

# The Subtle Chemistry of Colloidal, Quantum-Confined Semiconductor Nanostructures

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Solution-phase, benchtop synthesis of quantum-confined semiconductor nanocrystals has opened novel approaches in addressing long-standing challenges facing many scientific and technological endeavors. These research endeavors lie at the interface between chemistry, physics, engineering, materials science, and biology. “Bottom-up” nanocrystals and nanostructures offer numerous advantages over their bulk and thin film counterparts, such as higher and tunable catalytic activity, control over band gap and energy levels, and favorable excited-state carrier relaxation dynamics. Perhaps their greatest advantage is the prospect of synthesizing complex nanostructures that have tailored and synergistic properties by employing simple benchtop synthetic methods. There are, however, challenges and therefore research opportunities with regard to achieving fine control over nanocrystal monodispersity, structure, composition, and defects related to surfaces. Rapid progress in the deployment and use of these nanostructures requires that, at a minimum, the syntheses be reproducible. As will be discussed here, the literature is filled with examples of how trace impurities and choice of precursor can have profound effects on the end product. Researchers must be able to produce the same quality of material under similar reaction protocols but in different laboratories. Therefore, greater understanding of the mechanistic nature of colloidal quantum nanostructure synthesis will enable much needed control over properties such as size and shape dispersion, ligand surface coverage, and composition.

A multitude of bulk crystalline materials have been reproduced in the 1–10 nm length scale and display unique size-dependent properties. Compound semiconductors that

**ABSTRACT**

Nanoscale colloidal semiconductor structures with at least one dimension small enough to experience quantum confinement effects have captured the imagination and attention of scientists interested in controlling various chemical and photophysical processes. Aside from having desirable quantum confinement properties, colloidal nanocrystals are attractive because they are often synthesized in low-temperature, low-cost, and potentially scalable manners using simple benchtop reaction baths. Considerable progress in producing a variety of shapes, compositions, and complex structures has been achieved. However, there are challenges to overcome in order for these novel materials to reach their full potential and become new drivers for commercial applications. The final shape, composition, nanocrystal-ligand structure, and size can depend on a delicate interplay of precursors, surface ligands, and other compounds that may or may not participate in the reaction. In this Perspective, we discuss current efforts toward better understanding how the reactivity of the reagents can be used to produce unique and complex nanostructures.

have ionic character, such as those composed of atoms from groups II–VI, IV–VI, and III–V, have received the greatest attention because of their lower lattice energy. Great effort has gone into understanding nanoparticle growth, composition, and shape, with the intent of ensuring reproducibility and control. Reaction mechanisms have been explored both in light of solid-state crystal growth and kinetics as well as in the classic synthetic mechanistic approach as it pertains to monomer addition and catalytic delivery agents.

Currently, there are three major solution-based approaches to synthesize semiconductor nanostructures: hot injection,<sup>1</sup> the

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heating-up method,<sup>2,3</sup> and the reduction method.<sup>2,4,5</sup> Inherent to each of these methodologies is a certain amount parameter space that can be explored and manipulated not only in the form of reaction conditions, but also important are elemental and molecular precursors, solvents, terminating ligands, and even chemical impurities, which have been shown to play an important role in the end product.<sup>6,7</sup> These synthetic “knobs”, when turned, enable distinct control over composition and architecture, though they are subtle at times and their mechanisms are often not fully understood.

Significant advances have been made toward purposeful chemical manipulation of nanostructures. The II–VI material CdSe (which has a relatively uneventful past in bulk/film form) is likely the most studied colloidal, quantum-confined semiconductor and, as such, it has become the prototypical system for exploring directed size and shape synthesis. CdSe can occur in three distinct crystal forms: hexagonal wurtzite, cubic rock salt (observed only at high pressure), and cubic zinc blende, which relaxes to the wurtzite phase upon heating. At nanoscale dimensions, the surface free energy can play an important role in determining nanocrystal shape. For example, the metastable zinc blende structure can be stabilized *via* surface strain effects, enabling shape engineering in CdSe structures by tailoring crystal phases derived from both zinc blende and wurtzite phases. In this way, tetrapodal structures of CdSe and CdTe have been synthesized.<sup>8</sup>

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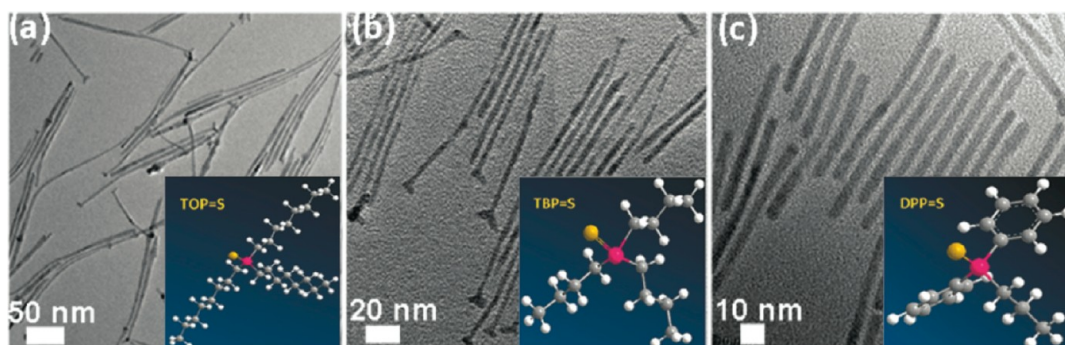
The crystalline and thus faceted nature of nanocrystals opens a door to controlled nanoparticle shape

design by mediating surface ligand protecting groups, which energetically favor particular surface facets.<sup>9,10</sup> Surface ligands aid in stabilizing and isolating nanoparticles in aqueous or organic solvents, and in most cases, they act as stabilizers by reducing the surface energies through bonding with surface metals to reduce surface charge. The ligand–nanoparticle interface is highly dynamic, and its structure depends on factors such as temperature, binding strength of the ligand functional groups to the nanocrystal surface, steric hindrance, and ligand–solvent interactions. Even at room temperature, ligands are in dynamic equilibrium between bound and unbound states as surface-bound ligands continually exchange with neutral ligands at a rate that is inversely proportional to the binding strength and increases substantially as heat is applied to the system. During nanoparticle growth, kinetics can dominate over thermodynamics, and therefore, the binding strength and the time constant at which ligands self-exchange at the surface affect the growth rates of individual facets. Surfaces to which ligands are strongly bound exhibit hindered growth in their respective crystal directions. As a result, the addition of various surface-selective ligands to the reaction mixture alters growth kinetics along different axes, enabling nanocrystal shape control. This kind of ligand-assisted shape control has been exploited in CdSe nanostructures where strongly binding ligands, such as alkyl phosphonic acids, enable well-controlled nanoscale dimensions in CdSe rods, whereas using alkyl phosphonic oxides alone results in large, irregularly shaped rods.<sup>1</sup>

Elemental and molecular delivery agents and their impurities have proven crucial to our understanding of nanoparticle shape evolution. Trioctylphosphine oxide (TOPO) is often used as the solvent in the hot-injection synthesis of CdSe

nanoparticles. Interestingly, the impurities in TOPO have been determined to be at the heart of sample-to-sample variations and monodispersity issues found during typical synthesis. In the past few years, careful study has helped to identify and to elucidate the synthetic influences of the common impurities in commercially available TOPO, and up to 10 alkylphosphonic acids, alkylphosphonates, and alkyl phosphine oxides have been identified.<sup>11</sup> The mechanisms by which these compounds affect colloid growth range from changing the reactivity of precursors to changing rates of colloid growth through selective binding to specific crystal facets. Changing the reactivity of precursors through the formation of more stable reactant complexes increases monomer concentrations and allows anisotropic growth in CdSe nanoparticles. Thus, by selective addition of specific phosphorus-containing compounds to the recrystallized TOPO, the length and diameter uniformity of CdSe nanorods can be tuned and different morphologies, such as branched structures, can be achieved.<sup>11,12</sup> Therefore, apart from acting as a solvent, the role of TOPO in Cd-chalcogenide nanoparticle synthesis is merely as a vehicle to deliver these necessary phosphorus-containing compounds. In fact, it has been shown that in mixed phosphonic acid/phosphine oxide CdSe reactions, passivation of Se surface sites is achieved solely by phosphonic acids, and TOPO is not a necessary component of the reaction as long as the critical phosphonic acids are present.<sup>13,14</sup>

In this issue of *ACS Nano*, Ruberu *et al.* have achieved control of both nanoparticle architecture and composition by exploiting the reactivity of different phosphine–chalcogenide precursors, and they present a model to describe these results in terms of chalcogen–phosphine bond strengths.<sup>15</sup> The reactivity of chalcogenide–phosphines was explored using five



**Figure 1.** Varying aspect ratios for CdS nanorods as a function of phosphine precursors. Adapted from ref 15. Copyright 2012 American Chemical Society. (a) Longest CdS nanorods prepared using trioctylphosphine-S, the least reactive precursor. (b) Intermediate CdS rods using TBP-S. (c) Short CdS nanorods prepared using the most reactive sulfur precursor, diphenylpropylphosphine-S.

commercially available phosphines. The authors find that phosphine–chalcogen bond strength dictates the precursor reactivity, with the weakest bonds producing the most reactive molecular precursors. Figure 1 depicts representative data for how nanoarchitecture can be manipulated using three different phosphine precursors whose bond energies decrease in the following order: trioctylphosphine-S > tributylphosphine-S > diphenylpropylphosphine-S. The length-to-diameter ratio in CdS nanorods is strongly affected by precursor reactivity, showing a decrease in the rod aspect ratio with decreasing bond energy (increasing precursor reactivity).

Subtle differences in reactivity rates enable the synthesis of unique materials with composition-dependent properties that cannot be achieved in bulk or in thin film forms. In order to tune these properties, controlled materials integration must be achieved. For example, alloyed nanomaterials have been pursued in order to control band gap independent from other size-dependent properties. To achieve a homogeneous alloyed nanostructure, the relative reactivity of the anion precursors must be balanced. With knowledge of precursor reactivities in hand, Ruberu *et al.* found that nanoparticle stoichiometries could also be adjusted according to the concentrations of different phosphine–chalcogenide precursors in CdSe/S

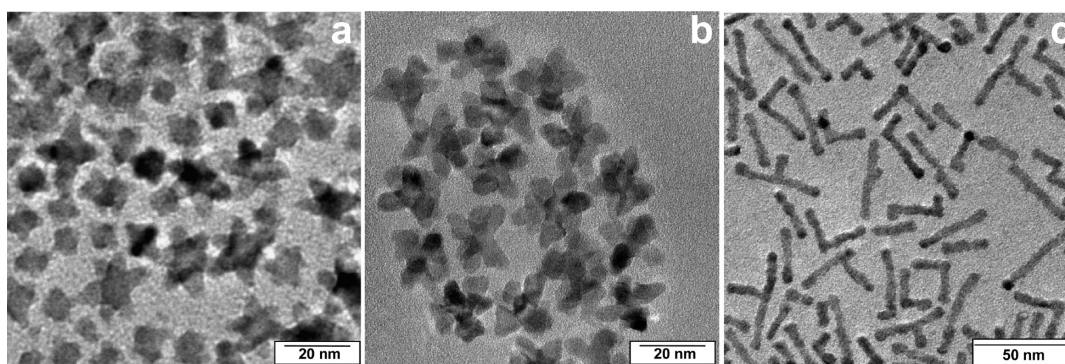
systems, moving from alloyed to core–shell structures.<sup>15</sup> The degree of radial alloying was changed by pairing precursors with similar or dissimilar reactivity, leading in some cases to the formation of asymmetric structures due to the disparities in nucleation rates.

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A wealth of unique properties results from such shape control in nanostructures; however, in many cases, the precise application of these anisotropic shaped nanostructures is still to be uncovered and exploited. One particular application that has seen many beneficial attributes from quasi-one-dimensional (1D) (*i.e.*, “rod-like”) nanocrystals is solar photoconversion. For photovoltaics (electricity derived from sunlight), nanorods of CdSe show improved electron

transport properties compared to spherical crystals in solar cells where the nanocrystals are blended with light-absorbing, hole-conducting polymers.<sup>16</sup> For photoelectrochemistry (chemical fuels derived from sunlight), complex heterostructured nanorods consisting of a small CdSe quantum dot (QD) embedded in a CdS nanorod with a Pt catalyst grown on the tip provide the unique advantage of being able to control the separation distance between the photogenerated electron and hole by changing the rod length.<sup>17</sup> Another enticing avenue of research involves exploring the phenomenon of multiple exciton generation (MEG) as a function of nanocrystal shape. Multiple exciton generation has shown to benefit from quantum confinement (QDs more efficiently undergo MEG than bulk crystals),<sup>18</sup> and further enhancement is also observed upon 1D shape manipulation.<sup>19</sup> Enhancement of MEG in 1D structures occurs due to the larger Coulomb interaction in anisotropic systems over isotropic structures.<sup>20</sup> Further increases in the MEG efficiency are needed to have the largest impact on solar photoconversion, and shape control may be a critical “knob” for enhancing this process.

The high level of complexity achieved for CdX (X = S, Se, Te) has allowed researchers to build an arsenal of tools for creating unique nanostructures, and these tools have, in turn, been used as a basis



**Figure 2.** Selective oriented attachment/growth of  $\{100\}$  faces during PbSe nanoparticle growth results in (a) nanostars which in time evolve into (b) large hexapodal structures. (c) PbSe nanorods prepared by oriented attachment using the Koh *et al.* synthesis.<sup>29</sup>

for synthetic shape control in other material systems. However, the same techniques do not always translate to other semiconductors, and shape control has become a new challenge in systems with greater symmetry such as the rock salt crystal lattice. The lead chalcogenides serve as a particularly good model system for understanding unique quantum confinement effects because they possess large bulk Bohr exciton radii and thus are under extreme confinement when their dimensions are reduced to less than 20 nm.<sup>21</sup> For example, although bulk PbSe has a band gap of 0.279 eV, high-quality nanocrystals of PbSe are easily synthesized that can exhibit band gaps as high as 2.0 eV. Unlike the II–VI materials, however, where a unique crystallographic direction lends itself to high levels of structural complexity, the crystal structure of the Pb-chalcogenides is highly symmetric, and thus symmetrically shaped crystals (quasi-spherical to cube-like crystals) are favored during growth. For the IV–VI materials, not only do ligand–QD interactions play a role in deliberate shape control, but also QD–QD, ligand–ligand, and ligand–solvent interactions are likely important factors that must be considered. Precursor reactivity is, however, still an important parameter for tuning composition as well as shape.

In much the same way that ligand-assisted shape control can

be achieved in the II–VI system, the surface growth in PbX salts can likewise be tuned. For instance, selective strong binding of aliphatic primary amines to the  $\{111\}$ <sup>22</sup> facets of PbSe leads to the formation of octahedral particles due to growth of the  $\{100\}$  faces.<sup>23</sup> Recently, we demonstrated similar facet-selective binding when applying a new octadecylselenide ligand to PbSe QDs, where the ligand primarily attaches to the  $\{111\}$  facets, thus retarding further growth, and leading to multipodal structures as seen in Figure 2a and b.<sup>24</sup> Amines also play important roles in the formation of PbSe 1D structures. Koh *et al.* found that by incorporating tris(diethylamino)phosphine selenide in place of TOP-Se, but otherwise using similar reaction conditions, produced 1D structures rather than isotropic structures (Figure 2c).<sup>25</sup> While the role of the amine is unclear, it likely plays a role in hindering growth in certain crystal directions. However, the kinetics and mechanism must be quite different than in the CdSe system, as simply blocking one face over another will not lead to anisotropic growth in the isotropic PbSe system. Therefore, the mechanism must include some component of QD–QD or ligand–ligand interaction that is generally termed “oriented attachment”.

In the oriented attachment mechanism, isotropic QDs first form and then fuse along a specific

crystallographic direction during the reaction, which has been recorded in real-time by Yuk *et al.* with Pt nanocrystals.<sup>26</sup> Oriented attachment is distinct from continued growth along a specific crystallographic axis and is a powerful tool that has been invoked in the preparation of complex PbSe structures such as nanowires, rings, and other complex anisotropic structures. Cho *et al.*<sup>23</sup> originally proposed that oriented attachment proceeds due to large dipoles that result due to Se- and Pb-rich  $\{111\}$  surfaces on an otherwise isotropic nanocrystal. However, further studies have tended to contradict this assessment by showing that PbSe nanocrystal surfaces reconstruct to lower their surface energy and, thereby, greatly reduce any dipoles that might otherwise form.<sup>27</sup> Furthermore, the majority of PbSe nanocrystals tend to be Pb-rich with Pb atoms terminating all surfaces, which results in an isotropic structure with greatly reduced dipole moments. Another approach to shape control in the IV–VI system is ion exchange, whereby a template nanocrystal structure can first be built and then chemically transformed into the material of interest. Luther *et al.* introduced a procedure to convert CdS to PbS via a two-step ion-exchange reaction.<sup>28</sup> Therefore, any shape or structure that can be synthesized using the well-known techniques discussed above for CdX synthesis

can be converted to PbX *via* this chemical reaction.

For the Pb salts, attempts have been made to elucidate the roles of certain precursors and to describe accurate reaction schemes from monomer formation to monomer addition in the growth of stable colloids.<sup>22,30</sup> In the same way that phosphorus-containing impurities in TOPO are responsible for tuning reaction conditions during the synthesis of CdSe quantum structures, secondary phosphine impurities in TOP play important roles in the growth of the lead salts. Evans *et al.* determined that the irreproducibility of QD size and variations in chemical yield were due in part to batch-to-batch variation in the amount of higher reactivity secondary phosphine impurities that exist in technical grade TOP, whose role may only be to serve as a means of homogeneous Se delivery to the reaction mixture.<sup>22</sup> <sup>1</sup>H and <sup>31</sup>P nuclear magnetic resonance analyses revealed that, following postsynthetic isolation of PbX quantum dots, no appreciable amount of TOP remained in solution, indicating that it does not contribute significantly to surface passivation.<sup>31</sup>

Small quantities of secondary phosphines found in TOP were determined to be responsible for higher conversion yields through the creation of a reactive intermediate formed upon introduction of secondary phosphines to reaction baths containing metal carboxylate species. Despite this adventitious behavior, there remain many unknowns about how to fine-tune growth conditions using pure secondary phosphine-Se and, as a result, standard QD synthetic procedures continue to employ TOP-Se as the phosphine–chalcogenide precursor. However, TOP is not the only potential source for trace impurities during the synthesis of PbSe nanoparticles. Houtepen *et al.* observed that during PbSe syntheses, when using lead acetate as the lead precursor, trace amounts of acetate impurities inhibited growth

of spherical nanocrystals.<sup>32</sup> Instead, star-shaped particles formed as a result of faster oriented attachment of small PbSe crystals to the {100} surface, presumably from acetate blocking the {111} surface.

Phosphines are not the only vehicles for delivering chalcogen substituents during QD growth of IV–VI materials, and more reactive compounds such as TMS<sub>2</sub>-based precursors have also been employed to affect both yield and composition. Following the previously mentioned approach to changing the anion precursor reactivity in order to tune the growth of ionic nanocrystals, Smith *et al.* demonstrated unique control in the alloying of the entire Pb-chalcogenide family.<sup>6</sup> Highly reactive TMS<sub>2</sub>-based anion precursors, rather than TOP-X (X = S, Se, Te), ensure incorporation of the desired anion into the nanoarchitecture, and combinations thereof can be exploited to form gradient core–shell rather than uniformly alloyed crystals, which are promising tools for engineering electronic properties.<sup>33</sup>

#### OUTLOOK AND FUTURE CHALLENGES

We are constantly amazed by the continued growth of research in this field. Each week brings new insights into the chemistry of semiconductor nanocrystals, new material combinations, and finer control over morphology, surface composition, and structure. Nanocrystal syntheses are generally performed with simple, safe, and solution-phase procedures that can be widely replicated by a diverse set of scientists. The ability to incorporate these structures into novel functional solids is increasing at an encouraging rate and is a testament to the growing knowledge base of nanocrystal synthesis. In order for quantum-confined nanostructures to have the largest technological impact, we must continually seek to move beyond these basic challenges of reproducibility and growth mechanisms to a deeper

understanding of obtaining precise control over nanocrystal formation that will enable further engineering of nanostructures with unique and desirable properties. However, incorporation of these novel nanostructures in new approaches and strategies for controlling excited-state dynamics, energy flow, photoluminescence, and other beneficial effects needs not wait for a complete mechanistic understanding of the QD synthesis. Already, proof-of-principle demonstrations utilizing QDs in photovoltaic devices have shown the potential benefits of quantum-confined semiconductor nanocrystals for enhancing solar photoconversion.

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We conclude by highlighting two recent areas that demonstrate a fraction of the exciting prospects in store for quantum-confined nanostructures. The anisotropic structures discussed above have opened new avenues for constructing

complex functional nanostructures. The reactivity of 1D nanostructures differs along the length of the structure, with the ends having different reactivity than the middle. Researchers have exploited this difference in reactivity to deposit a different material selectively at the more reactive site, such as at the tip of the nanostructure. For example, Alemseghed *et al.* demonstrated selective deposition of Pt and Pd on CdS/Se alloyed 1D nanostructures.<sup>34</sup> The metal could be deposited in different locations depending upon the irradiation wavelength. New types of nanoheterostructures can be envisioned and constructed using this approach with great promise for controlling electron–hole separation, energy flow toward reactive sites, or approaches and applications yet to be imagined. Elsewhere, Iturria and Dubertret discovered that CdSe nanoplatelets can be produced with great precision over the thickness of the sheet.<sup>35</sup> In this case, Cd acetate salts are shown to be critical for platelet formation. The optical properties of these nanoplates are governed mainly by the thickness of the nanoplates, and the dispersion in thickness is one CdSe monolayer. These examples and others demonstrate that, due to the ingenuity, imagination, and dedication of researchers worldwide, the field of quantum-confined semiconductors will continue to have a bright and exciting future.

*Conflict of Interest:* The authors declare no competing financial interest.

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