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.

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 frequency. These optical properties are accounted for extremely well by classical electromagnetic theory (Mie scattering theory). Although the general Mie scattering solution for a spherical particle consisting of concentric layers has been known for decades, 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 spectrum.

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. Historically, microgravity conditions have been used successfully to produce latex dielectric particles in the micron size range that were more highly monodisperse and more spherical than the highest quality particles produced 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.

We have recently confirmed the original theoretical predictions of Mie scattering from nanoshell geometry by studying the growth of gold sulfide (Au_2S) nanoparticles in a series of ground-based experiments. These nanoparticles are naturally 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 sizable blue shift, during particle growth. We have shown 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 time.

We have also studied the ultrafast electron dynamics of gold-coated Au_2S nanoshells embedded in poly-vinyl alcohol films via femtosecond pump-probe spectroscopy utilizing a cavity-dumped Ti:sapphire laser. The induced change in the transmission of the gold nanoshell films studied has a

lifetime of ~ 1.6 ps. 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 electron-dissipative interactions with the nanoparticle core and the embedding medium. In the gold-terminated Au_2S 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, in order to obtain control over the optical resonances of these types of nanoparticles, 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 dielectric cores. 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 added. The solid gold nanoparticles bond covalently to the organosilane linkage molecules via the amine group. A subsequent reduction of an aged mixture of chloroauric acid and potassium carbonate by a solution of sodium borohydride, where the gold-decorated silica nanoparticles are used as nucleation sites for the reduction, results in an increasing coverage of gold on the nanoparticle surface. The successful growth of the gold shell has been verified using UV-visible absorption spectroscopy and transmission electron microscopy.

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. Studies of the optical properties of these nanoshell particles are currently underway, where a variety of spectroscopic methods, including time-resolved methods, are being used to elucidate their interaction with incident fields and with embedding media. 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. These crystallization and deposition studies will provide another experimental arena where terrestrial gravitational effects are expected to be sizable and where a microgravity environment may provide the opportunity to produce crystalline structures not obtainable using a ground-based approach.