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Nanoengineering of optical resonances

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Abstract

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. We report a general approach to the making of metal nanoshell composite nanoparticles based on molecular self-assembly and colloid reduction chemistry. © 1998 Elsevier Science B.V. All rights reserved.

There is currently an intense interest in the creation of functional materials by judicious selection of their nanoscale constituents or their microscopic structure [1,2]. A particularly important goal is the customized design of a material's interaction with electromagnetic radiation. Quantum confinement effects in semiconductor nanoparticles [3] and bandgap engineered solids [4] have provided the ability to modify optical characteristics of certain materials over limited wavelength ranges. Recently, photonic bandgap structures [5] have been fabricated that demonstrate true designed-in optical properties in the microwave and millimeter wave regions of the spectrum [6].

By combining classical electromagnetic scattering theory with molecular self-assembly and colloidal growth chemistry, we have fabricated a new type of composite nanoparticle whose optical properties can be ''designed in'' in a highly predictive manner. These nanoparticles, which we call metal nanoshells, consist of a dielectric or semiconducting core coated with a nanometer scale metallic shell. These nanoparticles manifest a strong optical resonance that is dependent on the relative thickness of the nanoparticle core and its metallic shell. By varying the core and shell thicknesses, this optical resonance can be placed virtually anywhere across the visible or infrared regions of the optical 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 [7–9]. These optical properties are accounted for extremely well by classical electromagnetic theory (Mie scattering) [10,11]. Although the general Mie scattering solution for a spherical particle consisting of concentric layers has been known for decades [12], it was only recently theoretically established that a configuration consisting of a

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metallic shell and a dielectric core should result in a particle with a plasmon-derived optical resonance variable over large regions of the electromagnetic spectrum [13].

This sensitive dependence of the optical resonance frequency on the structure of metal nanoshells is illustrated in Fig. 1. Fig. 1a shows the theoretical optical resonances for gold nanoshells with a 120 nm diameter silica core. In this example, as the core radius-shell thickness ratio is varied between 3 and 12, the predicted resonances of the nanoparticles span a range of 300 nm in wavelength. If the order of these layers were inverted, that is, a metallic core and a dielectric shell, less than a 20 nm optical resonance shift would be expected. In Fig. 1b, the optical resonance as a function of core-shell ratio is calculated for the same silica-gold nanoshell system in the quasi-static limit. These calculations, using the experimental dielectric function for gold [14], agree well with predictions based on a simple Drude model

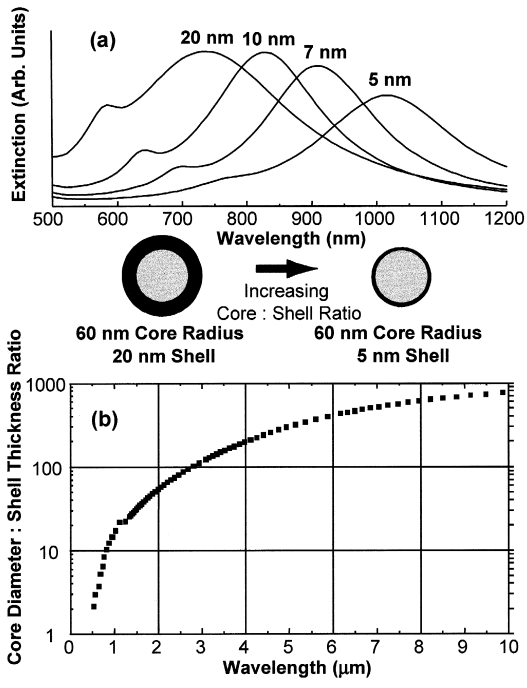

Fig. 1. (a) Theoretically calculated optical resonances of metal nanoshells (silica core, gold shell) over a range of core radius/shell thickness ratios. (b) Calculation of optical resonance wavelength versus core radius/shell thickness ratio for metal nanoshells (silica core, gold shell).

for the metal permittivity, indicating that this effect should be valid for other metals such as silver and copper. These theoretical studies indicate that silica-gold nanoshells with core-shell ratios of 10^2–10^3 could have optical resonances shifted into the infrared spectral range, as far as 10 microns in wavelength, spanning regions of the IR where wavelength-specific optical materials are either rare or entirely unavailable.

We have recently confirmed these theoretical predictions by studying the growth of gold sulfide (Au_2S) nanoparticles. These nanoparticles are gold-terminated during growth, providing a naturally occurring metal nanoshell system [15]. These nanoparticles typically manifest a large (200–300 nm) optical resonance red shift, followed by a sizeable 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. In the gold terminated-gold sulfide metal nanoshell system, the range over which the optical resonance varies is limited by the constraints of its complex growth chemistry.

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. We have grown monodisperse silica nanoparticles via the Stöber method as our dielectric cores [16]. 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 [17]. The gold particles bond covalently to the organosilane linkage molecules via the amine group [18]. In close agreement with the attachment of gold colloid on planar silica surfaces, we observe gold colloid coverage on our silica nanoshell surfaces of approximately thirty percent, most likely limited by interparticle Coulomb repulsion [19]. A transmission

electron micrograph of a 120 nm diameter silica colloid decorated with ~2000 gold nanoparticles is shown in Fig. 2a. 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.

In Fig. 2b–2f, a sequence of TEM images of 120 nm diameter nanoparticles illustrates the progression in metal nanoshell growth that occurs during the reduction. Initially, the seed colloid absorbates 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

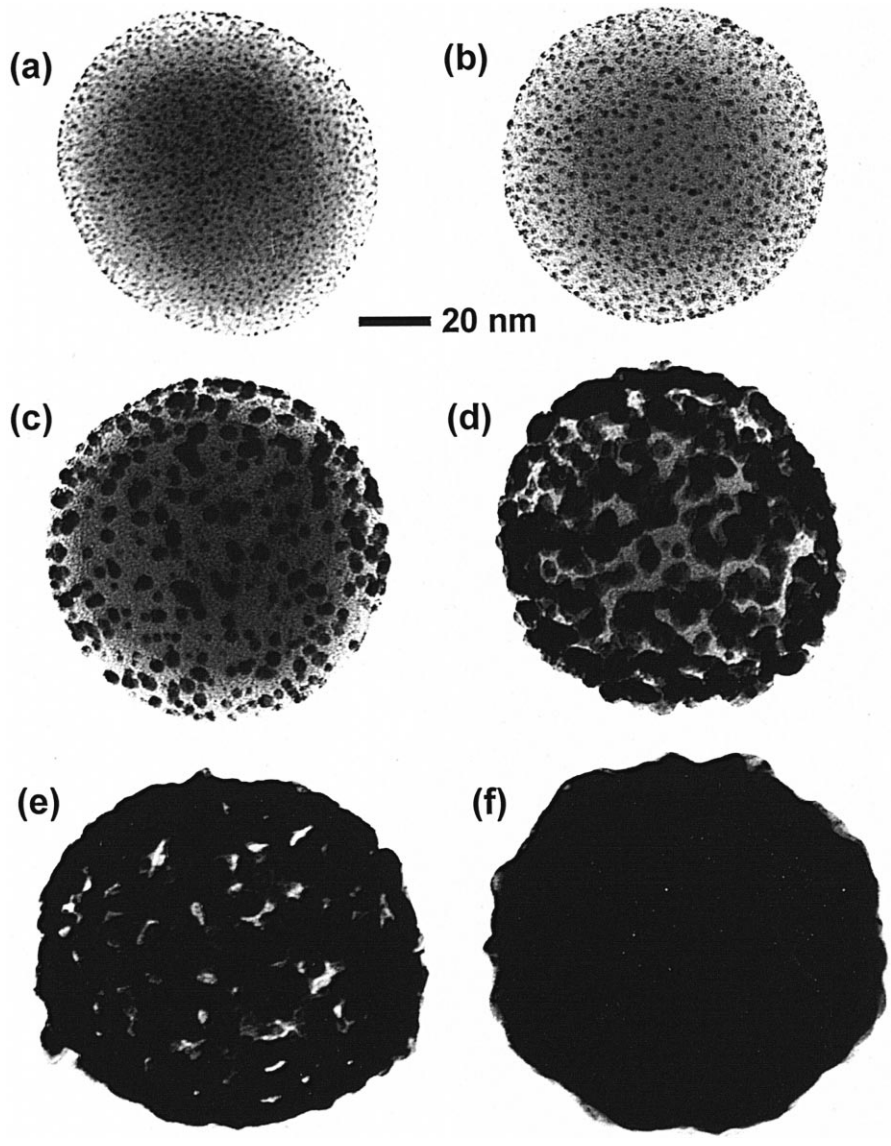

Fig. 2. (a)–(f) TEM images of nanoshell growth on 120 nm diameter silica dielectric nanoparticle. (a) Initial gold colloid-decorated silica nanoparticle. (b)–(e) Gradual growth and coalescence of gold colloid on silica nanoparticle surface. (f) Completed growth of metallic nanoshell.

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 Fig. 3, 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, with a well-defined plasmon peak at 520 nm. As the colloidal adsorbates grow, their plasmon peak becomes slightly red shifted [20]. 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 ratios [21], a lineshape similar to that previously observed in spectroscopic studies of gold platelets in solution [22]. A pronounced nanoshell resonance peak abruptly rises when the shell growth is ''complete''. In Fig. 3a, the peak of the plasmon absorbance has shifted from 520 to over 800 nm while in Fig. 3b, 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 [23]. The higher order contributions give rise to the secondary peak to the left of the plasmon resonance in Fig. 3a and the modulated peak in Fig. 3b. 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.

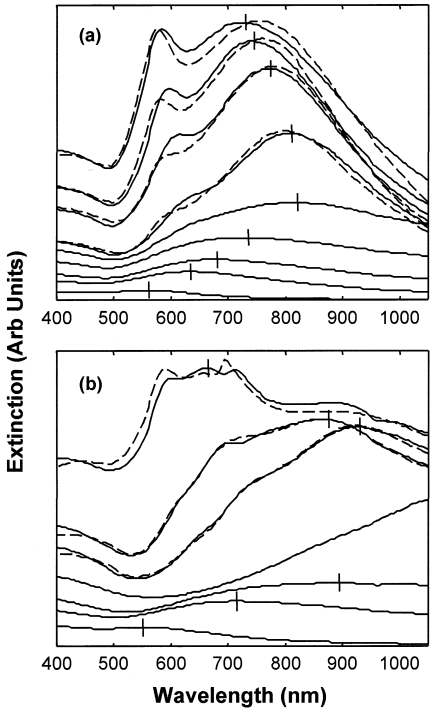

Fig. 3. (a) Growth of gold shell on 120 nm diameter silica nanoparticle. The lower spectral curves follow the evolution of the optical absorption as coalescence of the gold layer progresses. This is responsible for the initial red shift in the peak absorbance from 550 nm to 800 nm. Once the shell is 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 $\sim$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.

In conclusion, we have developed a method for synthesizing a new, frequency-agile nanoparticle whose optical resonance is highly dependent on the dimensions of its dielectric core and its metallic shell. The synthesis of such particles and their incorporation into various supporting media should give rise to materials with unique optical functionalities, and will permit the detailed design of optical proper-

ties across wavelength regions of the electromagnetic spectrum where few appropriate materials may exist.

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