groups are displaced by APS molecules, with the silanol groups believed to be pointing into solution, as sketched in Figure 1. This is driven by the large complexation constant for gold amines. Hydrolysis of the surface-bonded siloxane moieties to form silane triols occurs within minutes, while condensation is much slower, especially at low concentrations.<sup>19</sup> At pH 7, there is ionization of the silane triols (their isoelectric point is pH 2–3), and this ensures that there is adequate negative surface charge on the gold sol during stabilizer exchange to maintain sol stability. In the second step, active silica (sodium silicate solution at a pH just low enough to allow for a slow polymerization of silicate groups) is added to the dispersion, which promotes the formation of a thin, dense, and relatively homogeneous silica layer around the particles,<sup>14</sup> using the silanol groups as anchor points. At this stage, the particles can be transferred into ethanol and the silica layer thickness can be increased in a controlled way.

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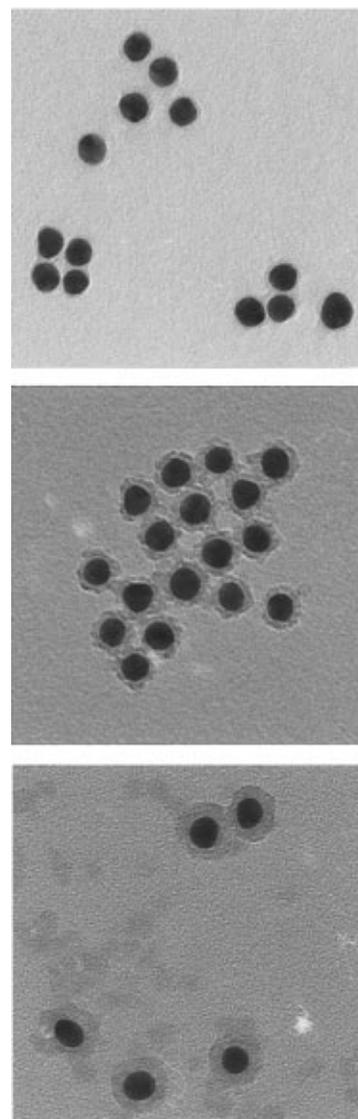
**Figure 2.** UV-visible spectra of sodium citrate-stabilized, 15 nm diameter gold colloids 1 day after addition of different amounts of APS.

**Influence of APS Concentration.** The APS concentration used in the standard preparation ( $5 \times 10^{-6}$  M) supplies the system with ca. 1300 APS molecules per gold particle. Assuming a surface coverage of  $40 \text{ \AA}^2$  per APS molecule<sup>24</sup> and taking the specific surface area of gold  $S_{\text{Au}}$  ( $\text{cm}^2 \text{ L}^{-1}$ ) as

$$S_{\text{Au}} = 3[\text{Au}] \bar{V}_{\text{Au}} R_{\text{Au}}^{-1} \quad (2)$$

the added amount of APS is close to one monolayer (but still slightly below it), and it has been observed to be sufficient for the preparation of homogeneous coatings. At this APS concentration, the dispersion remains stable for days and no clear change in the absorption spectrum is observed. After longer periods of time, some black precipitate is observed (often present in the citrate-stabilized sol too), while the rest of the sol retains the original red color. When more than one monolayer is added, bridging flocculation occurs over minutes to days depending on the APS concentration. This can easily be monitored through the shape of the UV-visible spectrum of the dispersion (see Figure 2). This bridging flocculation can even be observed visually; initially the color of the dispersion becomes dark brown, and finally total precipitation occurs. The structure of the APS monolayer at the particle surface is thought to be uniform, with the amino groups complexed to gold surface atoms and the silane groups facing the solvent (see Figure 1). There may be some surface condensation of the silane groups when the coverage of APS is close to a monolayer, but this would not significantly affect the affinity toward silicate ions.

**Role of Active Silica.** Two parameters are important for the first silica coating: pH and silicate concentration. As indicated by Iler,<sup>14</sup> the pH should be kept between 8 and 10, so that the solubility of the silicate species present in the solution is reduced, and polymerization/precipitation must occur at a sufficient rate to homogeneously coat the particles but still slow enough to avoid the formation of silica nuclei. At the same time, the silicate concentration also plays a role in determining the coating rate. We find that a large excess of silicate ( $[\text{SiO}_2]/[\text{Au}] \approx 10$ ) is necessary to achieve a visible silica layer in a rather short period of time. With a silicate concentration of 0.021 wt %, a 2–4 nm layer is formed after 24 h. In Figure 3, transmission electron micrographs taken at various stages of the coating process are shown. After 18 h in the active silica solution the silica layer is not perfectly homogeneous, but practically the entire surface of all the gold particles appears to be coated. One day later, the shell perfectly covers all the particles; however, the particle surface is rough. This



**Figure 3.** Transmission electron micrographs of 15 nm gold particles coated with thin silica layers: (a, top) 18 hours after addition of active silica; (b, center) 42 h after addition; (c, bottom) 5 days after addition. The silica shell keeps on growing, but eventually small silica particles also nucleate out of the solution.

roughness is due to the oligomeric nature of active silica. Direct adsorption of silica oligomers takes place as aging proceeds. Finally after 5 days a further increase in silica layer thickness is observed, but small silica particles also nucleate out of the solution.

To avoid coprecipitation of silica nuclei, dialysis can be performed at several stages of the coating process (MW cutoff = 12 000, 10 mL of Au–silica sol, 5 L reservoir of distilled water) as a way to remove unreacted silicate ions from the solution. With thin coatings (even after short term dialysis), partial aggregation of the colloid takes place, as indicated by an increased absorbance at longer wavelengths and a decreased plasmon band.<sup>25,26</sup> On the other hand, when the layer is thick, the dialysis is not very useful because small silica particles are already present in the dispersion and they cannot be removed by dialysis. This means that the preparation of aqueous dispersions of gold with thin silica shells that are free of silica particles is hard to achieve.

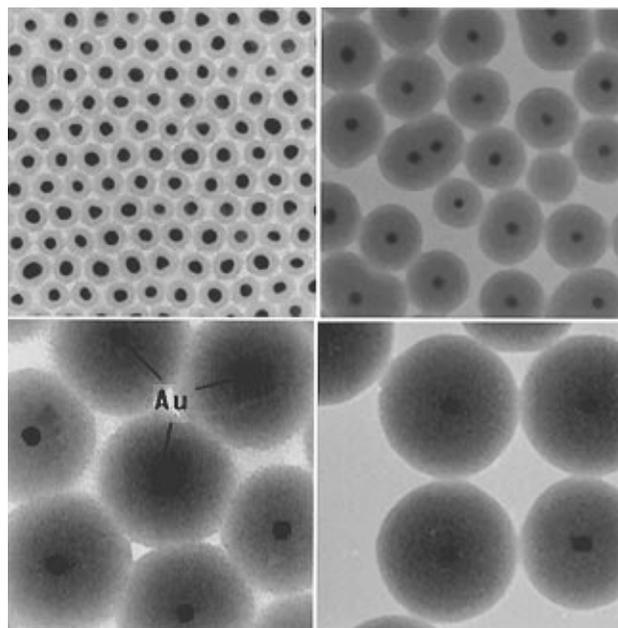
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**Transfer into Ethanol.** The control of the silica layer thickness is much easier to achieve if the particles are dispersed in ethanol or in ethanol/water mixtures. In such mixtures, the addition of tetraalkoxylated silanes provides the system with monomeric silica, which leads to slow homogeneous particle growth.<sup>27</sup> However, prior to the preparation of stable dispersions in ethanol, the silica layer formed in the aqueous dispersion must be sufficiently thick to shield the strong van der Waals interactions between the gold particles.<sup>28</sup> When the particles are transferred from water into a solvent with a lower polarity, such as ethanol, there is a reduction in surface charge. If the silica layer around the particles is too thin, the van der Waals forces are still very strong and partial flocculation occurs, even if TES and ammonia are added immediately after the transfer. This problem is partially offset by the fact that when the aqueous dispersion of precoated particles is diluted with ethanol, the solubility of silicate is drastically lowered, and therefore polymerization occurs.<sup>29</sup> Consequently the transfer into ethanol causes (most of) the silicate ions still remaining in solution to condense onto the gold-silica nuclei already present in the dispersion. The extent of the polymerization depends mainly on the ethanol/water ratio. When small ratios (up to 2:1) are used, the condensation is not complete (part of the silicate stays in solution) but deposition takes place exclusively on the gold-silica nuclei. When ratios larger than 2:1 are used, most of the silica still polymerizes on the particle surface, thus increasing the thickness of the shell, but small gold-free silica particles are formed as well. If the aim of the transfer is the seeded growth of the particles via the Stöber method, high water concentration leads to less monodisperse particles and inhomogeneous surfaces.<sup>30</sup> Therefore, the ethanol/water ratio is chosen as a compromise between these two extremes and again depends on the ultimate application of the particles. Clean (silicate-free) dispersions in ethanol can however be obtained by repeated centrifugation (3000 rpm for at least 6 h) and redispersion of the particles in an ethanol/water mixture.

**Extensive Growth.** Further growth of the particles is achieved in the ethanol/water mixtures using the well-known Stöber method,<sup>27</sup> based on the hydroxide-catalyzed hydrolysis of tetraethoxy silane (TES) and condensation of the resulting silanol groups. It is important to note that, if the first silica coating in water is skipped, significant aggregation takes place in ethanol before silica from TES hydrolysis can grow onto the particles. This is mainly due to a reduction in electrostatic stabilization of gold particles in ethanol, when stabilized only with APS/citrate. Philipse et al. have previously shown that only a combination of silicate and TES deposition produces homogeneously coated colloid particles.<sup>16</sup> By this method the formation of alcosols of silica particles of any selected size with the gold particles placed precisely at their centers is possible. Figure 4 shows several steps in the seeded growth of a sample prepared with the concentrations described above. Gold-free silica particles were also present during the growth because of nucleation during the transfer into ethanol. These particles were smaller than the core-shell particles because of the smaller size of the nuclei on which they initially grew. When the particle size increases, the system becomes more monodisperse because of a reduction in the relative size



**Figure 4.** Transmission electron micrographs of silica-coated gold particles produced during the extensive growth of the silica shell around 15 nm Au particles with TES in 4:1 ethanol/water mixtures. The shell thicknesses are (a, top left) 10 nm, (b, top right) 23 nm, (c, bottom left) 58 nm, and (d, bottom right) 83 nm.

distribution. This extensive growth also leads to a smoothing of the particle surface because the growth takes place through monomer addition. It can even be observed in Figure 4 that, for thin shells, the sometimes non-spherical shape of the gold particles is maintained during silicate deposition in water but that all the particles become spherical after extensive growth in ethanol/water mixtures.

During the growth process, care must be taken (by addition of relatively small amounts of TES) to ensure that all the hydrolyzed TES polymerizes on the existing particles and that no new silica nuclei form. If this happens, the growth experiment should be stopped because further TES additions will preferentially promote the growth of the new, smaller particles.<sup>30</sup>

**II. Optical Properties.** Nanosized gold colloids show a very intense surface plasmon absorption band in the visible (typically around 520 nm). The exact position of this plasmon band is extremely sensitive both to particle size and shape and to the optical and electronic properties of the medium surrounding the particles.<sup>31-33</sup> Silica is electronically inert (it does not exchange charge with the gold particles), but its refractive index is different from that of both water and ethanol (and of course from that of gold).

The extinction coefficients for dispersions of spherical particles can be calculated by using the equations derived by Mie. These equations have been modified for the case of core-shell particles by Aden and Kerker.<sup>34</sup> We calculated the extinction coefficients using the algorithm in the book by Bohren and Huffman.<sup>32</sup> The optical constants for gold were taken from values for evaporated gold films.<sup>35</sup> Values at intermediate wavelengths were calculated by interpolation and were corrected for the effect

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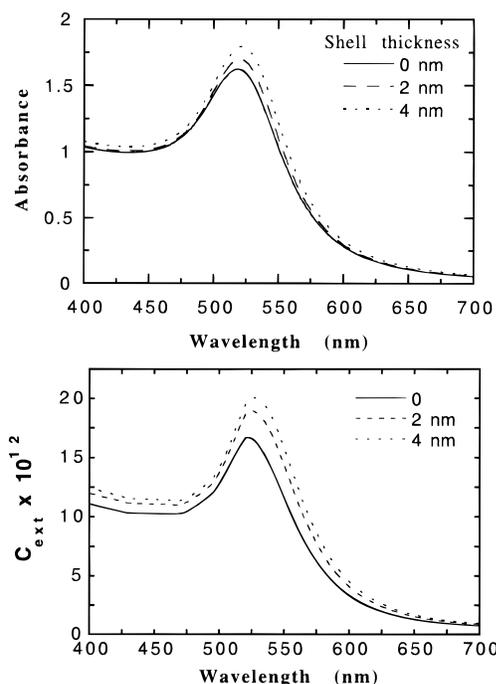
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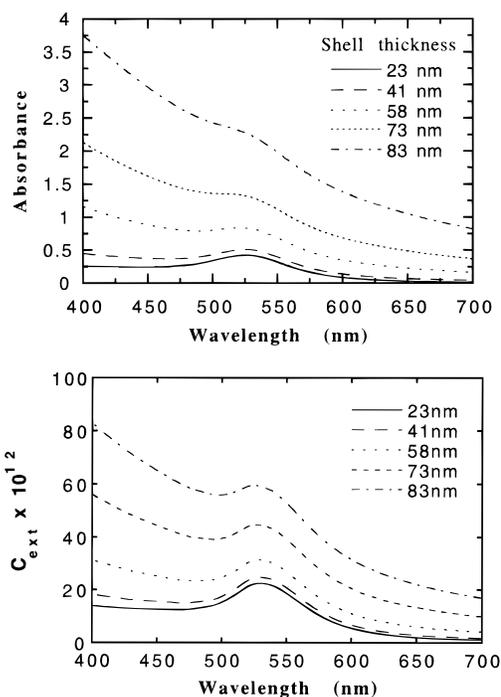
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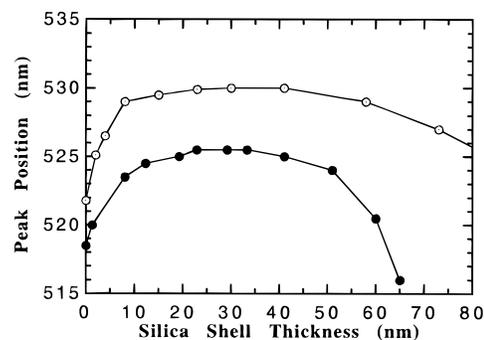
**Figure 5.** Influence of thin silica shells on the UV-visible spectra of aqueous gold colloids: (a, top) experimental; (b, bottom) calculated.

of the small particle size on the dielectric constants for gold.<sup>33,36</sup> These data have been shown to give good agreement for a variety of solvents,<sup>33</sup> but there can be a slight mismatch because the position of the surface plasmon band maximum depends weakly on the particle size, and peak positions for aqueous gold sols have been reported to lie variously between 514 and 521 nm.<sup>3a,8i,25</sup> The gold sols used here had a maximum at 518 nm, whereas calculated spectra obtained using the dielectric data of Johnson and Christy had peaks at 521.5 nm, a difference of 3.5 nm. This difference is probably due to the limited accuracy with which the dielectric function of the bulk metal can be determined. Johnson and Christy claim that the values are only accurate to 3%, and the discrepancy is much smaller than this.<sup>36</sup> It has been shown previously that if the particles have a surface plasmon band at 520 nm initially, the shift in peak position with solvent refractive index is accurately predicted using the dielectric data of Johnson and Christy.<sup>33</sup> The main effect of the discrepancy is that the peak positions will be systematically observed to be at shorter wavelengths than predicted using Mie theory. For silica, a (dispersionless) dielectric constant was used, taken as the square of the refractive index (1.456),<sup>22</sup> whilst for ethanol the value at 589 nm of 1.362 was adopted, since experimental values were obtained at this wavelength and this value is close to the plasmon absorption band.

The influence of the silica layer on the optical properties of the suspension is shown in Figures 5 and 6 for thin and thick silica shells in water and ethanol, respectively. Initially, as the shell thickness is increased, there is an increase in the intensity of the plasmon absorption band, as well as a red shift in the position of the absorption maximum. This is due to the increase in the local refractive index around the particles. However, when the silica shell is sufficiently large, scattering becomes significant, resulting in a strong increase in the absorbance at shorter wavelengths. This effect promotes a blue shift



**Figure 6.** Influence of thick silica shells on the UV-visible spectra of ethanolic gold colloids. (a, top) experimental; (b, bottom) calculated.



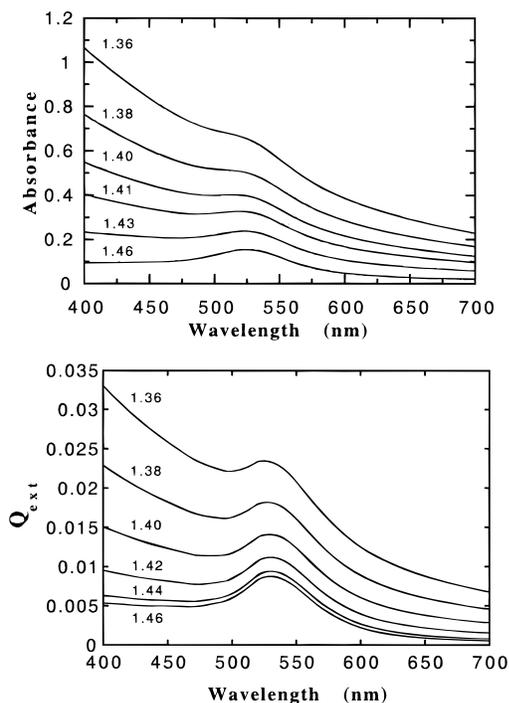
**Figure 7.** Variation in the position of the plasmon band of 15 nm gold particles with silica shell thickness ( $n = 1.456$ ): (solid circles) experimental data; (open circles) calculated positions.

of the surface plasmon band and a weakening in the apparent intensity of the plasmon band. Eventually at shell thicknesses above 80 nm, the scattering almost completely masks the surface plasmon band. The final colloid is very turbid and slightly pink in appearance. All these effects are accounted for by Mie's theory for core-shell particles described above, as shown in Figures 5b and 6b.

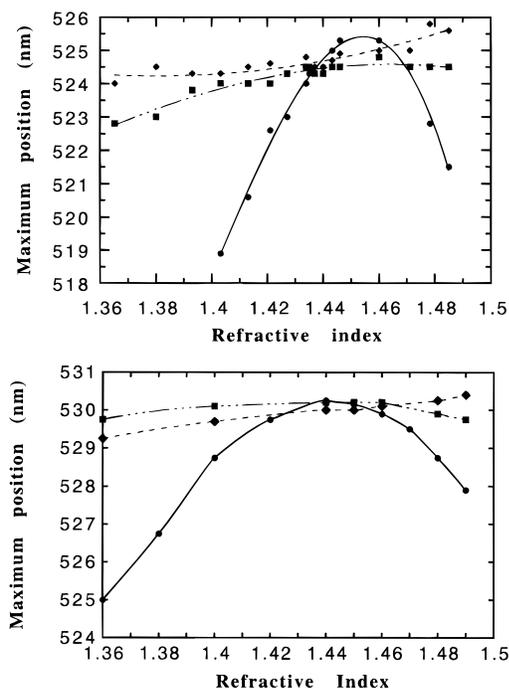
In Figure 7, the observed position of the maximum of the plasmon band is plotted vs shell thickness and compared to the calculated spectra. The same trends are present in the experimental and the calculated spectra, though the precise peak position is not the same. The larger scattering contribution observed experimentally is due partly to the presence of gold-free silica particles, which scatter but do not absorb.

Strong changes to the absorption spectra are also observed when the particles are coated with TPM and dispersed in ethanol/toluene mixtures of different concentrations. These mixtures cover a wide range of refractive indices (between 1.36 and 1.49), which allows optical index matching of the silica with the solvent. As the refractive index of the solvent approaches that of silica, the scattering decreases dramatically, and the gold

(36) (a) Kreibig, U. *J. Phys. (Paris)* **1977**, C2-97. (b) Kreibig, U. *J. Phys. F* **1974**, 4, 999.

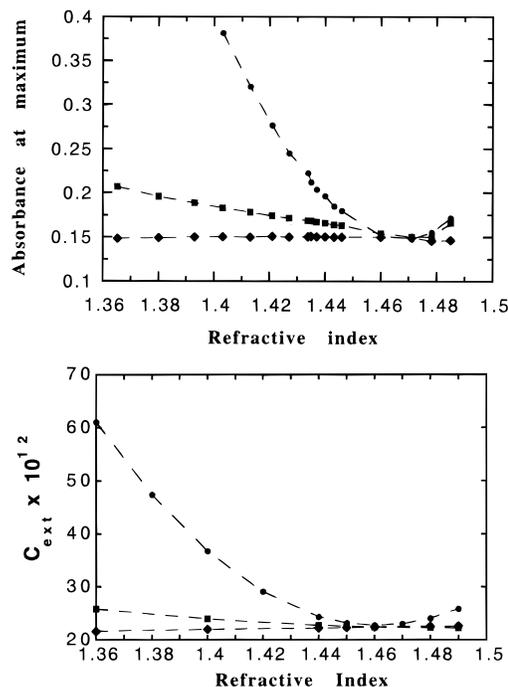


**Figure 8.** UV-visible spectra of dispersions of 15 nm gold particles with a silica shell 83 nm thick, in solvents with different refractive indices, as indicated. Both (a, top) experimentally and (b, bottom) theoretically, the gold plasmon band is recovered as the match point for silica is approached.



**Figure 9.** Variation of the plasmon band position with solvent refractive index for gold particles coated with thin (diamonds, 10 nm), intermediate (squares, 45 nm), and thick (circles, 83 nm) silica shells: (a, top) experimental; (b, bottom) calculated. Dielectric data for gold are taken from Johnson and Christy and corrected for a particle radius of 8 nm. For silica, a refractive index of  $n = 1.456$  was used.

plasmon band becomes more pronounced. Figure 8 shows both experimental and calculated spectra for dispersions of particles with an 83 nm thick silica shell in ethanol/toluene mixtures with selected refractive indices. Again the tendency is exactly the same in both cases. Conversely, when the silica layer is thin, scattering is not important



**Figure 10.** Variation of the peak intensity with solvent refractive index for gold particles coated with thin (diamonds, 10 nm), intermediate (squares, 45 nm), and thick (circles, 83 nm) silica shells: (a, top) experimental; (b, bottom) calculated.



**Figure 11.** Effect of solvent refractive index on the color of dispersions of 15 nm gold particles with a 60 nm silica shell. The solvent refractive indices (left to right) are 1.45, 1.42, 1.39, and 1.36.

enough to exert a large effect on the spectrum. In Figures 9 and 10, the peak position and the absorbance at the maximum, respectively, are compared for identical gold particles coated with thin (10 nm), intermediate (45 nm), and thick (83 nm) silica shells in solvents with different refractive indices. As expected, the effect is larger for particles with thicker shells, and the peak position at the match point (equal refractive index of silica and solvent) basically coincides in all three cases. The slow increase in peak position for the thin silica shell particles is due to the fact that the red shift due to the increase in solvent refractive index is larger than the blue shift due to scattering.<sup>33</sup> Predictions using Mie's theory are shown in the same figures. There is again a systematic error in the

predicted position of the peak, but the qualitative trend is exactly the same as for the measured values.

The striking effect of solvent refractive index on the color of the dispersions is illustrated more clearly in Figure 11 for 15 nm gold particles with a 60 nm silica shell. While the particle size and concentration are the same in every case, the dispersions change from cloudy to transparent as the solvent refractive index increases from 1.36 to 1.45, at which point the silica shell is almost perfectly index matched and only the gold cores are visible.

### Conclusions

The preparation of silica-coated gold particles can be achieved by a combination of standard procedures, provided that a gold-complexing, silane coupling agent is previously attached to the particle surface. The thickness of the silica shell can be varied from a few to several hundred nanometers, though special procedures must be utilized to completely avoid the formation of multiple-gold-core or gold-free silica particles.

The optical properties of the dispersions of silica-coated gold particles with varying shell thickness agree extremely well with the predictions of Mie theory. If furthermore the refractive index of silica is matched to that of the solvent, the particles interact with light in the same way as they would do without the silica layer.

Although the method is presented here in detail for gold colloids only, it is readily applied to other kinds of colloids which have typically been difficult to silica coat, such as silver, copper, and semiconductor particles. Specific synthetic routes for the preparation of coated nanosized semiconductors and other metals will be presented elsewhere. These coated particles are more reactive than silica-coated gold, and chemical reactions can be performed on them using the silica shell as a semipermeable stabilizer.<sup>37</sup> In addition, as is apparent from the micrographs in Figure 4, these layered insulator–metal nanocomposites may form 2D and 3D crystals. Diffraction and diffusion studies on these coated crystals are currently being undertaken.

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(37) Ung, T.; Liz-Marzan, L. M.; Giersig, M.; Mulvaney, P. In preparation.