



REVIEW

Formation of supercrystals through self-assembly of polyhedral nanocrystals



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Summary Compared to the number of reports on the self-assembly of spherical nanoparticles forming superlattices, relatively fewer studies have addressed the assembly of polyhedral metal and semiconductor nanocrystals for the formation of supercrystals with well-defined geometric shapes. These polyhedral supercrystals are considered as a new class of superlattice structures in which particle morphology strongly dictates the shapes of resulting supercrystals if the particles are larger than 20 nm. This review provides examples and advances in fabricating supercrystals on a substrate during the process of solvent evaporation and through diffusion transport of surfactant to generate free-standing supercrystals. The diversity of supercrystal morphologies observed is illustrated. In many cases, the supercrystal formation process has been found to be surfactant-mediated with surfactant molecules residing between adjacent nanocrystals. Polyhedral nanocrystal assembly was found to be strongly shape-guided. Thus, the formation of polyhedral supercrystals offers a unique opportunity to reconsider the forces involved from a more global perspective instead of focusing on mainly local interactions. Efforts have been made to record the entire supercrystal formation process. Finally, some results of properties of supercrystals and future directions for supercrystal research are provided.

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Introduction

Advances in the syntheses of polyhedral metal and semiconductor nanocrystals with excellent size and shape control have not only given us valuable particles for the examination of their facet-dependent properties, but have also naturally

led to the observation of their self-assembled structures on substrates [1–20]. Because of their spontaneous organization after particle formation, it becomes necessary to describe the superlattice structures formed. Previously the focus of extensive studies on the assembly of nanoparticles involves mostly spherical particles of single or multiple sizes [21–27]. The particles therefore can be viewed as artificial atoms forming lattice structures which resemble those seen in unit cells of metals and binary compounds with face-centered cubic (fcc) and body-centered cubic (bcc) packing arrangements. Conversion from one packing structure to

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another is also possible with spherical particles by varying the temperature [24,25]. While assembly by polyhedral particles should involve similar mechanisms and forces, the effect of particle shape becomes important, and accommodation of small spheres or polyhedra filling the interstitial spaces can be more difficult or show no positional uniformity. Their packing arrangements therefore deviate from those of spherical building blocks. An exception may be the coassembly of nanospheres and very short nanorods with curved ends to form binary superlattices [28]. Another interesting aspect of polyhedral nanoparticle assembly is the formation of supercrystals with geometric shapes, which are much less observed or discussed. These features makes supercrystals organized by polyhedra a new class of superstructures that can yield different structural diversity and allow the exploration of pore accessibility and novel physical properties.

This review focuses on the formation of supercrystals with geometric shapes from the self-assembly of inorganic polyhedral nanocrystals. The scope of discussion is somewhat different from that of superlattices constructed from non-spherical building blocks, in which the formation of organized superstructures with well-defined morphologies is not emphasized [29]. Supercrystals fabricated from the assemblies of various building blocks and their packing structures are presented. Direct observation of the supercrystal formation process during droplet evaporation is provided. The forces involved in the formation of superlattices have been extensively discussed in the literature, so here the role of surfactant and the particle shape effects are emphasized to show how the use of simple surfactant can effectively yield polyhedral supercrystals in aqueous solution. A novel surfactant diffusion approach to generate free-standing supercrystals in bulk solution is also described. This method offers tremendous advantages of mass production of supercrystals in solution for easy collection and large-area deposition of supercrystals on a substrate to facilitate the availability of supercrystals for their property investigations. Some useful properties of supercrystals, particularly their catalytic activities, and future research directions are also given.

Supercrystals fabricated from diverse polyhedral metal and semiconductor nanocrystals

To best illustrate the morphological diversity achievable for supercrystals, it is necessary to use a variety of polyhedral building blocks with the same or similar solution environment including solvent and capping agents. This requirement limits the number and composition of nanomaterials available as building blocks. Polyhedral particles made with a series of shape evolution and uniform sizes of tens of nanometers such as Au, Au–Pd, and PbS nanocrystals are ideal for such demonstration [3,7,8,12]. Previously gold nanocubes, octahedra, truncated octahedra, and rhombic dodecahedra with sizes of tens of nanometers have been used as building blocks to form micrometer-sized supercrystals by slowly evaporating a water droplet on a substrate placed inside a vial containing water [30,31]. Supercrystals were generated by placing the vial in an

oven set at different temperatures. The droplet withdrawn from a centrifuged tube contains a high concentration of nanocrystals and a sufficiently high concentration of cetyltrimethylammonium chloride (CTAC) surfactant. Fig. 1 illustrates the variety of supercrystals formed using these building blocks. Supercrystals can be obtained at various droplet evaporation temperatures, although a higher temperature (e.g. 90 °C) favors the formation of high-quality supercrystals. Nanocubes form roughly cubic supercrystals. Rhombic dodecahedra were assembled into truncated triangular pyramidal supercrystals. Rhombic dodecahedral, octahedral, and hexapod-shaped supercrystals were produced from the assembly of octahedra. Corner-truncated octahedra formed mostly octahedral, truncated triangular pyramidal, and square pyramidal supercrystals. Remarkably, supercrystals are evenly scattered over the entire substrate surface covered by the evaporating droplet, rather than concentrated toward the perimeter of the droplet, suggesting that multiple supercrystals are formed by rapidly assembling nearby particles and then settling on the substrate (Fig. 2a). Despite the exhibited structural variety of the synthesized supercrystals, there is only one packing arrangement identified for each nanocrystal shape, as shown in Fig. 2. Such packing arrangements make maximum contacts with neighboring nanocrystals and should be the most stable assembly structures. For cubes with slight corner truncation, a variant packing structure in which a single cube residing at the cross-section of four cubes underneath is also frequently observed.

Superstructures and supercrystals fabricated from the assembly of various metal and semiconductor nanocrystals have been reported. Fig. 3 summarizes some of these examples. Tan et al. used *N*-hexadecylpyridinium chloride (CPC)-capped rhombic dodecahedral Au nanocrystals to form triangular superstructures with the same packing arrangement as shown in Fig. 2 by depositing the nanocrystal droplet to a vertically aligned silicon wafer and slowly evaporating the solution for 40 h under high humidity [32]. An optimal CPC concentration of 10 mM was found to yield the superstructures. Pd nanocubes with an edge length of 27 nm dispersed in an aqueous solution with a cetyltrimethylammonium bromide (CTAB) concentration of 25 mM have been used to grow into cubic supercrystals (Fig. 3a) [33]. The nanocrystal solution placed in a closed vial was completely vaporized in 12 h at room temperature to obtain the supercrystals. Petit and coworkers synthesized corner-truncated Pt cubes with sizes of ~5 nm in the presence of tetrakis(decyl)ammonium bromide (TDAB) and alkylamine in toluene [34]. The nanocubes were used to assemble into large supercrystals on a substrate with square pyramidal and triangular (or truncated tetrahedral) shapes by slowly evaporating toluene over the substrate over a period of 8 days (Fig. 3b and c). The formation of square pyramidal supercrystals can be understood by stacking the next layer of truncated cubes at the interstitial sites formed from regular packing of the first layer of cubes. This way the square area of the upper layer of cubes is slightly smaller than the lower layer and eventually leads to the formation of a square pyramid. What is puzzling is how cubes can form triangular or truncated tetrahedral supercrystals. The answer lies on the normally invisible shell or coating of surfactant on the surface of truncated cubes as seen in the inset of Fig. 4. The

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