

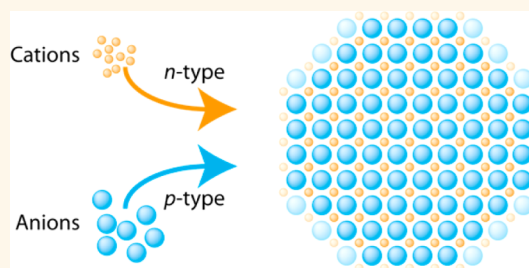
# Stoichiometry Control in Quantum Dots: A Viable Analog to Impurity Doping of Bulk Materials

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**ABSTRACT** A growing body of research indicates that the stoichiometry of compound semiconductor quantum dots (QDs) may offer control over the materials' optoelectronic properties in ways that could be invaluable in electronic devices. Quantum dots have been characterized as having a stoichiometric bulk-like core with a highly reconstructed surface of a more flexible composition, consisting essentially of ligated, weakly bound ions. As such, many efforts toward stoichiometry-based control over material properties have focused on ligand manipulation. In this issue of *ACS Nano*, Murray and Kagan's groups instead demonstrate control of the

conductive properties of QD arrays by altering the stoichiometry *via* atomic infusion using a thermal evaporation technique. In this work, PbSe and PbS QD films are made to show controlled *n*- or *p*-type behavior, which is key to developing optimized QD-based electronics. In this Perspective, we discuss recent developments and the future outlook in using stoichiometry as a tool to further manipulate QD material properties in this context.



At the heart of materials nanoscience is the familiar theme that “Size matters!”, which is to say that nanoscopic objects, almost as a rule, offer surprisingly different properties than larger “bulk” crystals of the same material. For instance, in crystals of semiconductor materials of sizes on the order of 1–10 nm, quantum confinement of electronic wave functions leads to quantized, size-dependent energy levels. These so-called “quantum dots” (QDs) can exhibit tunable absorption onsets, bright photoluminescence (PL), and other potentially useful properties. This confinement is particularly common in colloidal QDs, which are free-standing, solution-dispersible nanocrystals made *via* a “bottom-up” approach employing low-cost, scalable wet-chemical methods. This unique class of materials is the subject of intense research for a wide variety of applications in optoelectronic devices, photochemical and catalytic processes, bio labeling, *etc.*, and thus colloidal synthesis has become a key development in the advancement of nanotechnology. However, such small size can be a double-edged sword, as QDs are inherently surface dominated. Large, tunable surface-to-volume ratios can be innately beneficial in catalytic applications,

but historically, QD surfaces have required keen attention because surface termination critically affects growth kinetics as well as post-synthesis properties like optical properties.<sup>1</sup>

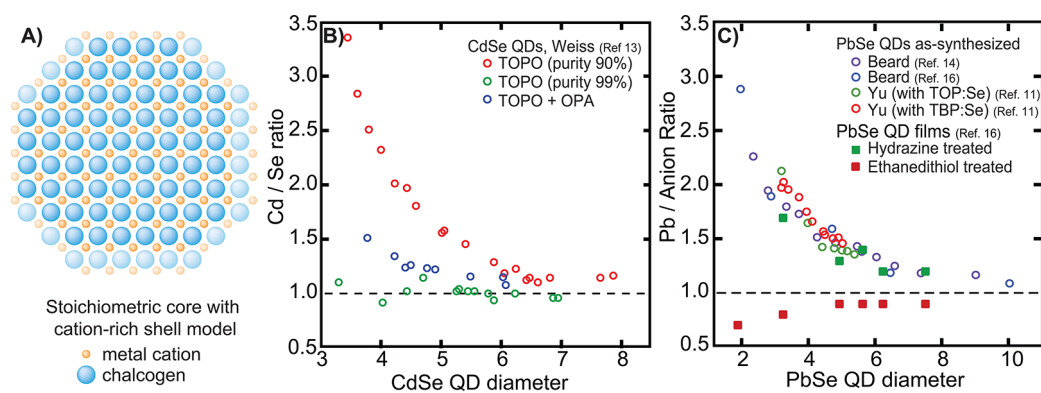
## Small size can be a double-edged sword, as QDs are inherently surface dominated

Being essentially all surface has been particularly frustrating to the development of QD-based electronic devices. In an important example, the electronics industry has long benefited from using impurity atoms (or “dopants”) as a powerful way to control the functionality of bulk semiconductors. This strategy enables, for instance, *p*–*n* junctions, which are at the heart of solid-state technology, including solar cells. While using impurity atoms in colloidal QDs has seen some success, persistent doping remains challenging due to the unavoidable proximity of the surface relative to dopant diffusion lengths, especially during growth or processing at elevated temperatures.<sup>2</sup> At surfaces, dopants can become electronically passive,

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**Figure 1.** 2D rendering of an atomic QD model showing a cation-rich shell (partially transparent) surrounding a stoichiometric core (solid). This model of a rock-salt structure specifically describes the size-dependent Pb/Se ratio, which trends with the surface/volume ratio. (b) Cd/Se ratios as a function of size from Weiss,<sup>13</sup> showing how the trends depend on the surfactant purity. *n*-Octylphosphonic acid (OPA) is added to high purity trioctylphosphine oxide (TOPO) to achieve intermediate size-dependent values. (c) Data compiled from literature reports of Pb/Se ratios in PbSe QDs synthesized and measured by varied methods,<sup>11,14,16</sup> including the use of different Se precursors (trioctylphosphine selenide, TOP:Se, and tributylphosphine selenide, TBP:Se, from Yu<sup>11</sup> are shown). Squares show data on conductive films of PbSe QDs treated either with hydrazine (green) or 1,2-ethanedithiol (red) to enhance electronic coupling. The hydrazine films show Pb/Se ratios similar to as-synthesized QDs, whereas EDT-treated films show anion-rich (Se+S) stoichiometry.<sup>16</sup>

and can even be expelled from the QD entirely. However, lately a growing body of research suggests that these troublesome surfaces may actually offer completely new and uniquely accessible means for achieving controllable doping in QD films.

**Stoichiometry of colloidal QDs.** Quantum dots of metal chalcogenides, and of CdSe, PbS, and PbSe in particular, have been at the forefront of progress in the development of QD electronic devices. Syntheses of these materials, accordingly, have been heavily studied and greatly refined; nonetheless, the principles behind the organic-solvent-based synthetic methods remain similar to those of early reports.<sup>3–6</sup> These so-called “colloidal” syntheses bring together metal and chalcogenide precursors in hot (typically 150–300 °C) mixtures of organic solvents and surfactants to create conditions analogous to those described decades ago by LaMer and Dinegar for the formation of monodisperse colloids.<sup>7</sup> According to this model, supersaturation of precursors causes a singular “nucleation” of small metal chalcogenide clusters. These nascent QDs then “grow” by reactively adding precursors until the precursor concentrations are diminished enough to reach an equilibrium point, at which the forward reaction of precursor addition

occurs at a similar rate to the reverse reaction of surface redissolution. The ligands serve a number of important functions during colloidal QD synthesis, including promoting and/or controlling the precursor reactivity during nucleation, and stabilizing the QDs during growth. In fact, the strength of the interaction between the metal ions and chosen Lewis basic surfactant molecules, particularly for cadmium and lead chalcogenides, typically leads to formation of overall cation-rich stoichiometries in the product particles (Figure 1), as can be determined by techniques including X-ray photoelectron spectroscopy (XPS),<sup>1,8</sup> Rutherford backscattering (RBS),<sup>8–10</sup> and inductively coupled plasma optical or mass spectrometry.<sup>11–14</sup>

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In fact, studies of CdSe QDs have shown that the stoichiometry is heavily dependent on synthesis conditions, but is more sensitive to the purity and amount of surfactant ligands present in the synthesis than to the ratio of Cd/Se precursors.<sup>13</sup> Moreover, Weiss and colleagues have noted a size dependence in the stoichiometry variation of CdSe QDs<sup>13</sup> that correlates well with the surface-to-volume ratio, supporting Hens’ model that colloidal QDs combine a stoichiometric “bulk-like” core with an outer shell of ions in which faceting leads to a more varied composition.<sup>12</sup> In this model, surface (and near-surface) atoms are more mobile and will reconfigure to produce at least a local minimum surface energy.<sup>15</sup> Regardless of an imbalance of charges within the strictly inorganic part of QDs, they can achieve overall charge neutrality through binding to ionic ligands, although this functionalization can have important ramifications for their optical properties. Jasieniak and Mulvaney have described how the surface stoichiometry can affect carrier trapping and, in turn, photoluminescence (PL) quantum yield (QY), by intentionally terminating CdSe QDs with Se- or Cd-rich surfaces.<sup>1</sup> In each case, the surface ligand-passivation strategy changes: Se-rich

QDs are well-passivated by trioctylphosphine, whereas amines bind to Cd-rich QDs, and thus high PL QYs are possible in either configuration.<sup>1</sup>

Interestingly, metal/anion ratios in as-prepared PbSe QDs generally follow the same size-dependent trends observed in CdSe QDs,<sup>11,12,14</sup> but Yu specifically notes that the stoichiometry does *not* depend on reaction conditions, solvents, or precursors. This has made direct observation of the effect of surface composition on properties such as PL QY more challenging. Beard and colleagues recently reported the treatment of PbSe QDs with a long-chain alkylselenide ligand after synthesis.<sup>16</sup> The alkylselenide binds to Pb ions, particularly at the {111} surface facets, to reduce the overall Pb/Se ratio while maintaining complete surface passivation. As was found by Jasieniak and Mulvaney for CdSe,<sup>1</sup> surface anions on PbSe directly affect valence band states; the use of the alkylselenide ligand induces hole traps, but also diminishes the propensity of the QDs to oxidize under ambient conditions.<sup>16</sup> In contrast, Klimov and Pietryga found that postsynthesis exposure of PbSe QDs to dilute solutions of chlorine (Cl<sub>2</sub>) preferentially removes surface Se ions, leading to even greater overall enrichment of Pb.<sup>17</sup> Cl<sub>2</sub> oxidizes the Se ions, which are replaced by Cl<sup>-</sup> ions to create a thin inorganic passivating layer of PbCl<sub>2</sub> that greatly enhances the resistance of these QDs toward oxidation without creating new hole traps, resulting in increased PL QY.<sup>17</sup>

**Influence of Stoichiometry on Conductivity.** The conductive behavior of PbE (E = S or Se) QD thin-film arrays has gained significant attention of late because of the importance of such narrow-band gap materials to devices like photodetectors and solar cells. Indeed, PbE is an inherently interesting system in which to study the relationship between stoichiometry and electronic properties, because in bulk films, the majority carrier type can be manipulated *via* stoichiometry: For instance, Pb (or

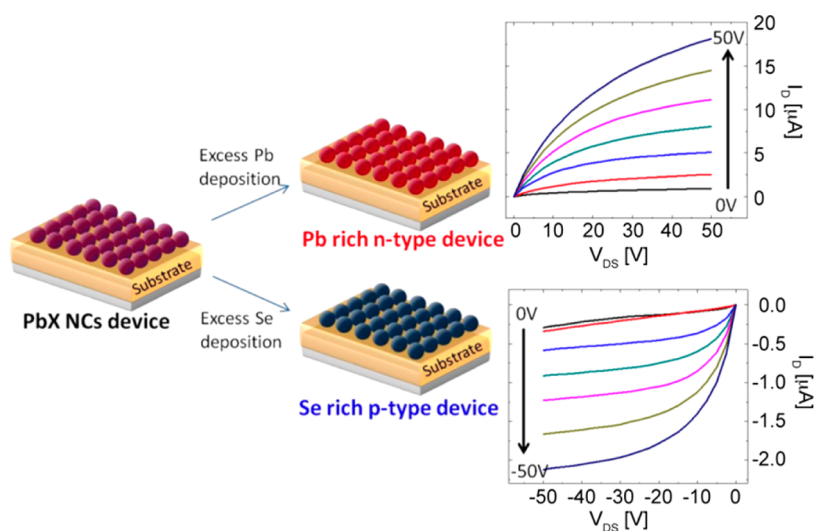
Se) deficient layers produce p-type (or n-type) films.<sup>18</sup> The concept of applying this type of control to QD arrays in general has recently been modeled,<sup>8</sup> supporting that the effect of stoichiometry on carrier properties might be especially pronounced in PbE QD films. Such systems witnessed a breakthrough in 2005 when Talapin and Murray found that PbSe QD arrays display appreciable long-range conductivity when treated with nucleophilic reagents that exchange or remove surface-bound ligands.<sup>19</sup> Specifically, hydrazine-treated films display strong n-type behavior in field-effect transistors, until a mild heat treatment (that removes hydrazine) switches the majority carrier to p-type.<sup>19</sup> Beard and colleagues found that hydrazine-treated PbSe arrays retain Pb-rich stoichiometries, whereas another popular surface treatment, 1,2-ethanedithiol (EDT), shifts the stoichiometry toward anion-rich, as thiols effectively append S ions to the surface.<sup>16</sup> As expected by stoichiometry arguments, EDT-treated films show persistent p-type conductivity under illumination<sup>20–22</sup> and form the basis for research on photovoltaics based on QD-arrays that exploit multiple exciton generation<sup>23</sup> (also known as carrier multiplication<sup>24</sup>) to boost the amount of current produced under solar illumination.<sup>20,25</sup>

In this issue of *ACS Nano*, Oh *et al.* from the groups of Murray and Kagan at the University of Pennsylvania use a novel approach to postsynthesis stoichiometry control, which is the direct thermal evaporation of Pb or Se atoms onto ligand-exchanged arrays, as a means to develop well-controlled n- and p-type PbE QD films.<sup>26</sup> Specifically, field-effect transistors (FETs) are fabricated from thiocyanate-treated<sup>27,28</sup> PbSe QDs, which display (on average) ambipolar behavior, reflecting the balance between the inherent n-type behavior arising from the slightly Pb-rich stoichiometry, and some amount of p-type character that can result from unintentional exposure to oxygen. A controlled amount

of Pb corresponding to a thickness between 1 and 4 Å, or of Se corresponding to between 0.1 and 0.4 Å, is then evaporated onto the transistor. The result is a shift of the threshold voltage to more negative values with Pb, or positive values with Se, as the Fermi level moves closer to the conduction or valence band, respectively. Additionally, as shown in Figure 2, the transistor output characteristics display conduction associated with n- or p-type behavior where the carrier concentration can be increased from the intrinsic level of 10<sup>16</sup> cm<sup>-3</sup> up to 10<sup>19</sup> cm<sup>-3</sup> for Pb-infused or 10<sup>18</sup> cm<sup>-3</sup> for Se-infused devices.<sup>26</sup>

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As a demonstration of the utility of these methods, Oh *et al.* probe the effects of Pb and Se deposition on the energetics of PbSe QD Schottky-junction solar cells.<sup>26</sup> Mild (0.2 Å) deposition of Se results in larger photovoltages and higher current densities, while a similar amount of Pb produces the opposite effects. These effects are attributed to changes in the degree of band-bending at the Schottky junction that result from the shift of the Fermi level in each case. Thus, extrinsic, postdeposition techniques for doping of QD thin films, whether the dopants are delivered as atomic vapor or, perhaps, in solution, may represent facile pathways to p–n and p–i–n structures for efficient charge separation, or even to graded doped layers, for example, n–n<sup>+</sup>



**Figure 2.** Schematic diagram of arrays of PbSe QDs that show enhanced n-type behavior with Pb-rich, or p-type behavior with Se-rich, stoichiometries. The output characteristics for an n-type (right, top) FET and p-type (bottom) FET show the effects of the enrichment, where the  $I_D$ - $V_{DS}$  curves are plotted for varying gate voltages as indicated in the plots. Adapted from ref 26. Copyright 2013 American Chemical Society.

layers, for improved carrier extraction at electrodes.<sup>29</sup>

While stoichiometry manipulation is an intriguing avenue toward effective doping of QDs, other research suggests that complete control over doping must also contend with, and perhaps even exploit, surface trap states, including those that can arise as a result of anion-rich stoichiometry.<sup>1,16</sup> In fact, Oh *et al.* raise the important issue of compensation of the intentional doping by “unintentional dopants” (*i.e.*, surface trap states) when comparing Hall-effect and FET mobility measurements, and Nagpal and Klimov show in similar measurements that trap states are the cause of p-type photoconductivity in films of EDT-treated PbS QDs.<sup>30</sup> Thus, generating n-type conductivity in QD films would seem to require either substantial excess dopant, or careful efforts to retain effective passivation. Recently, for instance, Sargent applied halide-ion passivation to PbS QD solids to render n-type behavior.<sup>31</sup> Similar to the hydrazine treatment initially developed by Talapin and Murray,<sup>19</sup> the QD solid remains as enriched in group-IV atoms as when the QDs were synthesized.<sup>8</sup> Surface chlorine has been shown to balance the extra cation charges

on cation-rich QD surfaces<sup>9</sup> without adding the chalcogen of thiols or alkylselenides, allowing the film to retain n-type properties.

More recent work by Talapin and colleagues demonstrates that one can take advantage of excellent binding properties of chalcogenides and still exert control over the dominant carrier type in films through the intercession of additional metal cations. For instance, films of CdSe QDs treated with molecular metal chalcogenide complexes<sup>32</sup> exhibit n-type behavior. The use of metal-free chalcogenide complexes as ligands in conjunction with additional metal cations offers even more flexible control over film stoichiometry and majority carrier type, particularly in QD films based on materials such as PbE or CdTe that do not exhibit a strong tendency toward one carrier type. In one specific example,  $K_2Te$  treatment produces p-type CdTe QD films,  $In_2Te_3$  yields ambipolar behavior, whereas  $In_2Se_4^{2-}/N_2H_5^+$  enables n-type behavior.<sup>33</sup>

**Outlook and Future Challenges.** The developments we have highlighted in this Perspective show that there has been tremendous progress in new strategies toward doping the undopable,<sup>34</sup> in particular involving

manipulation of QD stoichiometry. The ongoing development of methods for altering stoichiometry *after synthesis*, whether *via* thermal evaporation or perhaps through solution-based methods, offers intriguing flexibility relative to attempts to alter QD composition during colloidal growth. This is especially true for shape-controlled, heterostructured, and other complex classes of QDs in which parameters such as growth temperature, ligand identity, and precursor ratios are greatly restricted by the needs of a particular reaction. Finally, it is relatively easy to picture these methods achieving the level of finely graded doping control within films that the modern semiconductor electronics industry, using methods such as ion-implantation, is built on. A more intriguing possibility to consider, however, is whether these methods can offer control yet unimagined by today's industry, perhaps to induce junctions or to provide directional fields in single quantum-confined nanorods or nanowires. Undoubtedly, the complexity of colloidal nanoparticle surfaces, which seemingly adapt in response to numerous underappreciated stimuli at every point in their growth and processing, will present a substantial



stumbling block to reaching this level of structural command. However, if recent progress is any indication, every surface-based problem eventually yields a surface-based solution.

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

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