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Spherical ensembles of gold nanoparticles on silica: electrostatic and size effects

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Core–shell ensembles of citrate-stabilized gold nanoparticles (20–80 nm) on submicron silica cores (330–550 nm) have been prepared by electrostatic self-assembly with shell packing densities as high as $\phi = 0.55$.

Gold and silver nanoparticles are well known to produce strong optical responses (plasmons) by the excitation of free electrons at the metal surface.[1] The plasmonic behavior of individual metal nanoparticles have been extensively studied both experimentally and theoretically, but their collective behavior is less well understood and is presently a subject of great academic and practical interest.[2] Colloidal metal particles with midnanometer (20–100 nm) dimensions have a special appeal because of their intense plasmon responses and large scattering cross sections,[3] so their ensemble properties merit particular attention. Our earlier studies have shown that extended planar assemblies of close-packed, midnanometer-sized gold particles produce strong optical responses at visible and near-infrared wavelengths, which vary as a function of unit particle size and periodic spacing.[4] Here we report a method for assembling 20–80 nm colloidal gold particles into densely packed core–shell ensembles around submicron-sized (330–550 nm) silica spheres (see Fig. 1). The optical properties of such spherical ensembles may be tuned for use as optical contrast agents[5] or as probes capable of surface-enhanced Raman scattering (SERS),[6] as demonstrated in seminal studies on continuous gold nanoshells by Halas and coworkers.[7]

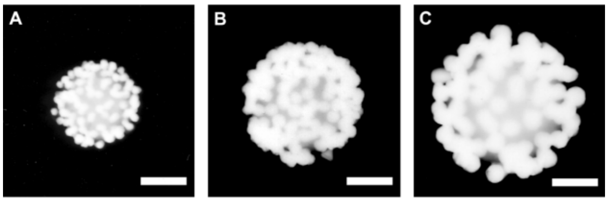

Fig. 1 TEM images (Philips EM-400, 100 kV) of spherical Au nanoparticle ensembles on silica. Au/SiO_2 diameters are (in nm): (A) 40/330, (B) 60/460, (C) 80/550. Scale bar = 200 nm.

Numerous examples of small (< 10 nm) metal nanoparticles assembled on oxide[8] or polymer[9] microspheres have been reported. Nearly all of these are formed with low or nonuniform particle densities in the shell layer, with the notable exception of Caruso and coworkers who used silica-coated gold nanoparticles to enhance their shell packing density on functionalized polystyrene microspheres.[10] Shell density can be affected by the strength of attraction between the core and shell particles, and also by the balance of attractive and repulsive forces between particles in the shell layer. These factors are in turn dependent on extrinsic parameters such as particle size and electrostatic charge. We reasoned that shell layers comprised of midnanometer-sized gold particles could be achieved with relatively high densities because of their strong van der Waals self-attraction, which can be expected to offset electrostatic repulsion at close range. The packing density could then be further adjusted by modulating the surface potential on the core and shell particles.

Silica particles were synthesized by the Stöber method[11] and functionalized with *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPTMS) or treated with polyethylenimine (PEI, $M_{av} = 750000$), then rinsed by several cycles of centrifugation and redispersion and diluted to concentrations on the order of 10^9 particles mL^{-1}. Aqueous suspensions of citrate-stabilized gold nanoparticles were either purchased (Ted Pella) or prepared by the method developed by Frens[12] and combined with silica at reflux temperatures, with the amount of gold particles in slight excess of that estimated for full monolayer coverage of the silica core.[13] The residual concentration of citrate in the colloidal gold dispersions was determined to be less than 0.2 mM based on the amount of sodium citrate used in the gold colloid preparation. Nonadsorbed gold particles were always observed after core–shell self-assembly, indicating that the silica particles were the limiting reagent. The resulting core–shell nanoparticle ensembles were then precipitated, rinsed, and redispersed several times to remove nonadsorbed nanoparticles. Transmission electron microscopy (TEM) images of the spherical nanoparticle ensembles were used to obtain approximate packing densities of the shell layer, which were calculated simply as $\phi = n\Omega/2\pi$ where n is the observable number of gold nanoparticles in a hemispherical ensemble and is the solid angle occupied per nanoparticle on the silica core.[14]

Surface potential was determined to be a critical factor for high packing density in the nanoparticle shell layer. Silica particles functionalized with AEAPTMS were much less effective at forming core–shell ensembles than PEI, whose high amine content allowed both greater and more uniform gold particle coverage. The shell density could be further increased by enhancing the negative surface potential of the gold particles. This was accomplished by raising the concentration of citrate ions in gold particle dispersions by 0.5–1.0 mM prior to introducing silica (see Fig. 2).[15] The effect of added sodium citrate increased shell densities up to $\phi = 0.55$ (see Fig. 3). Shell densities were calculated for several gold and silica particle size combinations, and were found to have little correlation with the core–shell diameter ratio for the size ranges examined. Removing citrate by exposing the gold particles to a mixed ion-exchange resin (Amberlite MB-3) resulted in no core–shell self-assembly. On the other hand, adding monovalent salts such as NaCl or adjusting the pH between 5 and 8 did not produce a significant change in shell density, indicating that the self-assembly process was not highly sensitive to mere changes in ionic strength or acidity. The remarkable effect of adsorbed citrate on shell density is somewhat counterintuitive, as the electrostatic repulsion between gold particles is also increased.[16] Nevertheless, this appears to be offset by the

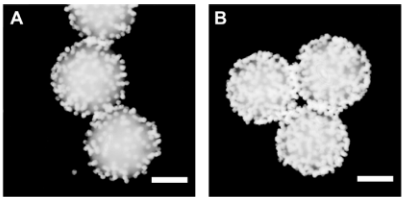

Fig. 2 TEM images (Philips EM-400, 100 kV) of 30-nm Au particles self-assembled onto PEI-functionalized 390-nm silica cores: (A) adsorption without added citrate, (B) adsorption with 0.5 mM added sodium citrate. Scale bar = 200 nm.

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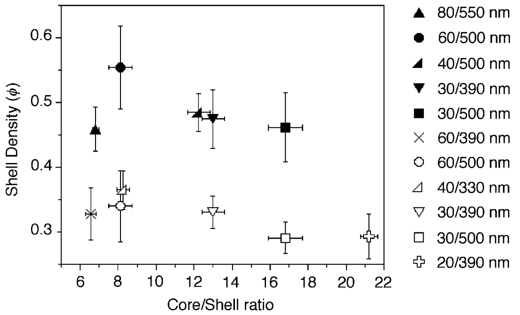

Fig. 3 Estimated packing densities of Au nanoparticle shell layer around SiO_2 core. Filled and open symbols correspond to ensembles formed with and without added citrate, respectively. Shell densities were obtained as an average of four ensembles for each core/shell size ratio: *x*- and *y*-error bars represent one standard deviation in core size and packing density, respectively.

nanoparticles' greater attraction to the postively charged PEI layer adsorbed on the silica surface.

Higher shell densities should strengthen the electromagnetic coupling between nanoparticles within core–shell ensembles, with a subsequent shift in their collective plasmon response.[4,17] Core–shell assemblies formed without added citrate displayed extinction spectra only slightly red-shifted from that of free gold nanoparticles, whereas those formed in the presence of added citrate exhibited bimodal extinction maxima, generated presumably by individual and collective plasmon responses (see Fig. 4(A)). Gold particle shell layers of 40 nm or more produced significant extinction in the near-infrared region, although less pronounced than that observed for planar arrays of close-packed nanoparticles (see Fig. 4(B)).[4] At the present time, it is unclear whether the optical responses are due solely to classic exchange interactions between nanoparticles, or if the size of the spherical ensemble also has an important effect.

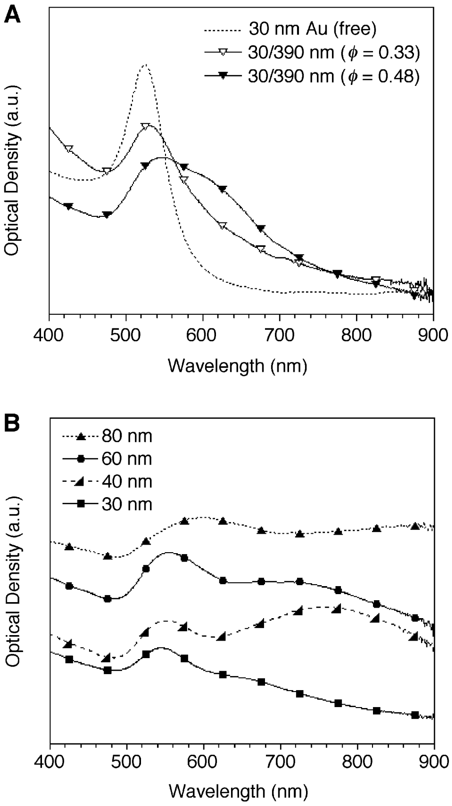

Fig. 4 (A) Extinction spectra of 30/390 nm Au/SiO_2 ensembles formed with no added citrate (ϕ = 0.33) and with 0.5 mM added citrate (ϕ = 0.48). (B) Extinction spectra of Au/SiO_2 ensembles with high shell densities (ϕ > 0.45) as a function of shell thickness (d_{SiO_2} = 500 nm).

In summary, the shell densities and subsequent optical responses of the spherical gold nanoparticle ensembles can be tuned for a wide range of core–shell size ratios by simple adjustment of electrolyte concentrations. Optical and Raman scattering studies are in progress and will be reported in due course.

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