Plasmon Resonance Shifts of Au-Coated Au_2S Nanoshells: Insight into Multicomponent Nanoparticle Growth

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In this Letter we present a coherent description of the optical properties of a unique type of nanoparticle, metal-coated dielectric nanoparticles. These structures occur naturally in the form of Au-coated Au_2S nanoparticles. During the course of nanoparticle growth, the plasmon-related absorption peak undergoes very large shifts in wavelength, from ~650 to ~900 nm. We show that this plasmon peak shift is purely classical in origin and is determined solely by the relative thickness of the Au shell and the Au_2S core diameter. This understanding of the optical properties of these nanoparticles is used to elucidate the nanoparticle growth kinetics. [S0031-9007(97)03286-9]

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Colloidal gold is, in many ways, the prototypical metallic nanoparticle. Its remarkable properties have been the subject of numerous investigations and applications since before the time of Faraday. In recent years, investigations of gold nanoparticles have increased due to their novel nanoscopic properties and device applications [1–4]. In this Letter, we describe the properties of Au-coated dielectric nanoparticles, or gold nanoshells. This configuration of a dielectric core coated with a metal nanoshell occurs naturally in the growth of Au/Au_2S nanoparticles. Gold nanoshells possess quite remarkable optical properties that differ dramatically from those of solid gold nanoparticles. During the course of nanoparticle growth, which takes place via reduction in solution, the plasmon absorption peak typically shifts from ~650 to ~900 nm or beyond, depending on reactant concentration. By comparison, the plasmon peak shifts observed in solid gold nanoparticles, via size variation or adsorption of molecular or dielectric species, are negligible (<10 nm) [5]. This unique redshifting of the nanoparticle plasmon resonance to wavelengths in the visible and near infrared regions of the spectrum, a wavelength region of extreme technological interest, may prove to be of tremendous importance for optical applications.

A previous study by Zhou *et al.* established the existence of the Au-coated Au_2S nanoparticles [6]. However, we conclude that various aspects of their analysis are contradictory to our results. Most importantly, Zhou *et al.* attribute the initial redshift of the Au-coated Au_2S nanoparticle absorption peak to quantum confinement in the thin Au nanoshell. Our calculations show that quantum confinement (or classically, surface electron scattering) does not result in a redshift of the absorption peak. We show that the reduced mean free path of conduction electrons in the Au shell does result in broadening of the plasmon peak, but this phenomenon does not shift the plasmon resonance. In short, our results show that the plasmon shift is classical in origin, and is determined by the dimensions and the dielectric properties of the Au_2S core and the Au shell. In addition, Zhou *et al.* state that at later times in the reaction S^{2-} diffuses through the gold shell and reduces the Au_2S core, resulting in an increase in the shell thickness with the core becoming smaller until the particles become pure gold. This kinetic scenario is unlikely for the following simple reason: S^{2-} does not exist in aqueous solution at any *p*H [7]. This improved understanding of the optical properties of Au nanoshells allows us to probe the growth kinetics of these nanoparticles, where our results indicate that the plasmon peak shift is consistent with a two-stage model of nanoparticle growth where first the Au_2S core, then the Au shell, grows linearly in time.

ACS reagent grade $HAuCl_4$ and Na_2S were obtained from Sigma. Either triply distilled or HPLC grade H_2O were used for making the aqueous solutions. The typical reaction was started by mixing 1 mM Na_2S in 2 mM $HAuCl_4$ with a 1.2:1 volume ratio.

Previous studies have demonstrated that S^{2-} is never a dominant aqueous species at any *p*H [7]. When Na_2S is mixed with water at *p*H 7, the S^{2-} reacts with the water to give HS^- and OH^-. Thus, the initial reactants are $AuCl_4^-$ and HS^-. This and simple electrochemical considerations lead us to propose the following reaction for the reduction process leading to the growth of Au-coated Au_2S nanoparticles:

$$2AuCl_4^- + 3HS^- \rightleftharpoons 2Au + 3S + 3H^+ + 8Cl^- . \quad (1)$$

Au and S are then available for subsequent nucleation and growth. Both Au and Au-coated Au_2S nanoparticles are grown simultaneously under these reaction conditions. Nanoparticle growth was monitored using a Hitachi U2000 spectrophotometer and the UV–visible spectrum was recorded from 400 to 1050 nm every few minutes. A sequence of UV–vis absorption spectra obtained during a typical reaction is shown in Fig. 1. There are two peaks in each spectrum due to the simultaneous formation

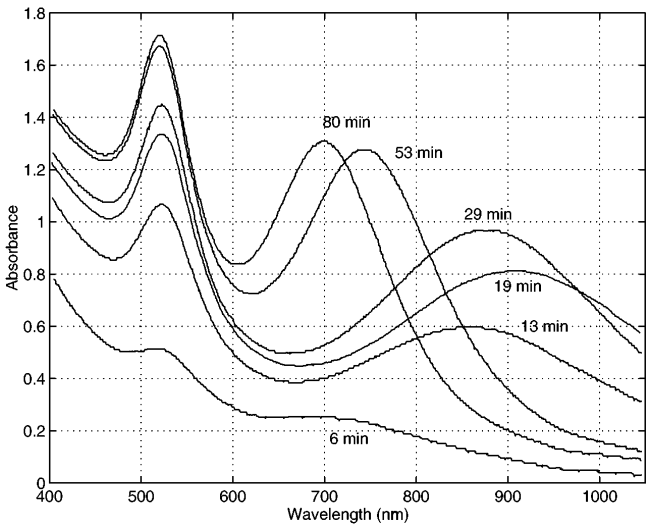

FIG. 1. Evolution of the UV–vis absorption spectrum as the nanoparticle growth proceeds. The peak at ~520 nm is due to the plasmon resonance of pure gold colloid. The second peak is due to the plasmon resonance of Au-coated Au_2S nanoparticles. Each spectrum is labeled by the corresponding reaction time.

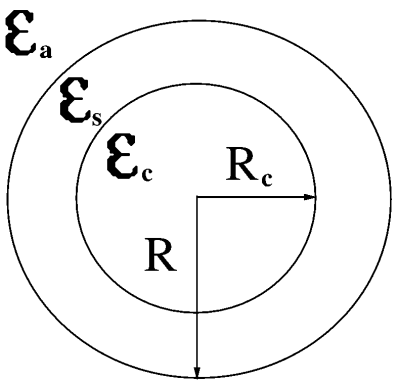

FIG. 2. Nanoshell geometry used in Mie scattering calculations. The Au_2S core has radius R_c and the total nanoparticle radius is R. Permittivities are given in text.

of solid Au nanoparticles and Au-coated Au_2S nanoparticles. The absorption peak which remains at ~520 nm throughout the reaction is due to the plasmon resonance of gold colloid. The second peak is due to Au-coated Au_2S nanoparticles as originally determined by Zhou *et al.* [6]. As the reaction proceeds, this peak first redshifts, and then at later times there is a dramatic blueshift. As the reaction progresses, the FWHM of the Au nanoshell peak narrows from 0.75 to 0.45 eV.

The size distribution of the Au-coated Au_2S nanoparticles was determined from transmission electron microscopy (TEM). A histogram was obtained using the NIH IMAGE program to measure the diameter of each particle [8]. The Au-coated Au_2S nanoparticles have an average diameter of 40 nm at the end of the reaction (with the reaction conditions as described above) and can be described by a Gaussian distribution. The standard deviation ranges from about 10% to 20% in different samples.

It is well established that the optical absorption spectra of alkali and noble metal nanoparticles consist of strong peaks that originate from plasmon excitations. Therefore, we would also expect the optical spectra of metal nanoshells to be plasmonic in origin. We employ a generalized Mie scattering approach [9,10] to calculate the absorption and scattering cross sections of metal nanoshells, using the specific geometry shown in Fig. 2. The core consists of a sphere of radius R_c with a dielectric constant $\varepsilon_c = 5.4$. The core dielectric constant was determined by using the calculated band gap for Au_2S [11] and the empirical expression $\varepsilon_c^2 E_g = 77$ where ε_c is the dielectric constant and E_g is the band gap [12]. Surrounding this core is a concentric shell for a total nanoparticle radius R, where values of the experimentally measured bulk permittivity $\varepsilon_s(\omega)$, modified as discussed below, were used [13]. The core-shell system is embedded in an aqueous medium of dielectric constant $\varepsilon_a = 1.78$.

For a complete description of the plasmon response of metal nanoshells, line broadening mechanisms must also be considered. Since the gold shells of these nanoparticles are thinner than the bulk electron mean free path in gold, a contribution to the dielectric function due to size-dependent electron scattering becomes important. The width of the absorption peak when size-dependent electron scattering becomes important can be described as a modification of the bulk collisional frequency [5],

$$\Gamma = \gamma_{\text{bulk}} + A \times V_F/a\,, \tag{2}$$

where γ_{bulk} is the bulk collisional frequency V_F is the Fermi velocity, and a is the reduced electron mean free path. For our nanoparticles, we take a equal to the shell thickness, $(R - R_c)$. A is a parameter which depends upon the geometry and theory used to derive this expression [14]. In the context of simple Drude theory and isotropic scattering, $A = 1$. The bulk dielectric function of the gold nanoshells is then modified as follows:

$$\varepsilon_s(a,\omega) = \varepsilon(\omega)_{\text{exp}} + \frac{\omega_p^2}{\omega^2 + i\omega\gamma_{\text{bulk}}} - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma}\,. \tag{3}$$

$\varepsilon_s(a,\omega)$ is the size-dependent dielectric function where $\varepsilon(\omega)_{\text{exp}}$ is the experimental dielectric function [13], and ω_p is the bulk plasmon frequency of gold. Additionally, in any colloidal precipitation process there is a distribution of nanoparticle sizes, leading to inhomogeneous broadening of the absorption spectrum. Although quite often a log-normal distribution describes the size population distribution [15], TEM statistics on Au-coated Au_2S nanoparticles indicate that they can be well described by a Gaussian size distribution with a standard deviation of 10%–20% for the total radius.

By including both size-dependent and inhomogeneous broadening in our Mie calculations, the plasmon peak width narrowing, in addition to the plasmon peak shifts, can be accounted for as nanoparticle growth proceeds. Figure 3 shows how the calculated plasmon peak compares in both peak location and width to the experimentally observed peaks, at six different times during the reaction. In these calculations, the specific values for the core radius R_c and total radius R are obtained via our growth model, as discussed below. For the gold shell, we use the size-dependent dielectric function [Eq. (3)]. The pure gold colloidal plasmon resonance is also included in this fit. For each spectrum, only the total particle radius R was adjusted within experimental uncertainties. A population size distribution of standard deviation $\sigma = 11\%$ in agreement with our experimentally obtained TEM statistics, was also included. Early in the growth reaction, the peak widths predicted by our model are slightly larger than those experimentally observed. This could be due to the fact that the size distribution is initially narrow and broadens as the reaction proceeds. In fact, if the broadening due to the population size distribution is neglected for the earliest reaction times (while still including size-dependent electron scattering), the agreement with experiment further improves. The pluses in Figs. 3(a) and 3(b) show the results of calculations where the size distribution of nanoparticles is neglected. In general, at all times during the reaction this theoretical approach yields excellent agreement with experiment.

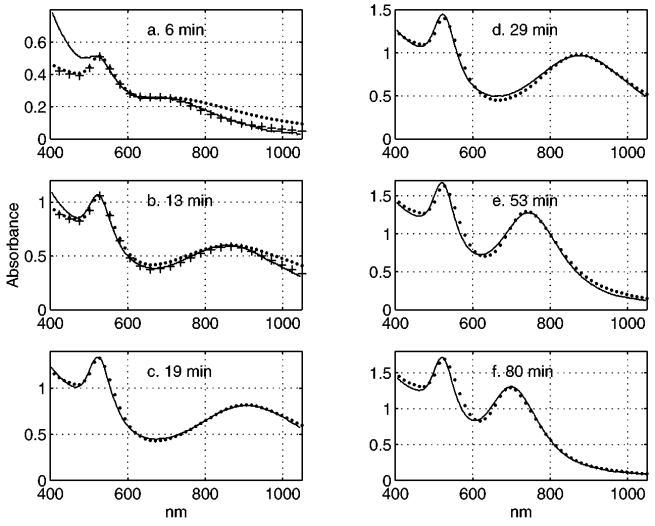

FIG. 3. (a)–(f) Comparison between Mie scattering calculations (dotted line), including the line broadening effects mentioned in text, and experimentally obtained UV–vis spectra (solid line) as nanoparticle growth proceeds. Calculations are obtained using a size distribution with standard deviation $\sigma = 11\%$. The + symbols in (a) and (b) are calculations performed with a standard deviation in the size distribution of $\sigma = 0\%$. (a) $R_c = 4.1$ nm, $R = 5.1$ nm. (b) $R_c = 8.6$ nm, $R = 9.9$ nm. (c) $R_c = 13.1$ nm, $R = 14.8$ nm. (d) $R_c = 15.1$ nm, $R = 17.3$ nm. (e) $R_c = 15.2$ nm, $R = 18.8$ nm. (f) $R_c = 15.2$ nm, $R = 19.3$ nm.

We have applied this quantitative understanding of the optical properties of metal nanoshells to gain insight into the growth kinetics of Au-coated Au_2S nanoshells. In general, the kinetics of colloid precipitation is quite complex and only specialized cases have been solved analytically. For example, for ideal diffusion limited growth the nanoparticle radius grows according to $(\text{time})^{1/2}$, whereas for surface-limited reactions, the particle radius follows a linear growth law [16,17]. During the initial ~20 min of Au-coated Au_2S nanoparticle growth, we assume that the core radius grows linearly in time. This model for Au_2S nanoparticle core growth is shown in Fig. 4(a). After ~20 min, and consistent with reactant depletion, the core growth stops, the core radius remains constant at ~15 nm, and the Au nanoshell increases in thickness. Comparison of plasmon shifts calculated for the nanoparticle geometry of Fig. 2 using this model for the core growth permits us to theoretically predict the Au nanoshell thickness as a function of time during nanoparticle growth. We also employ a constraint obtained from TEM analysis: the nanoparticle diameter must asymptotically approach the observed value of 40 nm. Figure 4(b) shows the calculated plasmon peak position vs time corresponding to the core radii of Fig. 4(a). The experimental plasmon peak location is also plotted in Fig. 4(b),

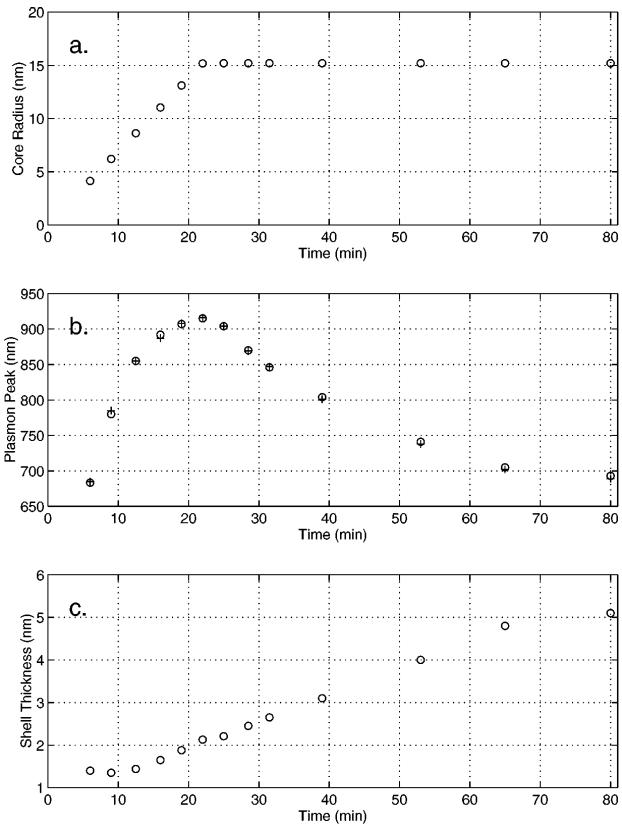

FIG. 4. (a) Postulated growth for the Au_2S core. (b) Calculated (∘) and experimental (+) plasmon peaks for the Au nanoshells as nanoparticle growth proceeds. (c) Calculated Au nanoshell thicknesses.

indicating that experimental observations and theoretical calculations agree for all times during nanoparticle growth. To obtain this agreement, only the relative shell thickness, $R - R_c$, is adjusted. The shell thickness obtained through this procedure is plotted in Fig. 4(c). Notice that the quantitative agreement between the experimental and theoretical plasmon shifts shown in Fig. 4(b) is consistent with a nanoparticle shell thickness that increases linearly with time. This result strongly reinforces a model of two-stage surface-limited growth, where first the core and then the nanoshell radius grow linearly with time.

In conclusion, we have explained the optical properties of Au-coated Au_2S nanoparticles, based on generalized Mie scattering calculations for the nanoshell geometry. The large plasmon peak shifts observed in this unique dielectric core-metal nanoshell system are classical in origin and dependent upon both the radius of the Au_2S nanoparticle core and the metal nanoshell thickness. Our results also show that the plasmon peak width is due to the reduced mean free path of the conduction electrons in the Au shell, as well as the size distribution of nanoparticles. The correlation between the optical properties and a linear growth model for the nanoparticle core permits us to invoke a two-stage linear growth scenario for both the core and the shell of this unique nanoparticle.

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