Pushing Nanocrystal Synthesis toward Nanomanufacturing

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ABSTRACT The potential of using nanocrystals in applications within the fields of catalysis, electronics, medicine, and others has fueled research into the preparation and assembly of these materials. For most applications, it is necessary to have nanocrystal samples in which the size, shape, composition, and structure are tightly controlled within a narrow distribution. This need has motivated researchers to explore different synthesis protocols, including a method featured in this issue of *ACS Nano* by Kitaev and co-workers, where decahedral silver nanoparticles were used as seed particles for the growth of faceted silver rods. In this Perspective, we describe recent advances in seeded growth as the ultimate approach to producing metal nanocrystals with precisely controlled sizes, shapes, and compositions—the necessary first step toward their use and assembly for large-scale applications.

See the accompanying Article by Pietrobon *et al.* on p 21.

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Owing to their fascinating and tunable properties, nanocrystals (*i.e.*, crystals with at least one dimension between 1 and 100 nm) have been an active subject of research for several decades. In particular, the confinement of electrons by the dimensions of a nanocrystal offers a powerful means of tuning the electronic, optical, and magnetic properties of a solid material. Thus, it is no surprise that the preparation of a new type of nanocrystal often correlates with the discovery and ensuing study of size effects, with notable examples including quantized excitation,[1] superparamagnetism,[2] and metal-to-insulator transition.[3] As the properties of a nanocrystal are determined by its size, shape, composition, and structure (*e.g.*, solid *vs* hollow), it is imperative that high-quality samples be produced in which all of these parameters are tightly controlled.[4] Additionally, the production of high-quality nanocrystals must be scalable to large volumes so they can be integrated into applications within the fields of catalysis, electronics, photonics, information storage, imaging, medicine, and sensing, among many others.[4] Luckily, over the past decade, it has become possible to prepare many classes of materials (*e.g.*, metals, metal oxides, and metal chalcogenides) as nanocrystals having well-controlled physical properties.[4,5] Such advances were achieved by controlling both the structure of the seeds present in the early stages of a synthesis and the conditions for their subsequent growth. In this Perspective, we consider seeded growth as the ultimate approach to producing metal nanocrystals with precisely controlled sizes, shapes, and compositions—the necessary first step toward nanomanufacturing.

Nanomanufacturing—the use of nanoscale building blocks in the fabrication or assembly of functional structures and/or devices—depends on our ability to provide the building blocks with a high degree of precision and complexity either by a top-down or bottom-up approach.[6] Compared to top-down methodology, the low costs associated with bottom-up techniques are favorable; however, as a prerequisite, high-quality nanocrystals must be produced and then assembled in a controllable fashion. For example, plasmonic gold and silver nanocrystals are being considered as substrates for chemical sensing applications *via* surface-enhanced Raman scattering (SERS); however, fundamental studies into their utility have been plagued by issues such as reproducibility. Interestingly, it was recently demonstrated that the size and shape of a nanoparticle substrate can influence the frequency and amplitude of light absorption, which in turn, can influence the SERS signal enhancement.[7] Additionally, when deposited on a surface (for use in a portable device, for example), the SERS signal enhancement that arises from nonspherical nanoparticles is dependent on its orientation relative to the laser polarization.[8] As this example illustrates, both the orientation and physical properties of nanoparticles can influence the performance and reproducibility of a potential device, making the synthesis and assembly of shape- and size-controlled nanocrystals essential for any practical application. However, early preparatory methods failed in providing such nanocrystals because multiple nucleation events and different nucleation pathways typically occurred during synthesis. Thus, at any time during a reaction, particles at different stages of growth would be present. Consequently, it has become critical to separate seed formation from nanocrystal growth. Only in doing so, can nanocrystals be synthesized with the high degrees of precision and complexity that are necessary for their integration into large-scale applications.

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Separating Seed Formation from Growth. The first solution-phase synthesis of metal nanocrystals can be traced back to the 1850s when Michael Faraday prepared stable Au colloids by reducing gold chloride (AuCl) with phosphorus in water.[9] Since this pioneering work, many different methods have been developed for preparing nanocrystals of various compositions; however, most samples from these early studies were plagued with problems that included widely distributed sizes, poorly defined shapes, and limited structures. In a typical synthesis of metal nanocrystals, nucleation must be separated from growth to achieve size uniformity for the final product.[10] To meet this condition, seeded growth has been exploited in which tiny metal nanocrystals or even well-defined metal clusters such as $Au_{101}(PPh_3)_{21}Cl_5$ were added to a synthesis and employed as nucleation centers, or seeds (nonfluxional assemblies of metal atoms), for the growth of larger nanocrystals.[10,11] In this way, the final products could be controllably altered in size, with their dimensions increasing with increasing precursor concentration (note: the seed concentration must be held constant to observe this trend). Additionally, as secondary nucleation events are eliminated due to the introduction of seeds, the size distribution is often narrower than those achieved through nonseeded methods.

Building upon this work, Murphy and co-workers found that Au nanocrystals could seed the growth of Au nanorods, a class of highly anisotropic nanostructures.[12] In such a synthesis, Au nanocrystals were first prepared *via* fast reduction of chloroauric acid ($HAuCl_4$) with sodium borohydride ($NaBH_4$). These tiny particles then served as seeds for further growth when additional precursor, typically $HAuCl_4$, was added and reduced with L-ascorbic acid in the presence of cetyltrimethylammonium bromide (CTAB), $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$. Although the initial synthesis of Au nanorods was reported over 10 years ago, the roles of both the seeds and CTAB in facilitating anisotropic growth have been contested until recently because the structure of the initial seeds were difficult to elucidate.[12,13]

A conceptual breakthrough in nanocrystal synthesis came when it was realized that the shape taken by nanocrystals produced in a solution phase directly correlated to the twinned structure of the seeds present in the synthesis.[4,14,15] This relationship was established by sampling metal nanocrystals at different stages of a synthesis and then analyzing their structures by electron microscopy. It was found that the seeds generated in the initial stage of a synthesis typically

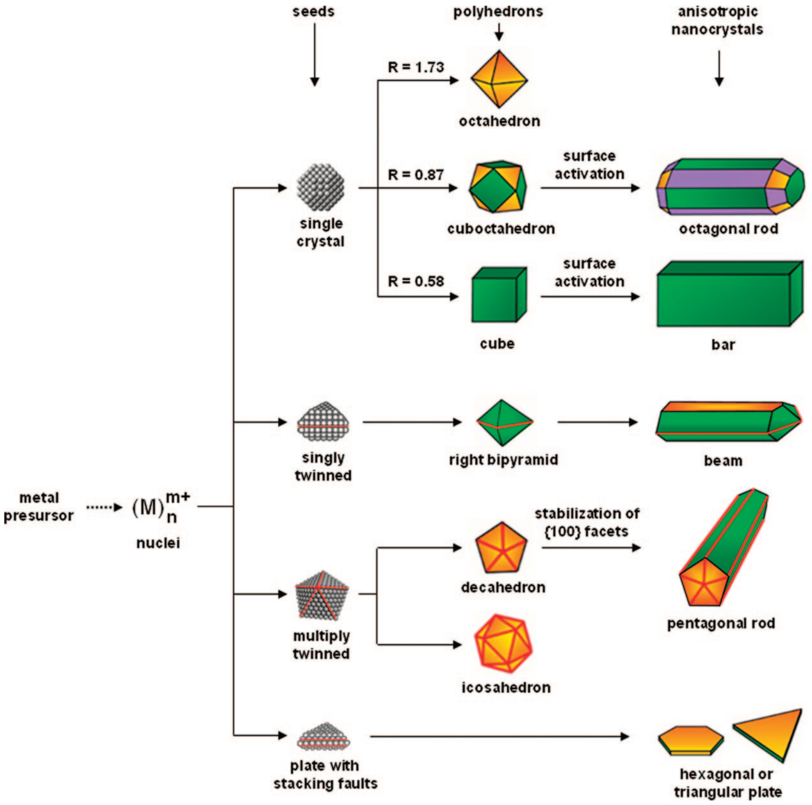

Figure 1. Schematic illustrating the correlations between seeds in single crystal, singly twinned, multiply twinned, and plate-like structures and nanocrystals of face-center-cubic metals with different shapes. Twin plains are delineated in the drawing with red lines. The green, orange, and purple colors represent the {100}, {111}, and {110} facets, respectively. The parameter *R* is defined as the ratio between the growth rates along the ⟨100⟩ and ⟨111⟩ direction. Reproduced with permission from ref 4, Copyright 2009, Wiley-VCH Verlag GmbH & Co.

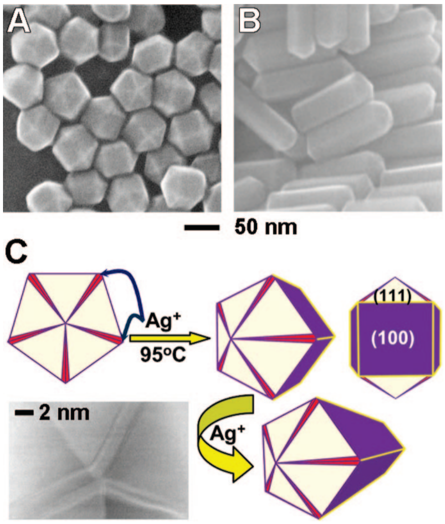

Figure 2. SEM images of Ag nanorods synthesized from decahedral Ag seeds, with edge lengths of (A) 62 ± 3 nm and (B) 142 ± 7 nm. (C) Proposed mechanism for transformation decahedra into nanorods, with a HRTEM image revealing the preferential deposition and reconstruction that occurs at the disclination wedges between facets. Image adapted with permission from ref 19, Copyright 2009 American Chemical Society.

adopted quasi-spherical single-crystal, singly twinned, or multiply twinned structures, which may or may not coexist depending on the experimental conditions. However, as the reaction proceeded, such seeds could grow and evolve into larger nanocrystals with well-defined facets and thus specific shapes. By studying systems in which only one structure was formed for the seeds, it has been shown that (Figure 1) (*i*) octahedrons, cubooctahedrons, octagonal rods, cubes, and rectangular bars all originate from single-crystal seeds; (*ii*) right bipyramids and nanobeams originate from singly twinned seeds; (*iii*) icosahedrons, decahedrons, and pentagonal rods originate from multiply twinned seeds; and (*iv*) triangular and hexagonal nanoplates originate from plate-like seeds containing defects such as stacking faults.[4] The variation in shape that originates from the same type of seed can be attributed to the degree to which a particular crystal facet is stabilized by the capping agent (*i.e.*, polymers or ionic species involved in a synthesis).[4] Thus, in order to prepare one type of metal nanocrystal to the exclusion of others, both the structure of the seed present in solution and the capping ability of solution additives must be controlled.

One of the major challenges to the synthesis of metal nanocrystals has been controlling the population of the various types of seeds involved in a synthesis. In many cases, a mixture of single-crystal, singly twinned, and multiply twinned seeds are present; however, by manipulating reaction kinetics and exploiting processes such as oxidative etching,[16−18] it is now possible to generate exclusively one type of seed over the others. When this condition is met, the synthesis can be thought of as "self-seeded". Such a synthesis can then be allowed to proceed, resulting in nanocrystal growth. Alternatively, these seeds with defined twinned structures can be isolated and then used in syntheses under different reaction conditions. With this ability in hand, better mechanistic studies can be undertaken. For example, Kitaev and co-workers recently reported the synthesis of pentagonal Ag nanorods of tunable lengths *via* a seed-mediated method, and this work provided critical insight into the role of decahedral seeds in forming one-dimensional metal nanocrystals.[19] In their synthesis, decahedral nanocrystals of Ag with a narrow size distribution were first prepared and then employed to seed the growth of pentagonal Ag nanorods; to the seed solution, silver nitrate ($AgNO_3$) was introduced and reduced with citrate. As they have found, the pentagonal cross sections of the resultant nanorods were identical to the dimensions of the initial decahedral seeds and the length of the nanorods increased with increasing $AgNO_3$ concentration. Figure 2A,B shows scanning electron microscopy (SEM) images of their Ag nanorods with two different lengths, grown from the same seed. This detailed analysis provides strong evidence for the following anisotropic growth mechanism: Ag^+ ions are reduced by citrate, with Ag atoms being deposited at locations of the highest surface energy. In the case of decahedral seeds, these locations correspond to the disclination wedges between facets that arise from a geometric mismatch of the five tetrahedral units that comprise a decahedral seed. Alternatively, the disclination wedges can be considered as line defects, in which the rotational symmetry is violated. These features were resolved for the first time in the high-resolution transmission electron microscopy (TEM) image shown in Figure 2C. Thus, with selective deposition of Ag atoms occurring onto the wedges, the {111} end facets of the decahedral seeds are continuously reconstructed, conserving the diameter, while new {100} edge facets are formed and continually elongated. As illustrated in Figure 2C, this process lends support to the mechanism proposed to account for the growth of pentagonal Ag nanowires by the popular polyol

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method.[20,21] As this example reiterates, the size, shape, and particle dispersity can all be controlled by controlling the seeds used in a synthesis.

Accessing New Structures through Seeded Growth. With the role of seeds better understood, it also becomes possible to use seeds with well-defined shapes to obtain increasingly complex nanocrystals that would otherwise be inaccessible by solution-phase methods. For example, with a method very similar to that used by Kitaev and co-workers, Song and co-workers have prepared Ag–Au–Ag heterometallic nanorods in which the ends of Au decahedral particles served as primary sites for Ag deposition, just as in the monometallic example.[22] Figure 3A,B shows a TEM and the elemental mapping of these unique bimetallic nanostructures.

The growth of nanorods *via* a seeded method can be thought of as an example of solution-phase epitaxial growth (or heteroepitaxial growth when the seeds and adatoms are chemically different as in the example by Song and co-workers). Yang and co-workers have explored such heteroepitaxial growth more thoroughly by preparing bimetallic core–shell nanocrystals in which the core consisted of the initial seed used in heteroepitaxial deposition.[23] They found that when there is a close lattice match between the seed and deposited atoms (*e.g.*, Pd and Pt have a lattice mismatch of only 0.77%) conformal deposition results; however, when the lattice mismatch is much greater, nonconformal deposition occurs, which results in shapes not directly correlated to the structure of the seed. Figure 3C–E shows electron micrographs of binary Pt/Pd core–shell nanocrystals obtained by heteroepitaxial deposition of Pd on cubic Pt seeds; the facets exposed on the nanocrystals can be tuned from the {100} to {111} (cubic *vs* octahedral particles) by changing the capping agent and growth conditions. In related work, Xia and co-workers found that by starting with Pd nanoplates heteroepitaxial growth of Pt shells was possible in which the plate-like morphology was maintained, giving rise to bimetallic Pd–Pt core–shell nanoplates as shown in Figure 3F–H.[24] Until the use of seeded methodology, preparation of Pt nanoplates was limited because the high strain energy associated with this structure tends to inhibit its formation in a solution phase. With this example, it appears that solution-phase heteroepitaxial deposition is a general phenomenon to which different starting seed structures may be employed to prepare increasingly complex nanostructures.

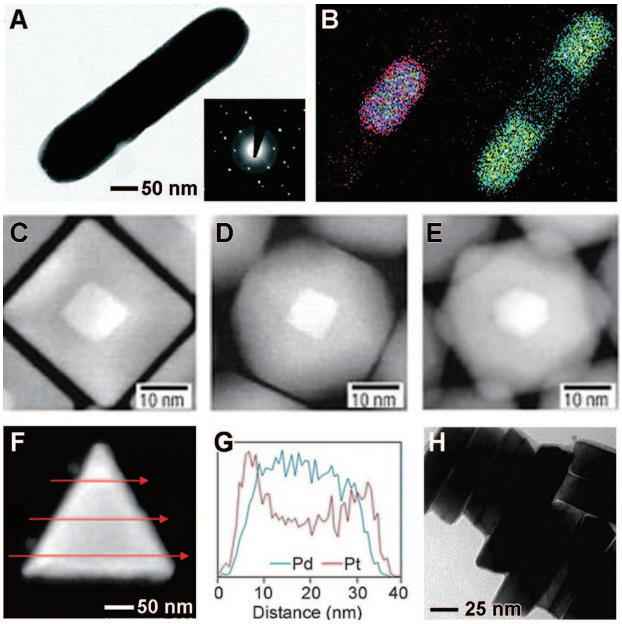

Figure 3. (A) TEM image of a Ag–Au–Ag heterometallic nanorod prepared by a seeded growth process. (B) Elemental mapping of a Ag–Au–Ag heterometallic nanorod; in red, the signal from Au, and in green, the signal from Ag. (C–E) EM images of Pt/Pd core–shell nanocrystals obtained by heteroepitaxial deposition of Pd on cubic Pt seeds. The overall shape of the particles can be tuned from (C) cubic to (D) cubooctahedral and finally (E) octahedral based on the nature of surface stabilization. (F) Binary Pd/Pt core–shell nanoplates prepared by heteroepitaxial deposition of Pt on triangular Pd seeds. (G) An elemental line scan showing the amount of Pd and Pt through the center of the plate. (H) TEM image of the binary Pd/Pt nanoplates in which the different layers can be resolved. (A and B) Reproduced from ref 22, Copyright 2008 American Chemical Society. (C–E) Reproduced with permission from ref 23, Copyright 2007 Macmillan Publishers Ltd. (http://www.nature.com/nmat/). (F–H) Adapted from ref 24, Copyright 2008 American Chemical Society.

In addition to conformal deposition on seeds, nonconformal growth or overgrowth on seeds can be exploited to increase the dimensionality of metal nanocrystals prepared by solution-phase methods. For example, in their study of solution-phase heteroepitaxial deposition, Yang and co-workers found that when there was a large lattice mismatch between the seed and the deposited atoms, the high strain energy would make heteroepitaxial deposition unfavorable.[23] Thus, in the case of Au and Pt, where the lattice mismatch is high (4.08%), Au nanorods with incorporated Pt nanocubes were produced in high yields (Figure 4A), rather than the core–shell structures shown in Figure 3C–E. Still, even in cases where there is minimal lattice mismatch, growth can deviate to give unpredictable structures when seeded techniques are employed. For example, Yang and co-workers recently prepared bimetallic Pt–Pd nanocrystals in which the deposition of Pd was localized to the corners of the cubic Pt seeds.[25] Single, double, and multiple nucleation of Pd on Pt seeds were observed depending on the reaction conditions, with a TEM of one class of nanocrystals shown in Figure 4B. The formation of multiple nucleation sites, rather than conformal growth, was attributed to the high rate of precursor reduction achieved with L-ascorbic acid at high solution pH. At pH 7, conformal deposition was observed. In a related study, Xia and co-workers also discovered the synthesis of Pd–Pt branched nanostructures through a seeded overgrowth process (unpublished results). As a final example of seed-mediated overgrowth, Vaia and co-workers reported the synthesis of complex Au–Ag nanorods.[26] In this case, they started with Au rods prepared by a method similar to the one

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developed by Murphy and coworkers. These Au rods were then used to seed the deposition of Ag, which occurred preferentially on the terminus of the rod. The final product displayed highly faceted, arrow-like Ag tips (Figure 4C). This unique structure was attributed to a competition between underpotential deposition of Ag^+ ions and galvanic replacement between Ag and Au. The capping agents present (CTAB and benzyldimethylhexadecylammonium chloride, BDAC) were also believed to be involved, leaving the ends of the Au rods poorly passivated and enabling localized deposition. As these examples illustrate, seeded growth techniques are enabling the integration of multiple features into one nanostructure. This ability will surely simplify the subsequent assembly of nanoscale building blocks into functional structures.

OUTLOOK AND TECHNICAL CHALLENGES

As these examples illustrate, seeded growth is facilitating the preparation of multicomponent nanocrystals with complex and highly tunable structures. While this Perspective has focused on the seeded growth of metal nanocrystals, a similar approach has also been used to increase the quality and functionality of metal oxide and metal chalcogenide nanocrystals. In particular, there has been a growing interest in constructing nanocrystals that incorporate both semiconductor and metal components (*e.g.*, CdSe–Au hybrids) into well-organized arrangements. In particular, the selective attachment or growth of shape-controlled metal nanocrystals to the ends of semiconductor nanorods represents a means of coupling the tunable optical and electrical properties of semiconductor nanocrystals with the unique properties of various metals.[27] Such hybrid structures may also find use in photonic or sensing applications in which metal-induced quenching or enhancement of photoluminescence signatures would be desirable.[28,29] They may also be useful in energy applications where hybrid assemblies could be used for the generation of electricity or H_2 *via* solar energy conversion.[30]

Yet, there are some technical challenges that will have to be addressed in order to fully utilize these nanostructures. For example, with hybrid metal–semiconductor nanocrystals, good interfacial contact must be established and the two components must be compatible with regards to chemical stability, reactivity, and mechanical properties.[30] With regards to the individual components, the initial seeds used in a synthesis may be dissolved by or corroded by the precursor solution, preventing deposition, and thus seeded growth.[18] In general, dissolution and growth always occur together, so special care must be taken to ensure that the rate of deposition is always greater than dissolution if seeded synthetic techniques are to be employed effectively. Additionally, the surface of the seeds may become oxidized or passivated during isolation, limiting their ability to serve as effective nucleation sites. However, as we have found with the synthesis of Pd nanobars and octagonal rods, it is possible to activate such seeds for growth by exploiting oxidative etching.[15] As illustrated in the previous discussion, these few technical challenges hardly limit the utility of seeded synthetic techniques toward preparing nanocrystals with the quality needed for nanomanufacturing. In fact, in some cases, competitive processes like oxidative etching can be exploited to in-

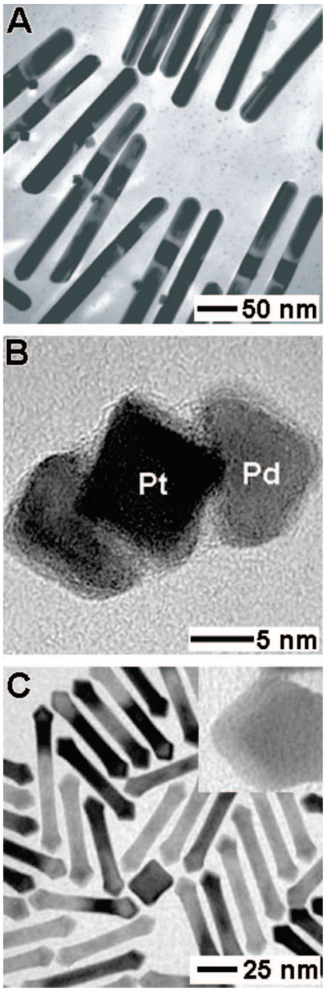

Figure 4. TEM images of bimetallic nanocrystals prepared by nonconformal growth and overgrowth on various types of seeds: (A) Au nanorods with Pt nanocubes incorporated; (B) Pd arms grown from the corners of Pt nanocubes; (C) Au nanorods with highly faceted, arrow-like Ag tips. (A) Reproduced with permission from ref 23, Copyright 2007 Macmillan Publishers Ltd. (http://www.nature.com/nmat/). (B) Reproduced from ref 25, Copyright 2008 American Chemical Society. (C) Adapted with permission from ref 26, Copyright 2008 Wiley-VCH Verlag GmbH & Co.

crease the complexity and quality of nanostructures prepared by seeded synthetic techniques.[18]

Seeded growth has a long history in material science, and with the advent of nanotechnology, it has emerged as a powerful means of precisely controlling the size, shape, composition, and yield of nanocrystals prepared using solution-phase methods. We anticipate that its use will continue to grow as both new types of seeds are generated and as methods for controlling the nonconformal deposition are developed. With these tools in hand, countless multifunctional nanocrystals can be envisioned and synthetically targeted. Additionally, as the size distribution associated with nanocrystals prepared by a seeded growth method is generally narrow, their assembly into larger structures and devices may be possible, having been recently demonstrated for both Ag nanocubes and nanorods.[19,31] The continued development of synthetic routes to increasingly multidimensional building blocks and their assembly into functional structures marks the next and critical stage in nanomanufacturing.

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