

## Controlled synthesis and quantum-size effect in gold-coated nanoparticles

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(Received 18 January 1994)

We have observed enormous shifts of the optical-absorption peak during the reduction of gold-sulfide particles ( $\text{Au}_2\text{S}$ ) to gold particles. A two-step colloidal method is used for the nanoparticle synthesis. We can explain our findings by assuming the colloidal particles have a gold coating on the surface. This is also consistent with our transmission-electron-microscopy figures, displaying a core-shell structure, and electron-diffraction data. The optical-absorption peak initially shifts toward the red and at later times toward the blue wavelengths. By controlling the initial size of the gold-sulfide particles, the resonance shift is correlated with a theoretical model that includes both quantum confinement and the resonance effects (the so-called surface-plasmon resonance). The use of metal-coated particles with a nonmetallic core material offers two advantages for studying quantum confinement. First, the particles are initially large, and have a large polarizability and consequently a large absorption cross section, and second, the thin metal layer confines the electron in one dimension and can extend itself in the other two dimensions.

### INTRODUCTION

Materials growth techniques have advanced the capability of researchers to design specific electronic and optical properties. This has led to rapid improvements in devices and different effects have been discovered, e.g., the quantum Hall effect. The required length scale for control over these structures is on the order of nanometers. This has been called the mesoscopic scale in the literature because macroscopic properties are altered, but the basic description of the carriers still uses bulk system parameters with the addition of boundary and interaction effects from quantum confinement. So-called quantum dots,<sup>1</sup> which are structures with nanometer sizes in all dimensions, are developing into an important research subfield.

A new challenge for scientists is the synthesis of heterostructure quantum dots. One example of these particles is a semiconductor coated by another semiconductor material. In this section, several attempts have been made.<sup>3-5</sup> In this paper we report the synthesis by colloidal methods of gold-coated nanoparticles with a nonmetallic core, and the extraordinary optical-absorption spectra of the coated samples. The results are consistent with a theoretical approach that includes electromagnetic-resonance effects<sup>2</sup> and quantum confinement of the carriers in the thin gold-shell layer. Interest in metal-coated particles stems from the expectation of a large nonlinear optical response due to the surface-plasmon resonance.<sup>6,7</sup>

### PREPARATION

The particles were prepared by a two-step process. First, we dissolved chloroauric acid ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ) and sodium sulphide ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) into super pure water at

room temperature to get a  $\text{HAuCl}_4$  solution and a  $\text{Na}_2\text{S}$  solution. We mix controlled amounts of the two solutions together to get the unstable gold sulfide,  $\text{Au}_2\text{S}$ , particles. The color of the  $\text{Au}_2\text{S}$  solution is shallow brown. In the second step, we inject a little  $\text{Na}_2\text{S}$  solution into the  $\text{Au}_2\text{S}$  solution. The color changes from shallow brown to gray, shallow red, and dark red.

In the reaction, the gold atom in the Au-S bond on the surface of  $\text{Au}_2\text{S}$  was reduced by the  $\text{S}^{2-}$  ion<sup>8</sup> and the surface became gold coated. The gold-surface layer grows thicker and the  $\text{Au}_2\text{S}$  core becomes small with time until all the particles become Au particles. This process is supported by transmission electron microscopy (TEM) and electron diffraction. TEM images of sample A show small spherical particles, whose average diameters are about 4 or 5 nm, coexisting with large particles, whose diameters are about 25 nm. The average particle diameter is determined by the concentration of the solution and the time interval before the addition of more  $\text{Na}_2\text{S}$  solution in the second step. Figure 1 displays TEM images of a sample at two magnifications and an electron-diffraction pattern. Detailed resolution of the larger particles in Figs. 1(a) and 1(b) reveals a surface coating. The diffraction pattern is close to the Au(111) lattice spacing and does not fit the  $\text{Au}_2\text{S}$  lattice spacing. The electron-diffraction pattern of the particles after gold precipitation includes the pattern of gold mixed with that of  $\text{Au}_2\text{S}$ .<sup>9</sup> We find no coating on the small particles, which are pure gold because the sulfur has been rapidly removed in the second step of the reaction; the larger particles naturally possess a longer diffusion and reducing time.

### ABSORPTION EXPERIMENTS

Our absorption experiments followed the reaction as it proceeded. The spectra were taken about every two

minutes; the reaction time is slow and takes about 30 min to complete. A selected data set on three samples taken during the gold overcoat growth process is shown in Fig. 2. The modified surface-plasmon-resonance absorption of the coated particles is measured with different average initial particle sizes. As the reduction proceeds, the thickness of the shell layer increases, and the absorption intensity increases. The peak positions move to longer wavelengths in the initial-time regime and then to shorter wavelengths at longer times. The turning point of the

surface-plasmon peak depends on the particle size. The bigger the initial particle size, the longer the wavelength of the turning point. At later times, the peak returns toward that of pure gold particles. Sample A was synthesized by taking 10 mL of 2 mM  $\text{HAuCl}_4$  and mixing with 10 mL of 1-mM  $\text{Na}_2\text{S}$  solution for the first step. After a few minutes, the second reduction step is begun by mixing in 5 mL of the 1-mM  $\text{Na}_2\text{S}$  solution. Sample B uses the same amounts of the solution in the first step, but the waiting time before beginning the second step is

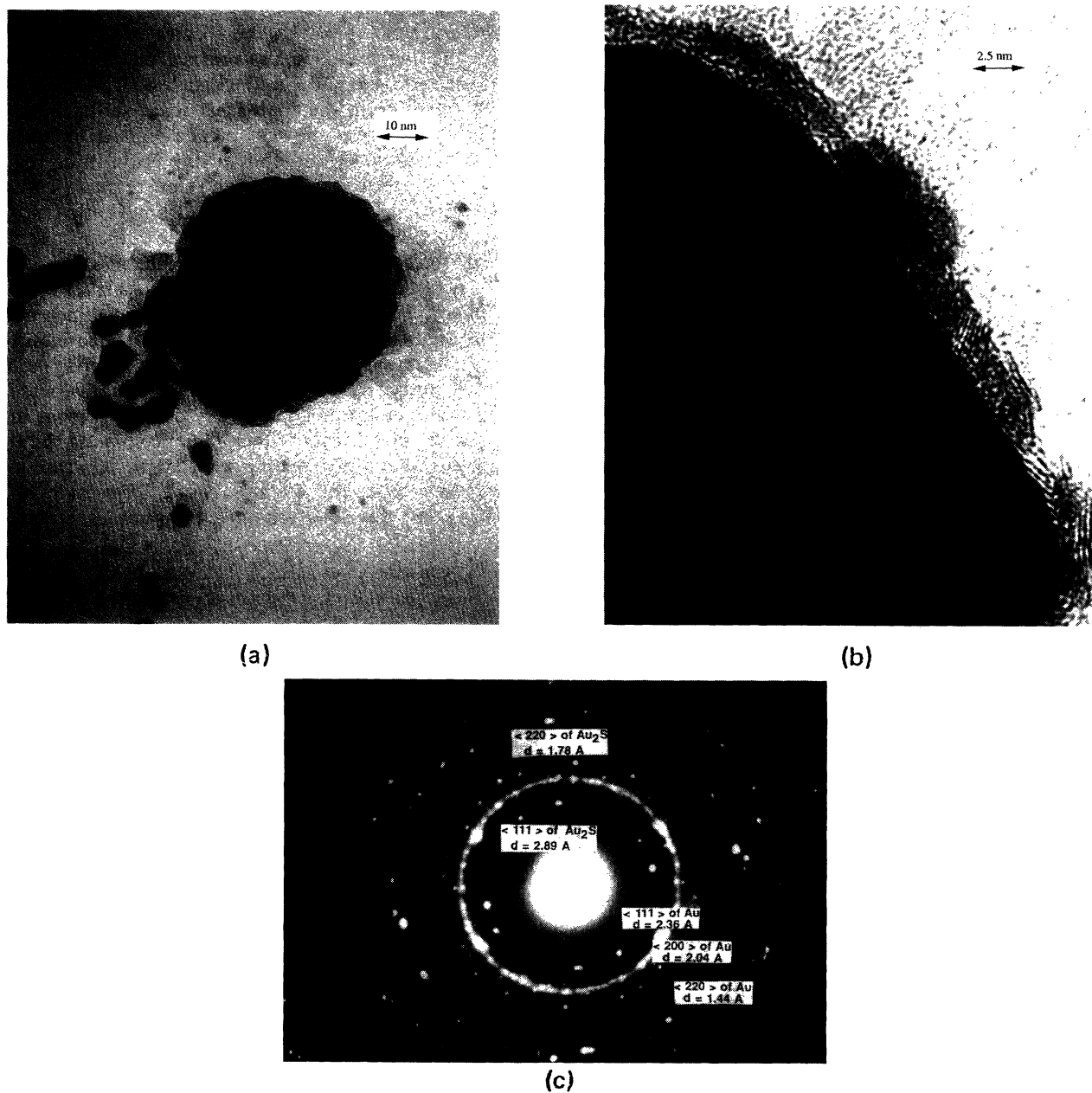


FIG. 1. TEM images display typical size and shape of the large particles. Two different magnifications of a 45-nm particle are used. (a) The large particle is coated and no coating is observed for the smaller particles. (b) A magnification of the large particle shows an electron-diffraction pattern from the surface layer, which yields a lattice spacing of 2.30 Å. This is consistent with the Au(111) lattice spacing of 2.355 Å;  $\text{Au}_2\text{S}$  does not have a corresponding lattice spacing close to these values. (c) The electron-diffraction pattern shows sharp Bragg reflections from the  $\text{Au}_2\text{S}$  single crystals and a powder pattern from the gold. This result further supports the interpretation that the larger particles have a  $\text{Au}_2\text{S}$  core and the smaller particles are pure gold.

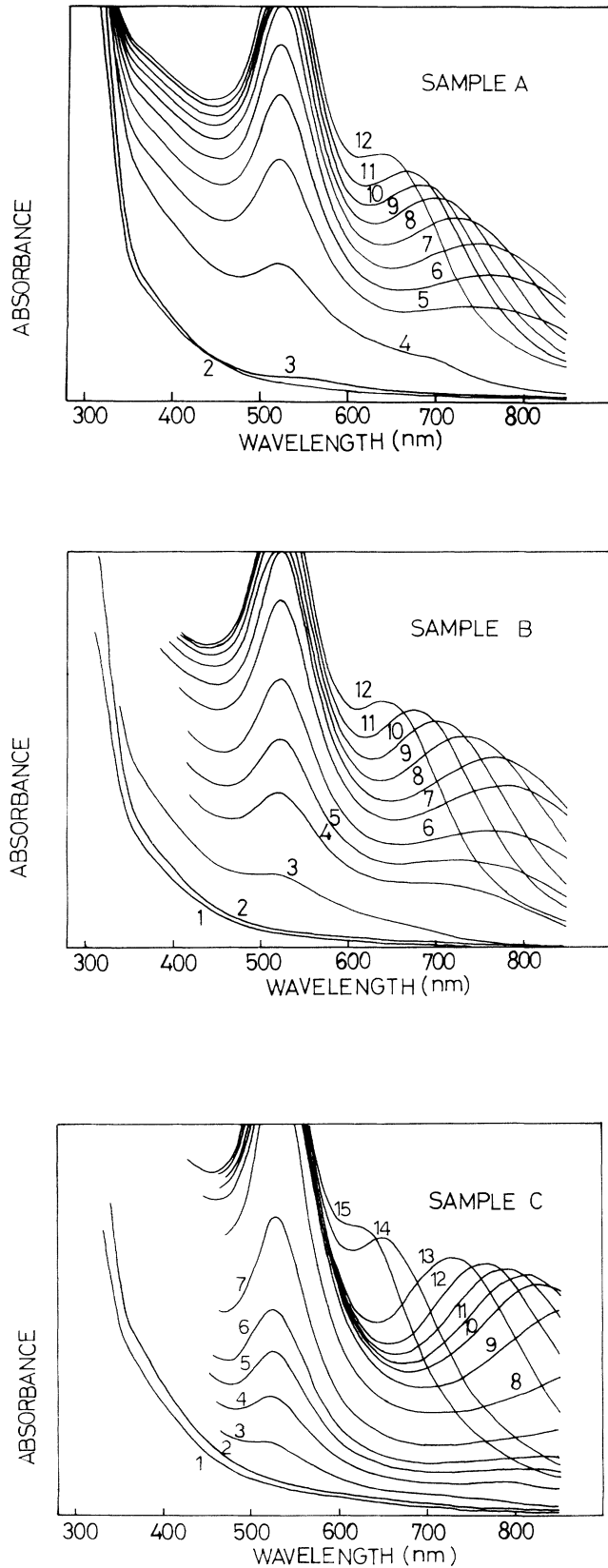


FIG. 2. The modified surface-plasmon-resonance absorption of the coated particles, which are measured during the gold overcoat growth process with different average initial particle sizes.

longer; this allows further growth of the  $\text{Au}_2\text{S}$  particles. The second reduction uses 3 mL of the 1-mM  $\text{Na}_2\text{S}$  solution. Sample C mixes 10 mL of 2-mM  $\text{HAuCl}_4$  with 12 mL of 1-mM  $\text{Na}_2\text{S}$ . After several minutes, the second step is begun by mixing 2 mL of the 1-mM  $\text{Na}_2\text{S}$  solution. In Fig. 2, curve 1 is the absorption of the  $\text{HAuCl}_4$  solution and curve 2 is from the  $\text{Au}_2\text{S}$  precipitated solution in the absorption spectra of samples A, B, and C; all the following sequences in the three sample were taken after the addition of the  $\text{Na}_2\text{S}$  solution again in the second step. They represent the characteristic absorption data for the gold-coated nanoparticles.

There are two peaks in the spectra of the three samples. The one at about 530 nm is from surface-plasmon resonance of the pure gold particles. The other one, which comes from the coated particles, shifts across the visible region and it shows two time regimes for all samples; the peak has a red shift in the initial time regime, and then a blue shift in the second time regime. The later time regime is described by the electromagnetic theory of coated nanoparticles, as discussed below; the resonance is shifted from the bulk particle resonance and depends on the ratio of the core and shell radii. The thicker the coating, then the closer the resonance is to that of homogeneous gold particles.<sup>7,10</sup> There is an unexpected feature in the initial time regime of the absorption spectra; namely, the shift initially is toward longer wavelengths, which is attributed to quantum confinement of the electrons in the thin surface metal layer. One difference among the three samples is the turning-point wavelength separating the first regime from the second regime. Variation of the turning-point wavelength among the samples is correlat-

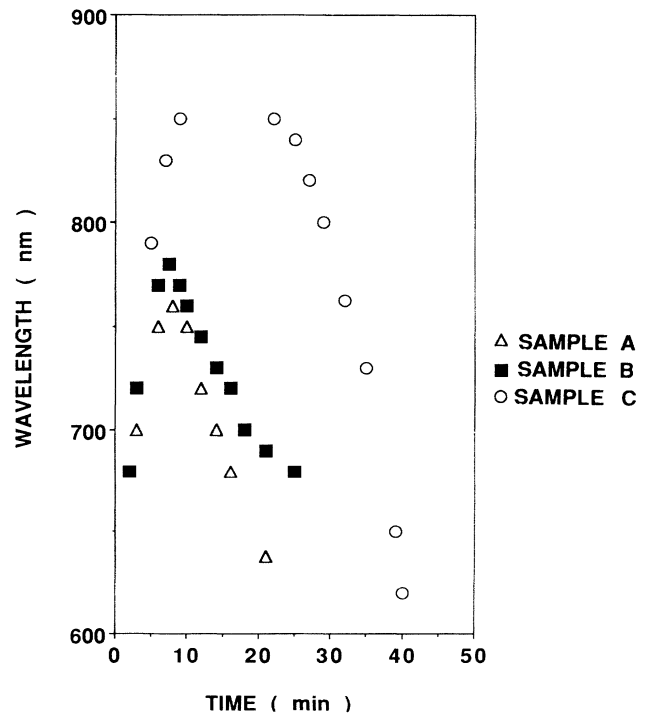


FIG. 3. The peak position of the surface-plasmon resonance vs reduction time.

ed with the different average particle size in each sample. The peak position of the absorption spectra of the three samples is plotted in Fig. 3, as a function of time.

### THEORETICAL MODEL

A model description of the optical-absorption results requires the dielectric function for the metal and the electromagnetic response of the coated particles. The latter function for coated nanoparticles can be analyzed within the Rayleigh regime, i.e., the coated particle's size is much smaller than an optical wavelength in the material.<sup>10</sup> The polarizability of coated particles dispersed in a host dielectric medium is given by<sup>10</sup>

$$p = \frac{(\epsilon_s - \epsilon_h)(\epsilon_c + 2\epsilon_s) + \Gamma(\epsilon_c - \epsilon_s)(\epsilon_h + 2\epsilon_s)}{(\epsilon_c + 2\epsilon_s)(2\epsilon_h + \epsilon_s) + 2\Gamma(\epsilon_s - \epsilon_h)(\epsilon_c - \epsilon_s)} a_s^3, \quad (1)$$

where

$$\Gamma = (a_c/a_s)^3. \quad (2)$$

The core, shell, and host dielectric constants are denoted by  $\epsilon_c$ ,  $\epsilon_s$ , and  $\epsilon_h$ , respectively; the radii of the core and shell are  $a_c$  and  $a_s$ , respectively. The core and host dielectric constants are real and the values  $\epsilon_c = 5$  (Au<sub>2</sub>S) and  $\epsilon_s = 1.78$  (water) are used. No dielectric data for Au<sub>2</sub>S was found, but its actual value is not critical to the analysis given here, using ten shift the maximum wavelength to about 10% longer wavelengths. Equation (1) is used in computing the absorption. The volume fraction is small (about  $10^{-5}$ ), so that the particles may be independently treated.<sup>10</sup>

Two models can be constructed to understand quantum confinement in coated particles. One model is a thin spherical shell, in which the energy spectrum is that of a particle in a one-dimensional box plus a transverse continue spectrum for the angular momentum. The other is a particle in a rectangular box with dimensions  $L$ ,  $L$ ,  $d$ , and  $d \ll L$ . Again, the spectrum is identical to the spherical-shell model. The particle is composed of six such boxes to cover the surface. The second type of model has been treated by Cini and Ascarelli for one rectangular box;<sup>13</sup> the lateral dimensions are treated as a continuum and the thin dimension is discretized.

Generally, the dielectric constant of the metal is described by the Drude model. While the Drude model works well in the infrared regime, it is not directly applicable to the visible regime. Moreover, when the shell layer is as thin as several monolayers of gold, there is the very strong quantum-confinement effect in the shell layer. To simplify the analysis, the quantum properties of the free electrons are modeled by a modified form of the Drude model,<sup>11</sup> in which individual electron resonances are replaced by an average resonant frequency  $\omega_0$ . The model reduces to Drude's model when  $d$  is large and, thus, it contains the collective plasmon properties in the macroscopic limit. On the other hand, the discrete individual-level structure is apparent in the model at the characteristic frequency of the transition. In the present case, though, an average over the energy-level structure must be made to account for the level statistics.<sup>11</sup>

$$\epsilon = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 + i\gamma\omega} + \epsilon_b. \quad (3)$$

To obtain an estimate of the effect of quantum confinement on the energy shift, we use the expression for the electron energy in the strong confinement regime<sup>11</sup>

$$\omega_0 = \frac{1.3V_F}{d}, \quad (4)$$

where  $V_F$  is the Fermi velocity, which for gold is  $V_F = 1.4 \times 10^6$  m/s and  $d$  is the thickness of the metal

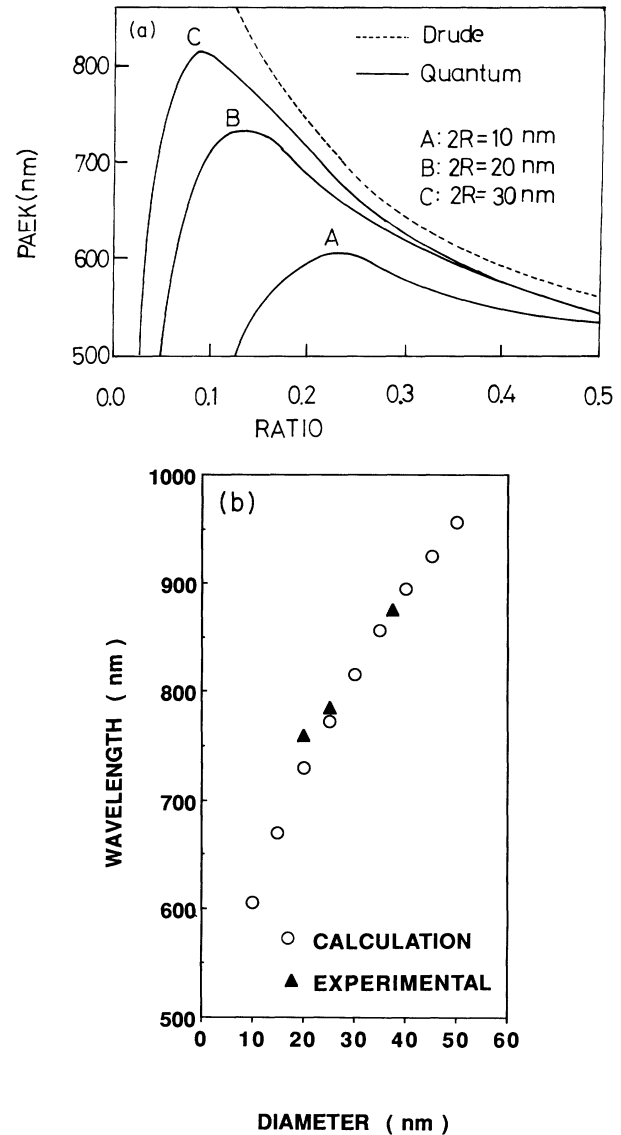


FIG. 4. (a) Peak position vs the shell-core ratio for different size nanoparticles calculated from the modified Drude model. The lines A, B, and C show the results from particles whose diameters are 10, 20, and 30 nm. The dashed line is computed with the Drude model, which assumes  $\omega_0 = 0$ . (b) The maximum wavelength of the surface-plasmon peak of samples A, B, and C (closed circles) vs the average particle radius. Sizes for samples A, B, and C were determined from TEM data. The open circles are the theoretical result.

shell. For the first few monolayers, it will have a significant effect on the dielectric constant through the visible regime. We find that the quantum behavior dominates when the layers are less than about six atomic layers. The width of the resonance is also strongly dependent on the width of the layer  $d$ . We use the expression,<sup>11</sup>

$$\gamma = \frac{V_F}{d} + \gamma_0, \quad (5)$$

with  $\gamma_0 = 4.1 \times 10^{13} \text{ s}^{-1}$ , the intrinsic width.<sup>12</sup> The values of the fixed parameters are  $\omega_p^2 = 1.9 \times 10^{32} \text{ s}^{-2}$  for the plasma frequency<sup>12</sup> and the contribution from the interband transition electrons<sup>11</sup> is taken as  $\epsilon_b = 9$ ; this value places the bulk surface-plasmon resonance near the observed value of 520 nm. The remaining parameters,  $\gamma$  and  $\omega_0^2$  depend on the layer thickness.

When the shell layer is thin enough, the resonance frequency  $\omega_0$  occurs in the visible regime. This strongly modifies the dielectric constant so that the absorption-resonance peak moves to longer wavelengths as the shell layer  $d$  becomes thicker. This is the reason that the first regime has a red shift. Also, since the polarizability depends on the particle volume [Eq. (1)], and the coated particles are large, they contribute a strong peak to the absorption spectrum. The model approaches Drude's model when  $d$  is large enough. In the Drude model regime, the thicker the coating, then the closer the resonance is to that of a homogeneous gold particle.<sup>10</sup>

The results of the theoretical analysis are displayed in Fig. 4. We have accounted for a 20% size dispersion of the initial particle sizes according to a log-normal distribution.<sup>11</sup> The quantum analysis includes the effect of the resonant frequency,  $\omega_0$ . Within this term, the frequency shift of the surface-plasmon resonance would be a mono-

tonic decreasing function as the shell is made thicker; this curve, which is the dashed one labeled Drude, is plotted in Fig. 4. The initial shift of the peak toward the infrared and then toward the ultraviolet compress well with the experimental data. The return position of the shift peak go longer wavelength when the size of the particles become large. The TEM image of sample B and C show that the average radius of sample B and C is about 12.5 and 17.5 nm, respectively.

## CONCLUSION

Similar two-step processes to synthesize metal-coated colloidal particles provide a unique method for extracting information on the quantum properties of metals. The particles are characterized by TEM and electron-diffraction data. The magnitude of the absorption-resonance shift is dependent on the size of the initial particle. Nonlinear response of the metal-coated particles are expected to exhibit a strong surface-plasmon-resonance enhancement;<sup>6,7</sup> such enhancements have been observed in the past with homogeneous metal particles.<sup>14</sup> These experiments could probe the quantum-level structure of thin goal coatings in the initial regime and provide further insight into the quantum properties of the coated particles.

## ACKNOWLEDGMENTS

Discussions with Professor E. Hanamura, Professor T. Arai, and Dr. D. Kundo are gratefully acknowledged and we thank Dr. E. Suzuki for the TEM analysis. J.W.H. acknowledges the kind hospitality and support of the Research Center for Advanced Science and Technology at University of Tokyo.

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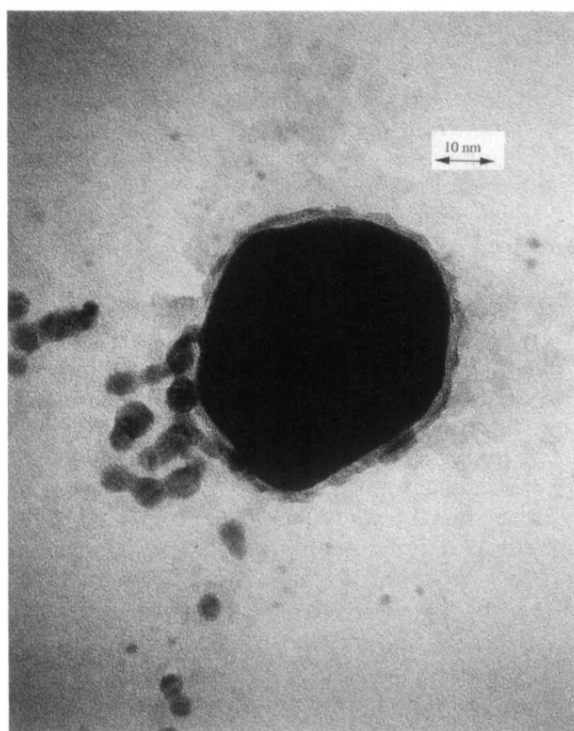
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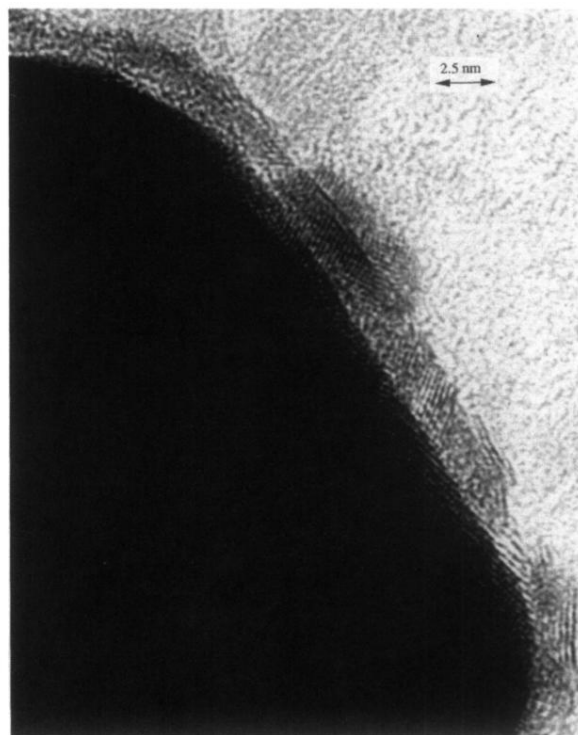
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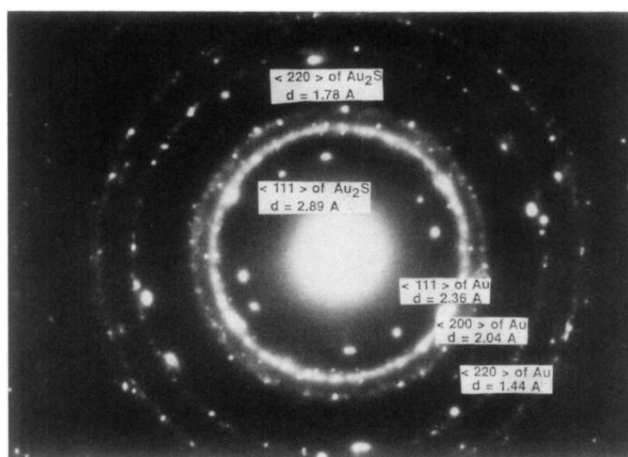
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(a)



(b)



(c)

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