

Optical Resonances of Gold Nanoshells

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Metal nanoshells, consisting of a dielectric core with a metallic shell of nanometer thickness, are a new, composite nanoparticle whose optical resonance can be "designed in" in a controlled manner. By varying the relative dimensions of the core and shell, the optical resonance of these nanoparticles can be varied over hundreds of nanometers in wavelength, across the visible and into the infrared region of the spectrum. These nanoparticles can serve as constituents in a new class of materials that are capable of uniquely controlling radiation in the visible and infrared spectral regions. Our current research focuses on two types of nanoshells: naturally occurring gold-coated Au₂S nanoshells and gold-coated silica nanoparticles that are formed utilizing colloid reduction chemistry and self-assembly^{1, 2}.

Solid metallic nanoparticles are well known for their attractive optical properties: a strong optical resonance and an extremely large and fast nonlinear optical (NLO) polarizability associated with their plasmon frequency³. These optical properties are accounted for extremely well by classical electromagnetic theory (Mie scattering theory)⁴. Although the general Mie scattering solution for a spherical particle consisting of concentric layers has been known for decades⁵, it was only recently theoretically established that a configuration consisting of a nanometer-scale metallic shell covering a submicron dielectric core should result in a particle with a plasmon-derived optical resonance tunable over large regions of the electromagnetic spectrum⁶. Figure 1 shows calculations using Mie scattering theory for a series of gold nanoshells with a shell thickness of 2 nm and a core radius that increases from 2 to 15 nm in going from a) to c). In this case the plasmon peak is shifted from ~550 nm to greater than 900 nm.

In order to construct nanoshell particles that will have their plasmon resonance shifted beyond the near infrared, a shell thickness/particle radius ratio of 10^{-2} to 10^{-4} is required. To achieve good optical quality in this regime, a high degree of sphericity of the dielectric core particles, a monodisperse distribution of dielectric core particles upon which to grow the metal nanoshell, and isotropic metal nanoshell growth onto the core particles is required. The growth and study of micron-scale spherical particles in space has a long history, dating from the Apollo program. During missions Apollo 14 and 16, the effect of reduced gravity on the electrophoresis of polystyrene latex spheres was studied. Extensive research into the reduced gravity growth of latex spheres, directed by Vanderhoff et al., flew on early Space Shuttle missions STS-003, STS-004, STS-006, STS-007, and STS-011⁷. The conclusions of this project were that highly monodisperse spherical latex particles in the micron size range could be grown with a higher degree of sphericity than was achievable on earth. Since we are exploring a similar size regime for our composite particles, it is apparent that a microgravity environment will result in higher quality particle growth, reducing deleterious effects such as sedimentation during growth. This will yield a more monodisperse distribution of nanoshells,

which will in turn improve the optical quality by reducing inhomogeneous broadening of the plasmon resonance.

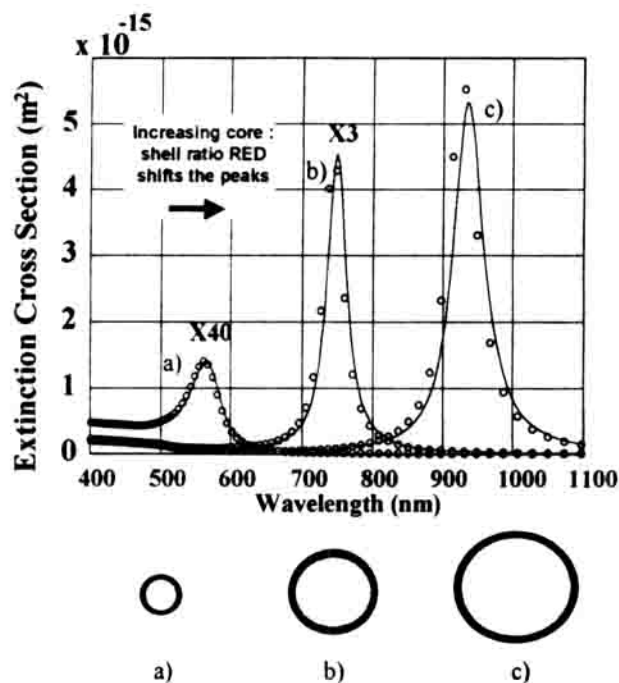


Figure 1: Mie scattering calculations of the plasmon resonance for metal nanoshells: (a) core radius = 2 nm, shell thickness = 2 nm; (b) core radius = 8 nm, shell thickness = 2 nm; (c) core radius = 15 nm, shell thickness = 2 nm.

Gold-Coated Au₂S Nanoshells

We have recently confirmed the original theoretical predictions of Mie scattering for the nanoshell geometry by studying the growth of gold sulfide (Au₂S) nanoparticles in a series of ground-based experiments. These nanoparticles, formed via reduction of AuCl₄⁻ with HS⁻ in water, are gold-terminated during growth, providing a naturally occurring metal nanoshell system. These nanoparticles typically manifest a large (200-300 nm) optical resonance red shift, followed by a sizeable blue shift, during particle growth. The solid lines in Figure 2 show a series of UV-vis spectra of the gold nanoshells during their growth. The peak at 520 nm is due to the simultaneous formation of solid gold nanoparticles. The shifting peak is associated with the gold nanoshells and the observed shifting is due to the changing core/shell ratio. The dashed lines are calculations using Mie scattering theory. At all times during the reaction, the calculations agree with experiment. This analysis has allowed us to show that these optical resonance shifts correspond to a two-stage growth model, where first the core and then the shell grow linearly as a function of time¹.

We have also studied the ultrafast electron dynamics of gold-coated Au₂S nanoshells embedded in poly-vinyl alcohol films via femtosecond pump-probe spectroscopy utilizing a cavity-dumped Ti:sapphire laser⁸. The induced change in the transmission of the gold nanoshell films studied has a lifetime of ~1.6 ps. Figure 3 (a) and (b) shows the UV-vis

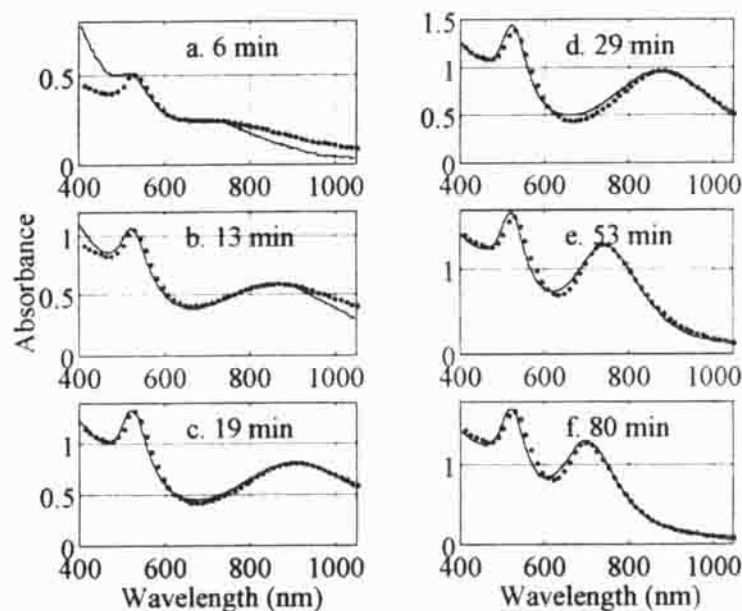


Figure 2: UV-vis spectra of Au-coated Au₂S nanoparticles at various stages of growth. Solid line: experimental data. Dotted line: theory. Radii: (a) core = 4.1 nm, shell = 1.0 nm; (b) core = 8.6 nm, shell = 1.3 nm; (c) core = 13.1 nm, shell = 1.7 nm; (d) core = 15.1 nm, shell = 2.2 nm, (e) core = 15.1 nm, shell = 3.4 nm; (f) core = 15.1 nm, shell = 4.1 nm.

and the corresponding transient induced changes in the transmission of this film. In tuning the laser from 780 nm to 840 nm, we observe a change from induced bleaching to induced absorption. Our analysis indicates that the origin of the measured signal is due to the creation of a hot electron distribution within the gold shell. The hot electrons return to equilibrium via energy-dissipative interactions with the nanoparticle core and the embedding medium.

Gold-Coated Silica Nanoparticles

In the gold-terminated Au₂S metal nanoshell system, the range over which the optical resonance is tunable (~ 600 to 1000 nm) is limited by the constraints of its complex growth chemistry. Thus, we have developed an approach to the construction of metal nanoshell particles that combines techniques of molecular self-assembly with the reduction chemistry of metal colloid synthesis. This approach is general and can potentially be adapted to a variety of core and shell materials allowing for the fabrication of nanoparticles whose plasmon resonance lies in the infrared. We have grown monodisperse silica nanoparticles via the Stober method as our cores⁹. Organosilane molecules (3-aminopropyltriethoxysilane) are then adsorbed onto these nanoparticles. These molecules bond to the surface of the silica nanoparticles, extending their amine groups outward as a new termination of the nanoparticle surface. After isolating the silane coated silica particles from residual reactants, a solution of very small gold colloid (1-2 nm in diameter) is added¹⁰. The solid gold nanoparticles bond covalently to the organosilane linkage molecules via the amine group. Subsequently, the gold-decorated silica nanoparticles are used as nucleation sites for the reduction of an aged mixture of chloroauric acid and potassium carbonate by a solution of sodium borohydride. This results

in an increasing coverage of gold on the nanoparticle surface.

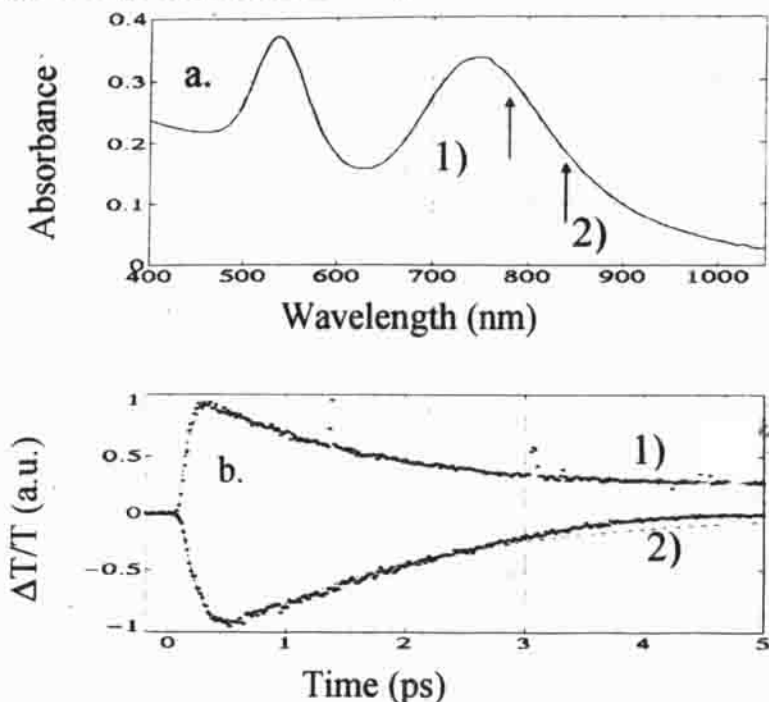


Figure 3: (a) UV-vis of gold nanoshell film. The labeled arrows correspond to the wavelength at which the time-resolved induced change in transmission was measured. (b) In tuning the Ti:sapphire laser from 780 nm to 840 nm the signal changes from induced bleaching to induced transmission.

In Figure 4(b-f), a sequence of transmission electron microscope (TEM) images of 120 nm diameter nanoparticles illustrates the progression in metal nanoshell growth that occurs during the reduction. Initially, the seed colloid adsorbates increase in size as reduction ensues (b,c). Then, the seed colloids begin to coalesce on the nanoparticle surface (d,e), until finally the apparent formation of a continuous metallic nanoshell (f) on the dielectric nanoparticle surface can be observed. Nanoshell growth is typically completed in a few seconds with a yield greater than 95 percent.

These dramatic changes in nanoshell structure give rise to a detailed optical signature of nanoshell formation and growth. This is shown in Figure 5, where (a) 120 nm and (b) 340 nm diameter silica spheres were used as the dielectric nanoparticle substrates. As the nanoshell growth progresses, these sequential UV-visible spectra increase in absorbance. In the initial stages of nanoshell growth, when gold is reduced exclusively onto the colloidal adsorbates, the spectrum is identical to that expected for gold colloid in solution. As the colloidal adsorbates grow, their plasmon peak becomes slightly red shifted. As the growing colloidal adsorbates begin to coalesce and form islands on the nanoparticle surface, this peak becomes distorted into a broad shoulder characteristic of particles with a distribution of aspect ratios, a lineshape similar to that previously observed in spectroscopic studies of gold platelets in solution¹¹.

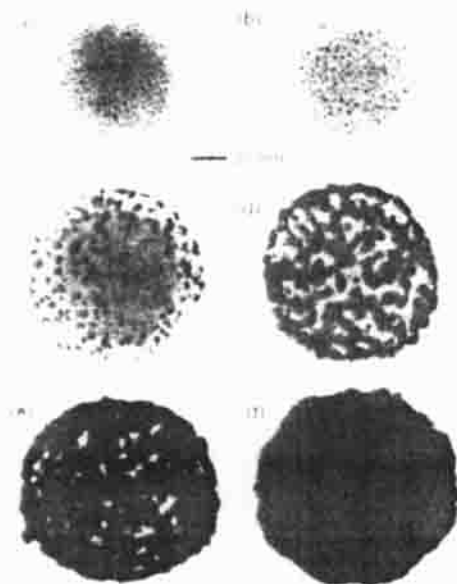


Figure 4. (a-f) TEM images of nanoshell growth on 120 nm diameter silica dielectric nanoparticle. (a) Initial gold colloid-decorated silica nanoparticle. (b)-(e) gradual growth and coalescence of gold colloid on silica nanoparticle surface (f) completed growth of metallic nanoshell.

A pronounced nanoshell resonance peak abruptly rises when the shell growth is “complete”. In Figure 5(a), the peak of the plasmon absorbance has shifted from 520 to over 800 nm while in Figure 5(b), a much greater shift is observed, leaving only the shoulder of the initial nanoshell peak observable for this core/shell ratio within our spectrophotometer range. At this stage, quantitative agreement between Mie scattering theory, the observed UV-visible absorption, and structural measurements obtained by TEM is achieved. A generalized version of Mie scattering theory incorporating the higher order multipoles of the scattering expansion is required here, since these slightly larger nanoparticles are no longer in the quasistatic limit. The higher order contributions give rise to the secondary peak to the left of the plasmon resonance in Figure 5(a) and the modulated peak in Figure 5(b). The relative positions and magnitudes of the secondary peaks with respect to the dipole resonance and the degree of absorbance versus scattering is a strong function of the overall particle size. Thus, in addition to core/shell ratio, the absolute size of the metal nanoshell provides additional control over the wavelength dependent optical response of the composite nanoparticles.

Future Directions

Current efforts in our laboratory focus on optimizing the present nanoshell growth process and extending and adapting this method to a broader range of core and shell materials. Within these studies, the limitations induced by terrestrial gravity regarding size and shape uniformity of nanoparticle cores and homogeneity of shell growth are being assessed. Several molecular functionalization strategies of these nanoparticles are being pursued, with the ultimate goal of condensing nanoshells into crystalline structures and well-ordered thin films.

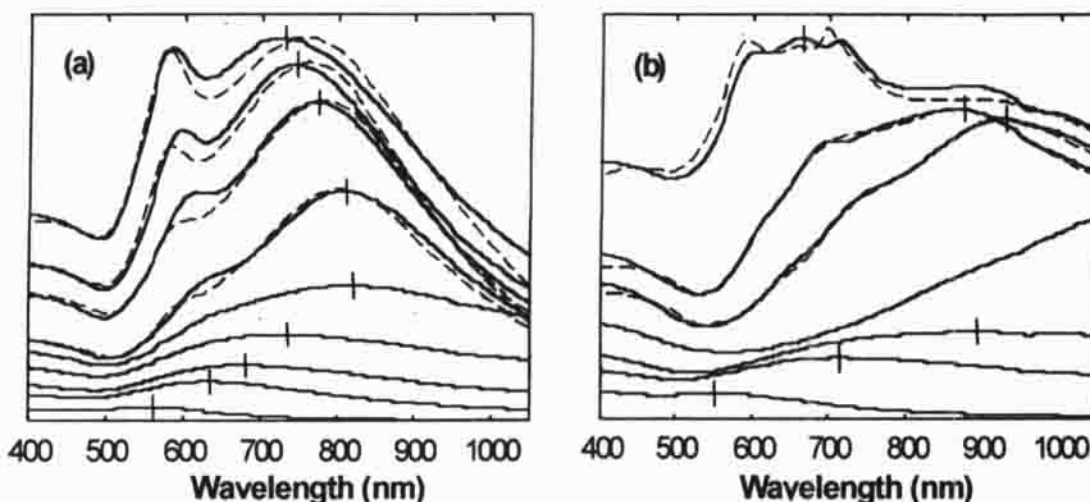


Figure 5 : (a) Growth of gold shell on 120 nm diameter silica nanoparticle. The lower spectral curves follow the evolution of the optical absorption as coalescence of the gold layer progresses. This is responsible for the initial red shift in the peak absorbance from 550 nm to 800 nm. Once the shell is complete, the peak absorbance is shifted to shorter wavelengths. Corresponding theoretical peaks are plotted with dotted lines. From right to left these spectra correspond to theoretical shell thicknesses of 14, 17, 24 and 30 nm. Experimental shell thicknesses determined by TEM are slightly larger at 20, 26, 29, 33 nm \pm 4 nm. This discrepancy is attributed to the \pm 4 nm surface roughness present on both the interior and exterior surfaces of the shell layer. The hash marks indicate the peak of each spectrum. (b) Growth of gold shell on 340 nm diameter silica nanoparticles. Here the peak shifts are much more pronounced with only the shoulder of the middle curve visible in our spectrophotometer range. The dotted lines from right to left, correspond to shell thicknesses of 17, 35, 48 nm. TEM determined shell thicknesses were 18, 39, 53 \pm 12 nm.

These crystallization and deposition studies will provide another experimental arena where terrestrial gravitational effects are expected to be sizeable and where a microgravity environment may provide the opportunity to produce crystalline structures not obtainable using a ground-based approach.

References

- 1 R. D. Averitt, D. Sarkar, N. J. Halas, *Phys. Rev. Lett.* **78**, 4217 (1997).
- 2 S. J. Oldenburg, R. D. Averitt, S. L. Westcott, N. J. Halas, *Chem. Phys. Lett.* **288**, 243 (1998).
- 3 F. Hache, D. Ricard, C. Flytzanis, *App. Phys. A* **47**, 347 (1988).
- 4 U. Kreibig, M. Vollmer, *Optical Properties of Metal Clusters* (Springer, New York, 1995).
- 5 A. L. Aden, M. Kerker, *J. App. Phys.* **22**, 1242 (1951).
- 6 A. E. Neeves, M. H. Birnboim, *J. Opt. Soc. Am. B* **6**, 787 (1989).
- 7 J. W. Vanderhoff, *et al.*, *J. Dispersion Sci. Tech.* **5**, 231 (1984).
- 8 R. D. Averitt, PhD thesis, Rice University, Houston, 1998.
- 9 W. Stober, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **26**, 62 (1968).
- 10 D. G. Duff, A. Baiker, *Langmuir* **9**, 2301 (1993).
- 11 J. Weisner, A. Wokaun, *Chem. Phys. Lett.* **157**, 569 (1989).