Nanostructures

Shape Effect in Nanoparticle Self-Assembly**

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The assembly of nanoparticles is a key step for their application as nanodevices. Self-assembly of nanomaterials strongly depends on interparticle interactions,[1,2] particle size distribution[1,2] and particle shape.[3–8] Current methods for assembling nanoparticles include capillary force,[9] template-directed patterning,[10] or surface derivatization of particles that modify interparticle interactions.[1,2] Spontaneous self-assembly of spherical nanoparticles occurs only with particles with a narrow size distribution, that is, those with a polydispersity $<5\%$, and leads to a compact 2D or 3D structure.[1,2] In contrast, nonspherical nanoparticles show different types of self-assembly. Oriented attachment-based self-assembly and crystallization was observed for inorganic colloids and nanoparticles.[4,11,12] Various liquid-crystalline order structures such as nematic, columnar, and smectic phases are observed for rodlike and platelike particles at high volume fractions.[13–21] Similarly, bundle structures have been observed for nanowires and nanotubes.[22,23] However, the colloidal systems available for experimental study had a limited length scales and aspect-ratio ranges, namely, the tobacco mosaic virus (TMV) nanorods, β-FeOOH nanorods, gibbsite plates, boehmite rods, and higher-order smectic phases, which are often inhibited either because of shape polydispersity or the kinetic arrest into the gel phase because of the lack of suitable surface modification.[17,24] Recent synthetic advances that provide anisotropic nanoparticles of various size, shape, and dimension, provide an opportunity to examine theoretical predictions and to use them for the ordering of nanomaterials.[6–8,20,25,26] We have studied the self-assembly of gold–silver nanoparticles with various aspect ratios (length to width ratio for spheroids/rods and diameter to width ratio for plates) from 1–25, all having short axis diameter between 10–30 nm. We observed various types of self-assembly depending on shape and extent of particle anisotropy. (Figures 1–5) The observed self-assemblies are analogous to the entropy-driven ordering into liquid-crystalline phases, as originally proposed by Onsager[27] and latter verified by computer simulations,[28,29] and experimental work.[17,18]

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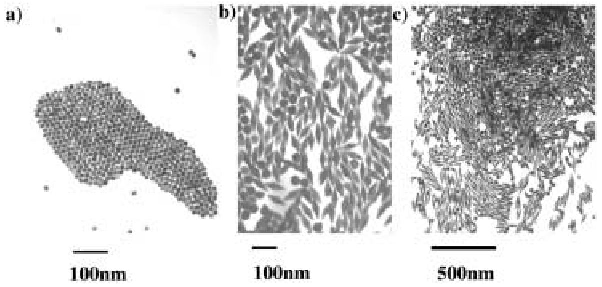

Figure 1. Honeycomb structures produced by gold spheroids of different anisotropy: a) aspect ratio 1.2, b) aspect ratio 3.5, and c) aspect ratio 6.5. Particle dispersion in water was ≈1% concentration by weight and 1–2 μL of this solution was deposited onto carbon-coated copper grid and solvent was slowly evaporated. The resulting dried film was investigated by transition electron microscopy (TEM).

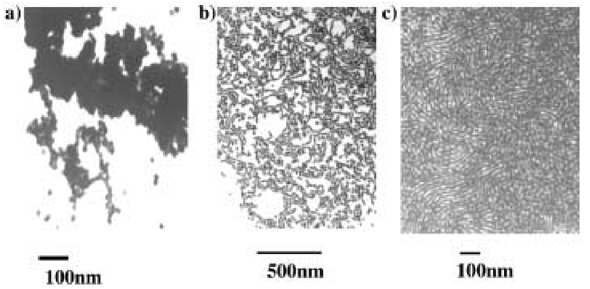

Figure 2. Oriented attachment observed by different anisotropic gold spheroids: a) aspect ratio 1.5 and b),c) aspect ratio 3.5. Particle dispersion in water was ≈0.1% concentration by weight. Concentration of free surfactants in solution was ≈0.0 as they were removed by successive centrifugation and redispersion cycles. TEM studies were carried out 48 h after preparing the dispersions by using 1–2 μL of the precipitated portion.

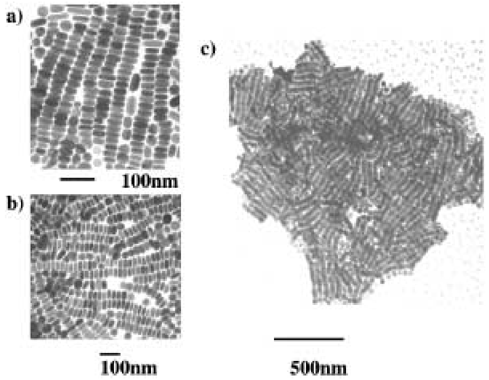

Figure 3. Smectic 2D ordering of silver nanorods/plates with aspect ratio 2–4: a) plates with aspect ratio of 2, b) rods with aspect ratio of 2, and c) rods with aspect ratio of 3.5 (some plates are also involved in this self-assembly). Particle dispersion in water was ≈2% concentration by weight. TEM studies were carried out 24 h after preparing the dispersions by using 1–2 μL of the precipitated portion.

According to the Onsager's theory, hard rods interacting with repulsive forces could exhibit orientational ordering at densities far below the closest packing. The thermodynamic stability of these order structures arises from a gain in translational entropy that overrules the loss of orientational entropy associated with particle alignment.[27] These order structures strongly depend on the particle anisotropy.[28] Short rods (< 7 aspect ratio) exhibit direct isotropic–smectic phase transition but long rods show isotropic–nematic–smectic transitions.[28] We observed that spheroids with aspect ratios between 1 and 7 show orientational ordering that often leads to honeycomb structures (Figure 1); cylindrical nanorods and platelets with aspect ratios between 2 and 4 show higher order smectic 2D structures (Figure 3), but particles with aspect ratios 5–15 have lower-order 1D ribbon structures (Figure 4). As the aspect ratio was further increased, nematic ordering, bundle structures, or a weak tendency to from smectic 3D structures were observed depending on the experimental conditions.

A closer look into the smectic 2D structures show that small nanorods/plates form ribbon structures through side-by-side alignment and those ribbons further self-assemble, side-by-side, into a smectic array. (Figure 3) The aspect-ratio window is relatively small for this smectic array and needs a narrow distribution (< 10%) of aspect ratio. However, we observed that the extent of anisotropy is more important than the nature of shape (i.e., rods or plates), thus both rods and plates can be involved in the same smectic array. In concentrated dispersions these rods slowly precipitate into these 2D structures. When this precipitate was observed under electron microscope, micrometer size 2D structures were observed without any isolated particles. No other type of ordering such as nematic or ribbon structure was observed, thus indicating that smectic ordering was only favorable as predicted earlier.[28] The precipitated nanorods can be redispersed in excess water and this diluted dispersion no longer produces a smectic array; mostly isolated particles are observed.

The honeycomb structures of spheroids do not show positional ordering, (Figure 1) however, 1D positional ordering occurs in the ribbon structures of particles with aspect ratios from 5 to 15. (Figure 4) The spheroids, plates, or

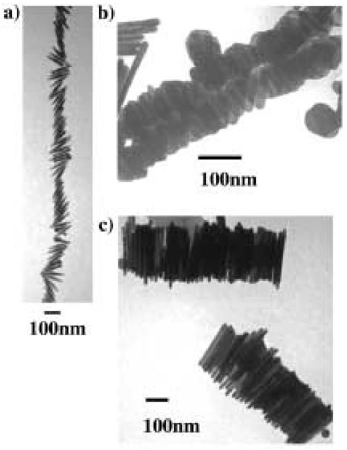

Figure 4. Ribbon structures of nanoparticles with higher aspect ratios: a) gold spheroids with aspect ratio of 7.5, b) gold plates with aspect ratio of 8 and two ribbons aligned size-by-size, and c) gold nanorods with aspect ratio 15. Particle dispersion in water was ≈5% concentrated. TEM study was carried out by using 1–2 μL of the dispersion.

nanorods align almost parallel to each other and form linear arrays of small groups in which the nanoparticle long axis is perpendicular to the array axis. (Figure 4) A similar array was present throughout the microscopic grid. In some cases 2 or 3 ribbons stack with each other, thus showing a weak smectic ordering. The frequency of occurrence of ribbon structures (compared with isolated particles) and the length of the ribbons increase with an increase in the aspect ratio. For example the spheroids seldom form ribbon structures (rather than honeycomb structures), but plates and rods form ribbon structures very frequently. The average number of monomer spheroids and plates present in a ribbon structure is between 25 and 50, but this number increases to a few hundred as the aspect ratio increases to 15. With a further increase in anisotropy (aspect ratio 15–25), the 1D ribbon structure extends into 2D bundle structures with occasional side-by-size alignment of 2 or 3 bundles into 3D superstructures. (Figure 5) At lower surfactant concentrations these long rods exhibit nematic ordering. (Figure 5) Our observations are in general agreement with the theoretical prediction that higher structures are more favorable with increasing particle anisotropy.[28]

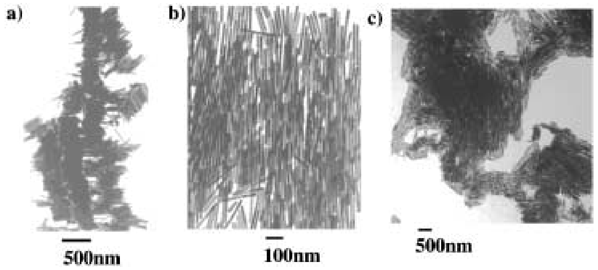

Figure 5. Self-assembly of gold nanorods with aspect of ratio 22: a) bundle structure at higher surfactant concentration with three bundles aligned size-by-size, and b,c) nematic order at lower surfactant concentration. Particle dispersion in water was ≈5% concentration by weight. TEM studies were carried out by using 1–2 μL of the dispersion.

A very different type of self-assembly, previously known as oriented attachment,[11,12] was observed for spheroids at lower stabilizing surfactant condition. Spheroids undergo irreversible oriented attachment and form a linear array. (Figure 2) In this oriented attachment, particles appear fused almost end-to-end along their longitudinal axis and form linear chains. The long chains were often bent and sometimes formed coils and globules. This oriented attachment also occurs in polydispersed samples in which the spheres are mixed, thus leading to the selective precipitation of spheroids. This oriented attachment is irreversible and particles could not be redispersed. This type of particle assembly occurs at 0.01–0.1% volume fractions, which is much lower than the condition required for entropy-driven ordering.[24] The irreversible attachment leads to a lowering of the surface energy after the elimination of highly curved surfaces of individual spheroids, and is an enthalpy-favorable processes.[11,12] We presumed that a lower concentration of stabilizing surfactant would induce slow 1D aggregation (then fusing) of charged particles to minimize the repulsive interactions between particles.[30]

The self-assembly process was influenced by the presence of stabilizer surfactant, which was used in the particle synthesis. As the concentration of surfactant increased relative to a fixed particle concentration, the formation of order structures appeared to be more favorable than the formation of isolated particles. This was evident with the precipitation of smectic 2D short rods, an increase of ribbon structures for rods with aspect ratios 5–15, and an increase of bundle structures for rods with aspect ratios 15–25. The volume fractions we used were relatively low compared to the theoretical values determined by hard particle approximation.[17,24,28] Similar self-assembly at lower volume fraction was recently reported.[21] This is expected as the interaction of real colloids or nanoparticles with each other depends on the presence of an ionic and/or an organic stabilizing shell surrounding each particle, and Onsager's theory may be applicable to those particles that have an effective increased diameter.[27] In the case presented here, the particles are coated with a cationic surfactant and the presence of excess surfactant induce self-assembly. This surfactant shell causes the particles to have a net positive charge, and can induce interdigitation between particles.[5,19] When the surfactant was replaced by a dodecanethiol monolayer, no order structures were observed as surface charge was eliminated. These facts indicate that the role of the surfactant is to balance the repulsive and attractive interactions between particles. The excess surfactant may behave similarly to polymer that is often used to induce depletion attraction between colloids and to widen the regions over which phase transition can occur.[24]

The lateral capillary force that occurs during the drying processes of the particle dispersion may induce the self-assembly.[6] However, self-assembly was observed only at higher particle concentrations or with precipitates. When the solution was diluted and the precipitate was redispersed to make a dilute solution, no self-assembly was observed under a microscope. The separation of nanorods from a bulk solution of rod–sphere mixture indicates that capillary forces do not have major role in the self-assembly processes. Liquid-crystalline order structures were further confirmed when the sample solution or the precipitates were investigated under polarized-light microscopy and by small-angle X-ray scattering.[19] However, we are unable to make very concentrated particle dispersions for light-scattering studies as most of our sample dispersion immediately precipitates or becomes too turbid. Earlier reports show that concentrated particle dispersions often form gels unless the particle surfaces are properly modified with stabilizer.[17,24] In this respect surfactants may not be a good stabilizer, as they themselves can form liquid crystals or gels; currently, we are trying to modify the particle surface with polymers.

In real colloids, the polydispersity often inhibits crystallization.[1,2,16] For example, in a binary colloid mixture, dilute solutions are homogeneous as the mixing entropy dominates, but at higher concentration spontaneous phase separation often occurs. This phase separation increases the free volume and thus increases the translational entropy of colloids that compensates for the loss of mixing entropy. In this concentrated dispersion, particles of the same shape attract each other—a phenomenon that is known as "macromolecular crowding" in biology and "depletion attraction" in chemistry and physics.[16,24] To understand the role of polydispersity in the self-assembly process, we performed some control experiments. When the samples were studied before shape separation from spheres (10–50% spheres, the rest spheroids or nanorods), the self-assembly processes often led to spontaneous shape separation in micrometer length scale. The rods or spheroids self-assembled with each other, formed groups, and separated from the spheres. In other words, nanorods or spheroids recognize each other in a polydispersed sample and assemble into groups (Figure 6), which is very similar to what occurs in the formation of bacteria colonies. Under similar conditions, spheres do not self-assemble. This is very similar to the recent observation by Lekkerkerker and co-workers in which the polydispersed (≈25%) plates show smectic transition during which spontaneous shape fractionation occurs.[18] Our results indicate that shape polydispersity may not inhibit crystallization under all experimental conditions, but may induce shape fractionation followed by the crystallization of each identical shapes—at least at the micrometer-length scale.

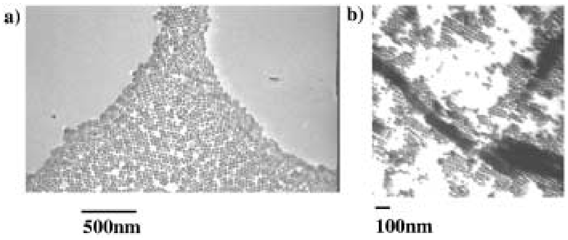

Figure 6. Self-assembly of gold nanorods in polydispersed sample: a) rods with aspect ratio of 2–4, and b) rods with aspect ratio of 5. In these samples rods are mixed with spheres (30–40% by number) of similar size and particles were 5% concentration by weight. TEM studies were carried out by using 1–2 μL of the dispersion.

The above microscopic shape separation phenomenon can be used for bulk shape separation of nanorods and plates, if the experimental condition are properly designed.[26] When the polydispersed samples are prepared at high volume fractions (0.5–5%), nanorods or plates precipitate leaving only spheres in solution. The purified nanorods can be redispersed in suitable solvents as the self-assembly is a reversible processes. As the self-assembly process depends on the particle anisotropy, the separation conditions can be tuned for the step-by-step separation of different anisotropic particles.[26] For example, in a mixture of gold rods (aspect ratio 10–25), plates (aspect ratio 8) and spheres, as the concentration of particle dispersion increased, long rods precipitated first followed by short rods and finally plates, but spheres remained in solution. Similarly, for the mixture of silver rods (aspect ratio 2–4) and spheres, rods precipitated but spheres remained in solution. Separation efficiency can be increased by repeated precipitation–redispersion cycles.[26] This shape separation technique can be used to prepare high-purity nanorods and plates.

Our results indicate that self-assembly is strongly induced by shape. While under similar experimental conditions the spheres of similar size do not self-assemble unless they have a very tight size distribution, other shapes do self-assemble despite shape polydispersity. Both the nature of the self-assembly and the driving force for self-assembly depends on particle shape and particularly on the extent of shape anisotropy. These types of self-assemblies may be used for mesoscale self-assembly of nanomaterials to overcome problems by using nanosphere precursors.

Experimental Section

The nanoparticles of various shapes were prepared according to seeding-growth processes in aqueous surfactant (cetyl-trimethylammonium bromide, CTAB) media.[25] In the first step, 3–4 nm seeds of citrate-stabilized silver or gold nanoparticles are prepared by borohydride reduction. In the next step, the seeds are grown in a growth solution that contains additional metal salts and weak reducing agents as previously reported. [25] Nanorods or plates of different anisotropy are formed depending on the ratio of seed to metal salt, presence of shape inducing agents (namely, Ag^+ ions or cyclohexane) or by changing solution pH. The prepared nanoparticles are then separated from the spherical nanoparticles and excess surfactant by centrifugation at different speeds. Nanoparticles thus prepared have a surfactant coating that stabilizes their aqueous dispersion. Thermogravimetric analysis of separated nanoparticles shows the presence of 15–20% surfactant by mass, which is larger that the monolayer coverage (≈3%) surrounding the particles. After removal of the excess surfactant, nanoparticles are then subjected to purification cycles.[26] Typically, a dispersion of nanoparticles (0.5–5% concentration by weight of the respective metals) is prepared and then either preserved for few days or excess CTAB is added until a precipitate is observed. The precipitate is redispersed in water or in a fresh CTAB solution. The precipitation–redispersion cycles are repeated 4 or 5 times, after which the concentrated nanoparticle dispersions (up to 20% by weight) are obtained. For dodecanethiol capping, nanoparticle hydrosol is mixed with a toluene solution of the thiol and stirred vigorously for one hour. The thiol-coated nanoparticle aggregates form films at the water–toluene phase boundary, which can be used for microscopic study.

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