Crystallization of Opals from Polydisperse Nanoparticles

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We report the reversible formation of crystals of nanoparticles (opals) from solutions of polydisperse gold nanocrystals. The structures are identified by transmission electron microscopy, and are characterized by hexagonal domains of large particles at the center, surrounded radially by successively smaller particles. Simulated annealing Monte Carlo calculations are used to demonstrate that these configurations correspond to minimization of the mesoscopic van der Waals energy of polydisperse particles, and the driving force for ordering is the size dependence of dispersional attractions.

Reversible crystallization of model colloids has been extensively studied in a broad-based theoretical and experimental effort to understand the freezing transition. Because the particles and lattice spacings are on the order of optical wavelengths, Bragg diffraction of light provides a particularly convenient probe of structure. In addition, the strength and range of the interparticle interactions in solution can be controlled by added electrolyte, free polymer or surfactant, or by surface treatment (e.g., adsorbed chain coating) of the particles. Special interest has been focused on "hard sphere" colloids, e.g., suspensions of submicron particles which have been polymer coated so that strong repulsions dominate the dispersional attractions [1]. For sufficiently *monodisperse* systems, the hard spheres have been shown [2] to crystallize reversibly due to *entropic effects:* the extra "packing" entropy associated with local motions about lattice sites—in contrast to that of the "gridlocked" random structures—is sufficient at high volume fractions to compensate for the loss of configurational entropy arising from long-range ordering. *Binary mixtures* of hard spheres can also crystallize, with freezing behavior sensitive to the size ratio [3]: When the size ratio is near $R_A/R_B \approx 0.58$, ordered crystalline supperlattice (e.g., AB_2 and AB_{13}) structures are observed [4], with packing entropy again the driving force for positional ordering. In the case of *sufficiently polydisperse mixtures,* however, crystallization is suppressed [5].

A great deal of effort has also been devoted to systematic studies of colloidal systems where particles interact through *strong attractive* forces—typically, these particles *aggregate irreversibly.* Here the particles "stick" to each other with energies large compared to those of thermal motion (i.e., $\gg k_B T$), thereby giving rise to out-of-equilibrium "floc" structures from which annealing to lower energy, more compact, configurations is no longer possible. Diffusion-limited-aggregation (DLA) models account well for the highly ramified, fractal objects that result [6].

In this Letter we report the observation of crystallization in solutions of polydisperse, charge-neutral [7], nanoparticles (Au nanocrystals capped with dodecanethiol, in hexane). This freezing process is seen to be driven by interparticle *attractions,* due to van der Waals (dispersional) energies. The crucial difference between the present study and previous ones mentioned is that the mutual attractions between our particles—while large enough to dominate over entropic effects—are *small* enough so that equilibrium configurations are involved. We also observe *size-selective crystallization and phase separation.* We show that the resulting structures, involving the biggest particles at the center surrounded by successively smaller ones, are consistent with energy minimization of a polydisperse sample of attracting hard spheres—and that the driving force for his ordering is the *size dependence of the dispersional interactions.* This finding suggests a general means for preparing quantum dot arrays for application in nanoelectronics.

The observation of opal formation from weakly interacting nanoparticles is not new. Dabbousi *et al.* [8] have formed 2D close-packed arrays from a Langmuir film of *monodisperse* (5.3 nm, $\sigma \approx 4\%$) CdSe nanocrystals. However, polydisperse distributions of these particles do not, apparently, form ordered domains. The observation of size-dependent aggregation is also not new. Nanocrystal size distributions are commonly narrowed via solvent-pair precipitation techniques [9]. A similar approach is pursued in *fractionated crystallization* [10], which takes advantage of the size dependence of entropic depletion interactions—which are effectively attractive, arising from the *addition of micelles (or nonadsorbing polymers)* to polydisperse emulsions (or colloidal particles). In these size-selective techniques, the largest particles aggregate and are *removed from solution successively.* In our system, the largest Au particles crystallize first, but remain in solution to serve as a *seed* for further crystallization. To the best of our knowledge, ordered opal formation has not previously been seen in systems of *polydisperse* particles.

Gold nanocrystals (diameter 1.5–6 nm) capped with covalently bound linear alkylthiols ($C_{12}H_{25}SH$) were synthesized according to a modified synthesis, originally de-

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scribed by Wyman et al. [11]. The reader is referred to Ref. [12] for details. The derivitization of the surface with dodecanethiol was confirmed by IR spectroscopy, and the final particle size distributions were characterized by lattice imaging the particles on a 200 keV transmission electron microscope (TEM) (0.17 nm point-to-point resolution). For the distributions presented here, between 200 and 400 individual particles were sized. Due to their organic surface groups, these nanocrystals are characterized by hydrophobic interactions. This enables the particle size distributions to be further narrowed or altered via the use of toluene/methanol solvent pair precipitation techniques.

Size-dependent phase separations and opal formation were probed using TEM. Figure 1(a) is a typical TEM micrograph showing size-dependent phase separations. This measurement was performed by evaporating a drop of Au nanocrystals in hexane on an amorphous carbon-coated TEM grid. The corresponding size distribution is indicated at the bottom right. There are three important features to note about this figure. (1) The radial distribution of particle sizes within this "island" is highly ordered, with the largest particles (ca. 5–6 nm diameter) positioned at the center, and the smallest particles at the extreme borders. (2) The separation between nearest neighbors is independent of the particular Au core sizes involved. (3) The large particles constitute only $\sim 2\%$ of the total size distribution, and yet they are able to nucleate and drive the formation of this opal. Without these large (i.e., $\gtrsim 4.5$ nm) particles, but still at comparable concentrations, there does not appear to be sufficient time for ordered arrays to form before the solvent evaporates. The particles are observed to randomly disperse upon the substrate.
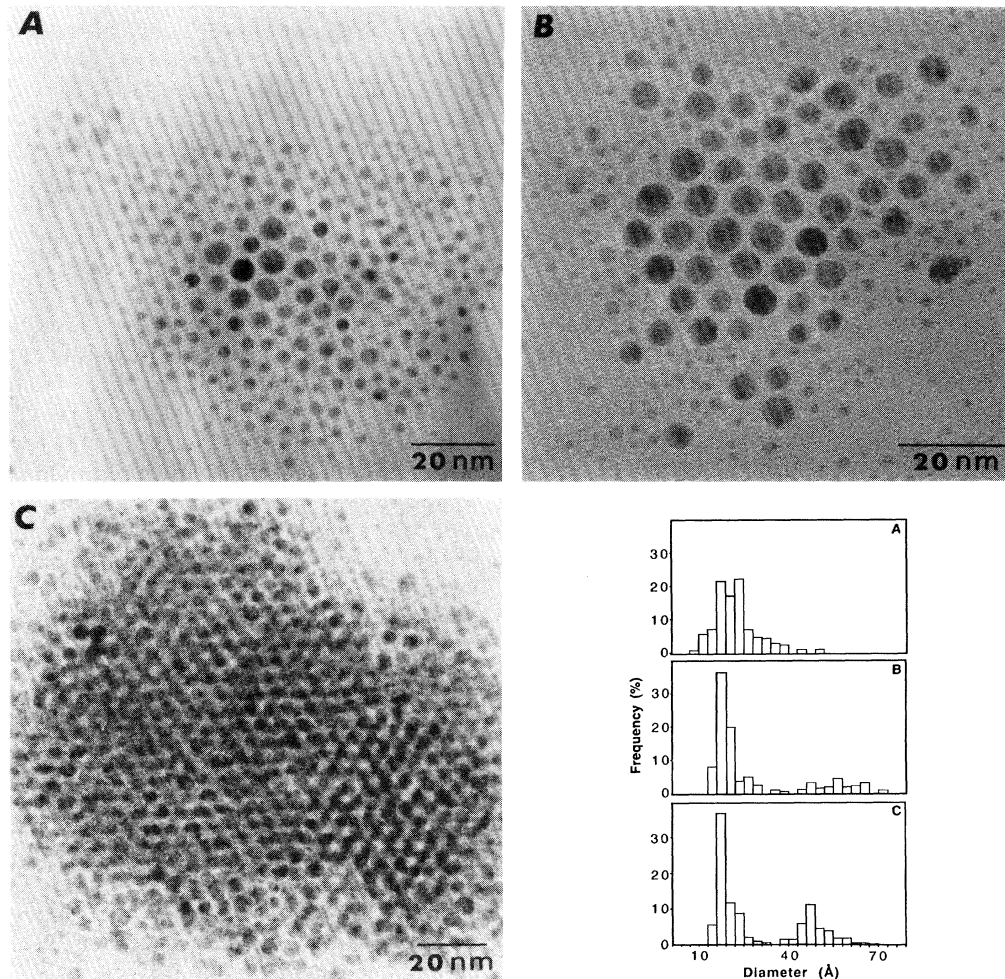

FIG. 1. TEM micrographs revealing the size-dependent phase separation and opal formation of weakly attracting alkylthiol-functionalized Au nanocrystals. Below (right) are the corresponding particle size distributions. As discussed in the text, only the largest particles (5–6 nm) attract each other sufficiently to order into closest packed domains. The transition from micrographs (a) to (b) shows the nucleation and 2D growth of such a domain. (c) A 3D hcp opal prepared by evaporating a hexane solution of particles on a water surface and lifting off the resulting Langmuir film onto a TEM grid.

Figure 1(b) is essentially a repeat of the above experiment, except that this particle size distribution contains a substantially larger relative fraction of 5–6 nm particles. Note the presence of extended 2D close-packed (cp) domains. Note also that, aside from the presence of these extended domains, the morphology of this particular "island" is similar to that of Fig. 1(a), with the largest particles again at the center.

A third experiment was performed in which an essentially bimodal size distribution of particles prepared in hexane was evaporated as a Langmuir film on a water surface in a 10 cm diameter Petri dish. The film, which did not extend to the edges of the Petri dish, was resoluble in hexane. After the hexane evaporated, a TEM grid was immediately dipped below the water through a region that did not have a film, and lifted up through a water/film interface to coat the grid. The grid was immediately loaded into the TEM. The whole process takes about 1 min. Figure 1(c) is a low resolution TEM micrograph of a region of this grid, and is typical of many areas of the grid. This micrograph is a view of the (110) zone axis of an hcp three-dimensional opal grown from 5 ± 1 nm Au nanocrystals. It is not obvious whether all the opals assume an hcp (rather than fcc) arrangement. Although this opal contains thousands of the larger nanocrystals, higher resolution images reveal that it is surrounded by smaller (1.5–3 nm) nanocrystals, as in Figs. 1(a) and 1(b).

We believe that the ordering of gold nanocrystals seen by TEM is due to the size dependence of van der Waals–type dispersional attractions between nanocrystals. For simplicity, we assume (see [13]) that the dielectric properties of the alkylthiol chain are roughly the same as those of the alkane solvent. The interaction between two nanocrystals in solution is then given by the dispersional attraction between the (approximately) spherical gold cores of the nanocrystal. Solid spheres of radii R_A and R_B, at a distance of closest approach D, have been shown (from direct pairwise summation over $-C/R^6$ atomic dispersional attractions) to attract each other with a potential given by [14]

$$V(D) = -\frac{A}{12}\left\{ \frac{R}{D[1 + D/2(R_A + R_B)]} \right.$$
$$+ \frac{1}{1 + D/R + D^2/4R_AR_B}$$
$$\left. + 2\ln\left(\frac{D[1 + D/2(R_A + R_B)]}{R[1 + D/R + D^2/4R_AR_B]} \right) \right\}.$$

A is the Hamaker constant, ≈ 1.95 eV for gold-gold attractions through dodecane [15], and $R = 2R_AR_B/(R_A + R_B)$ is the reduced radius. This interaction energy varies in the large D limit ($D \gg R$) as $-AR_A^3R_B^3/D^6$, similar in form to the fundamental $-C/R^6$ dispersional attractions. In the small D limit ($D \ll R$), $V(D)$ becomes proportional to $-AR/D$, consistent with the result derived using the Derjaguin approximation [16]. The size depen-

dence of the dispersional attractions between nanocrystals is readily apparent from these expressions, ranging from a linear (for small D) to sixth-power (for large D) dependence on particle radius [17]. Because the attractions between the largest spheres are strongest, they energetically prefer to be clustered together, with the next size preferring to "wet" this cluster rather than forming a separate domain. This argument can be extended successively to smaller and smaller spheres, thereby favoring the structures with radial size segregation seen by TEM.

To illustrate how the ordering of the energetics leads to radial size segregation, we performed a two-dimensional simulated annealing calculation with spheres of different sizes, where the total energy of the system—a pairwise sum over sphere-sphere dispersional attractions—is minimized via a Monte Carlo routine. We take the radius of the largest spheres (A) as our unit of length ($R_A = 1.0$), and choose B and C such that $R_B = 0.6$ and $R_C = 0.3$. Because of the thiol layer on the nanocrystal, the distance of closest approach between the gold spheres is taken to be $D = 0.5$, estimated from the TEM micrographs. The fact that the gold "cores" do not approach *closer* than a few nanometers is responsible for keeping the dispersional attractions comparable to k_BT, thereby allowing configurations to anneal as crystals. This contrasts with the familiar situation [6] where particles are separated by a few *angstroms,* making the energies at contact an order of magnitude larger and giving rise to out-of-equilibrium flocs. The *exact* choices of sizes and distances for the present calculations are not important, and will not affect the *qualitative* results seen here. We ran a simulated annealing routine with random initial configurations of 7 A, 21 B, and 36 C (64 total) spheres to find the lowest-energy two-dimensional structures. Our simulation was limited to two dimensions because the micrographs [see Figs. 1(a) and 1(b)] show only 2D structures, due to the wetting of the carbon TEM grid by hexane and/or to the strong interactions between these nanocrystals and the grid. We assert that these simulations are reflective of the TEM results because the nanocrystals apparently *are able to anneal* and rearrange into ordered structures on the grid before all solvent has evaporated.

Figure 2 shows the result for one of our initial simulations. This structure has an energy of -2.22 eV, slightly higher than that of the *lowest* energy structure. Note that these energies are also *underestimates* of the dispersional attractions between nanocrystals because we leave out the thiol shell-shell interactions [13]. This figure illustrates the *qualitative* trends that the large nanocrystals (A) cluster together in the middle, medium-sized crystals (B) tend to "wet" the large particles, and the small crystals (C) surround those of B. This behavior is precisely what is seen experimentally, and is consistent with our argument that the *size dependence of the energetics leads to radial size segregation.* Thus the gold opal formation can be viewed as a thermodynamic, energetic effect.
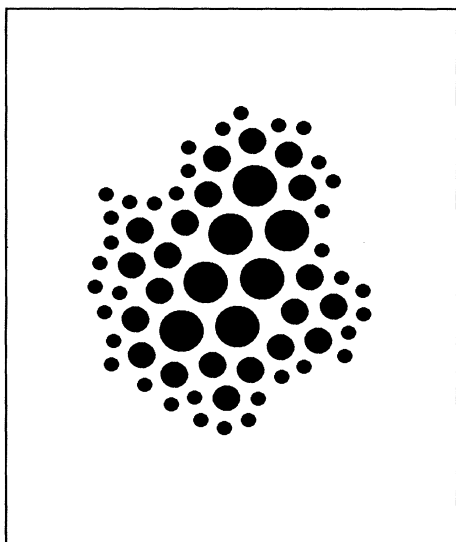
FIG. 2.   Simulated annealing calculation for a system containing three sizes of spheres. The energy of a system containing 64 spheres—7 A, 21 B, and 36 C, with radii $R_A = 1.0$, $R_B = 0.6$, and $R_C = 0.3$—was minimized via a Monte Carlo simulated annealing routine. This structure is one (typical) product obtained, after annealing from random initial configurations. Its energy is -2.22 eV, neglecting thiol-thiol contribution to the energetics [13]. The minimum allowable distance between gold cores is set to be $D = 0.5$.

In summary, we have presented the experimental finding that polydisperse mixtures of alkylthiol-capped gold nanocrystals in organic solvent crystallize into ordered, size-segregated opals on a TEM grid. Furthermore, we used Monte Carlo simulated annealing calculations to demonstrate that the resulting structures—showing radial size segregation with the largest particles in the center—are formed due to the *size dependence of the dispersional attractions*. This assembly process is possible because of the unique, intermediate range of the interactions: Dispersional attractions are strong enough to dominate over entropic effects, but weak enough to allow the nanocrystals to anneal into low-energy, equilibrium configurations.

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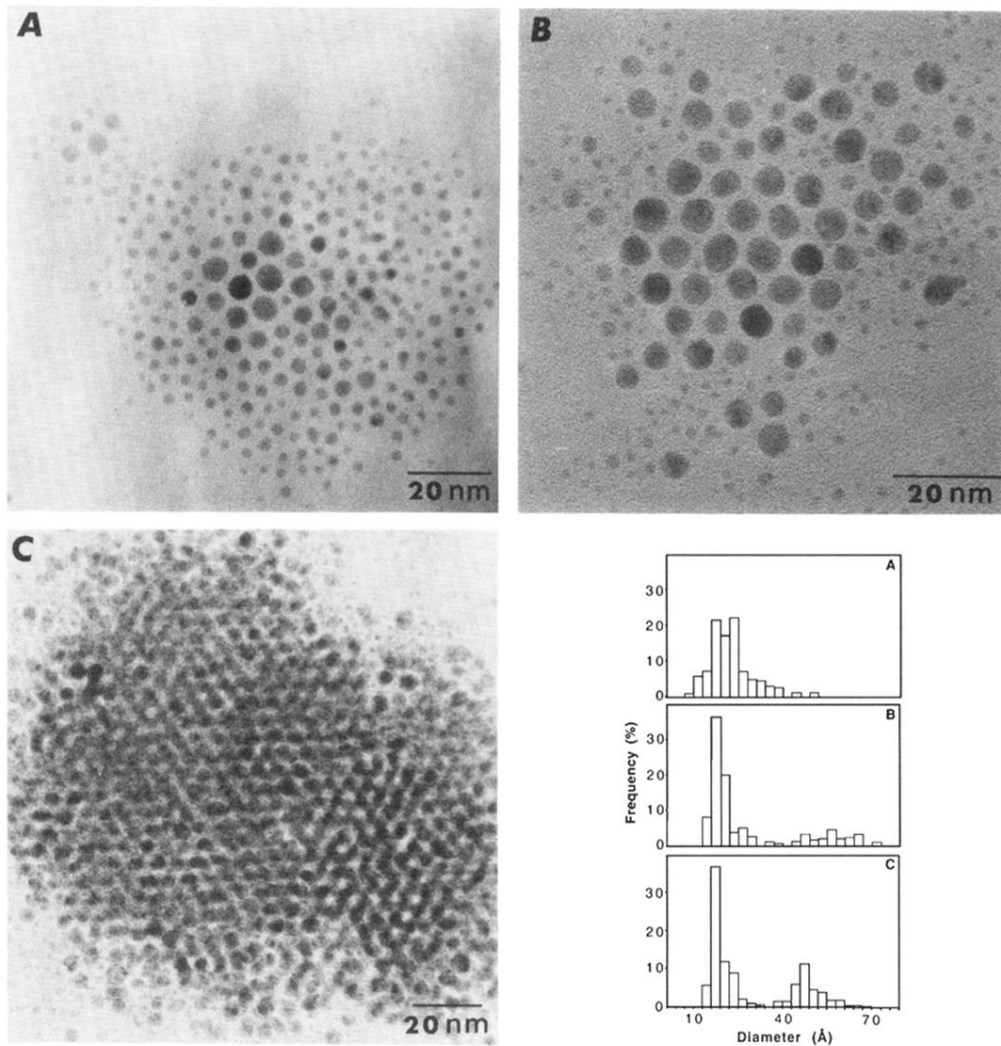
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