Self-Organization of Large Gold Nanoparticle Arrays

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The synthesis of nanostructured materials with tunable properties is central to developments in nanoscale science and technology. Nonlithographic approaches based on thermodynamically driven self-organization processes are especially appealing because of their potential for low overhead in large-scale production. The spontaneous organization of monolayer-protected metal nanoparticles into periodic two-dimensional (2D) arrays is archetypal of this approach, with many of these arrays demonstrating novel optical or electronic properties as a function of particle size or interparticle spacing.[1] Hydrophobic surfactants such as alkanethiols are often used to drive the nanoparticles toward self-organization at the aqueous interface; however, 2D array formation by this methodology has so far been successful only for small (<10 nm) metal particles.[2,3] Stabilized metal particles beyond this size threshold become increasingly prone to multilayer or three-dimensional aggregate formation, which can be attributed to the rapid increase in van der Waals attraction and the loss of surfactant chain mobility on the planar facets of the nanoparticles as a function of size.[4]

In this communication we describe conditions that enable large (16−170 nm) gold particles to self-organize at the air−water interface into monoparticulate films, which can subsequently be transferred onto substrates as 2D hexagonal close-packed (hcp) arrays. The choice of surfactant is crucial in the stabilization of these nanoparticle ensembles: the surfactant layer is required to be highly repulsive at close range but thin enough to maintain minimal interparticle separations, a critical parameter in the electromagnetic properties of metal nanoparticle assemblies.[1,5] Short-range repulsion can be enhanced by creating a surfactant layer with hydrophobic chains at intermediate packing densities[6] and an appreciable surface charge density for electrostatic double-layer repulsion.[7] These features also render the encapsulated nanoparticles amphiphilic and promote self-organization at the air−water interface. We recently demonstrated that calix[4]-resorcinarenes are excellent surfactants for steric stabilization, and we have used them to maintain dispersions of gold nanoparticles up to 20 nm in hydrocarbon solutions.[8] We now report that resorcinarene tetrathiol **1** is ideal for promoting the formation of 2D gold nanoparticle arrays with periodicities up to 170 nm, a length scale comparable to the resolution limits of conventional photolithography.

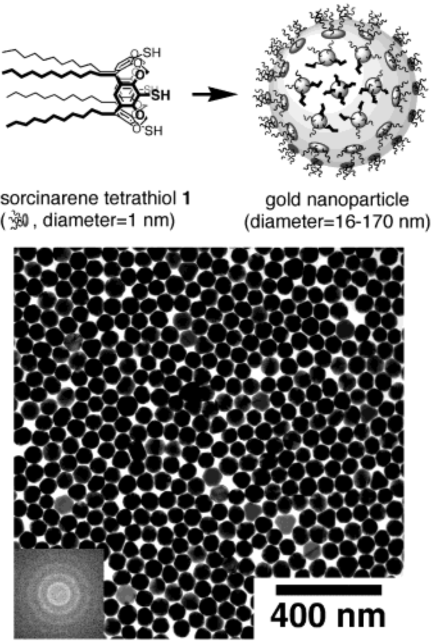

Figure 1. Transmission electron micrograph (Philips EM-400, 80 keV) of self-organized 2D array of 70 ± 5 nm gold particles encapsulated by **1**.The array was transferred onto Formvar-coated Cu grid (300 mesh) by manual Langmuir−Schaefer deposition in the absence of applied lateral compression. (Inset) Fourier transform of 70-nm particle array.

Resorcinarene-encapsulated gold nanoparticles of low size dispersity were prepared by treating aqueous suspensions of citrate-stabilized gold particles with a solution of **1** in THF, followed by several washes with toluene.[9] The adsorption of the tetrathiols onto the nanoparticle surfaces was expected to be robust, given the multivalent nature of the surfactants[10] and the low rates of desorption of aryl monothiols from gold surfaces.[11] The amphiphilic nanoparticles were confined to the solvent interface and could be carefully collected from the bulk solution using silanized pipets. Concentrated suspensions of nanoparticles were spread onto air−water interfaces and transferred as films in the absence of applied surface compression onto surfaces by horizontal (Langmuir−Schaefer) deposition or by slow vertical retraction of immersed substrates. Either method produced essentially monoparticulate films with hcp order as determined by transmission electron microscopy (TEM), demonstrating that the encapsulated nanoparticles organized spontaneously into 2D superlattices at the air−water interface (see Figure 1). The degree of order within the close-packed domains suggests that the uniformity of the arrays is determined largely by the size and shape dispersity of the nanoparticles themselves.[12]

Careful inspection of the TEM images reveals an inverse correlation between array periodicity and interparticle spacing, an indication of the increase in van der Waals attraction with unit particle size (see Figure 2).[9] Periodicities obtained by Fourier transform analysis were not sufficiently precise to provide meaningful estimates for average interparticle separations, which ranged from 6 to less than 1% of the average particle diameter

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[6] The importance of chain packing density on conformational entropy has been discussed for amphiphile monolayers at the air−water interface: Szleifer, I.; Ben-Shaul, A.; Gelbart, W. M. *J. Phys. Chem.* **1990**, *94*, 5081−89.

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[9] See Supporting Information for further details.

[10] Surfactants with several well-spaced thiol groups have been suggested for enhanced adsorption to gold surfaces because of cooperative binding as well as low probability of desorption via disulfide formation: Schlenoff, J. B.; Li, M.; Ly, H. *J. Am. Chem. Soc.* **1995**, *117*, 12528−36.

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[12] It has been noted that low size dispersity (5−10% relative standard deviation from the mean) is an important factor in the preparation of sterically stabilized colloidal crystals: Oxtoby, D. W. *Nature* **1990**, *347*, 725−30.

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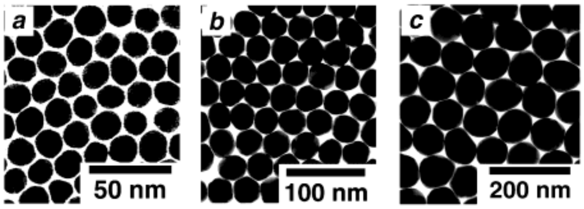

Figure 2. TEM images (Philips EM-400, 80−100 keV) of self-organized 2D arrays of (A) 16 ± 3 nm particles, (B) 34 ± 2 nm particles, and (C) 87 ± 7 nm particles. The images have been sized to emphasize the changes in particle diameter−spacing ratio.

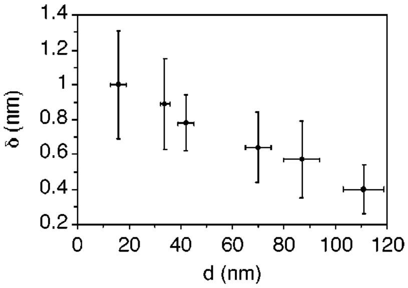

Figure 3. Average particle diameters (*d*) versus interparticle spacing parameters (δ) of large gold nanoparticle arrays based on TEM image analysis.[9] Errors are equal to one standard deviation from the mean.

(*d*). However, direct measurement of individual spacings within well-defined hcp domains enabled the calculation of spacing parameters (δ) with indeterminate errors defined by the digital resolution of the TEM images.[9] These relative values clearly demonstrate a trend toward decreasing average interparticle spacings with increasing periodicity (see Figure 3).

The particle size and the interparticle spacing have a strong influence on the optical properties of the large gold nanoparticle arrays. Arrays transferred onto smooth quartz substrates exhibit dipolar plasmon (Mie) resonances which shift and broaden by hundreds of nanometers into the near-infrared (NIR) with increasing periodicity (see Figure 4). Higher-order plasmon resonances (centered at 527 nm) are also produced by the larger arrays ($d \geq$ 70 nm) and increase in prominence with unit particle diameter. Size effects on the Mie extinction properties of isolated metal particles are well-known,[13] but the changes observed for the arrays are much more pronounced and are primarily due to the strong electromagnetic coupling between gold particles.[5,14,15] The periodicity-dependent broadening of the extinction band is particularly noteworthy as it may characterize the insulator-to-metal transition of the nanoparticulate film, and can be correlated with changes in δ. Heath and co-workers have performed extensive studies on the optical properties of small (2−4 nm) silver nanoparticle arrays as a function of interparticle separation, and have proposed quantum mechanical coupling as the basis for changes in optical response at low spacing−diameter ratios.[5,16]

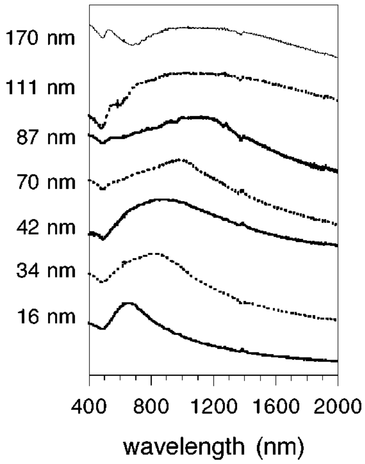

Figure 4. Extinction spectra of large gold nanoparticle arrays on smooth quartz substrates. Spectra were obtained using a HP 8452 spectrophotometer equipped with a diode array detector (400−1000 nm) and a modified Cary-14 spectrophotometer equipped with a NIR photodiode (850−2000 nm). Spectral intensities have been modulated for clarity of presentation with minimal effect on the extinction maxima. Inflections in the spectra near 1250 and 1400 nm are artifacts from instrumentation.

The self-organization of large gold nanoparticle arrays can be achieved with structural precision and has excellent potential in the fabrication of nanostructured films with tunable optical and optoelectronic properties. The large gold nanoparticle arrays are especially promising as substrates for surface-enhanced Raman scattering (SERS), and have been shown to generate stable and reproducible signal enhancements in excess of 10^7 with NIR excitation.[17] Other structure-dependent optical properties have been observed and will be reported in due course.

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Supporting Information Available: Fabrication procedures, additional TEM images, and full details of the TEM image analyses of the large gold nanoparticle arrays (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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