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Citation	Kim, Donghun, Dong-Ho Kim, Joo-Hyoung Lee, and Jeffrey C. Grossman. Impact of Stoichiometry on the Electronic Structure of PbS Quantum Dots. Physical Review Letters 110, no. 19 (May 2013). © 2013 American Physical Society.
As Published	http://dx.doi.org/10.1103/PhysRevLett.110.196802
Publisher	American Physical Society
Version	Final published version
Citable link	http://hdl.handle.net/1721.1/81326
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Impact of Stoichiometry on the Electronic Structure of PbS Quantum Dots

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(Received 17 September 2012; revised manuscript received 25 December 2012; published 7 May 2013)

Although the stoichiometry of bulk lead sulfide (PbS) is exactly 1:1, that of quantum dots (QDs) can be considerably different from this crystalline limit. Employing first-principles calculations, we show that the impact of PbS QD stoichiometry on the electronic structure can be enormous, suggesting that control over the overall stoichiometry in the QD will play a critical role for improving the efficiency of optoelectronic devices made with PbS QDs. In particular, for bare PbS QDs, we find that: (i) stoichiometric PbS QDs are free from midgap states even without ligand passivation and independent of shape, (ii) off stoichiometry in PbS QDs introduces new states in the gap that are highly localized on certain surface atoms, and (iii) further deviations in stoichiometry lead to QDs with “metallic” behavior, with a dense number of energy states near the Fermi level. We further demonstrate that this framework holds for the case of passivated QDs by considering the attachment of ligand molecules as stoichiometry variations. Our calculations show that an *optimal* number of ligands makes the QD stoichiometric and heals unfavorable electronic structure, whereas too few or too many ligands cause effective off stoichiometry, resulting in QDs with defect states in the gap.

DOI: [10.1103/PhysRevLett.110.196802](https://doi.org/10.1103/PhysRevLett.110.196802)

PACS numbers: 73.21.La, 71.15.–m, 73.63.Kv

Photovoltaic (PV) cells that utilize quantum dots (QDs) in the active layer have gained much attention recently because of their potential as high-efficiency, low-cost, and air-stable devices for sustainable solar energy conversion. The power conversion efficiencies of QD-PVs based on lead sulfide (PbS) have been enhanced dramatically in only several years to the current record of 7.0% [1], owing to the favorable optical properties of PbS QDs including facile tunability of band gaps with the variation in dot sizes or shapes [2,3], wide spectral responses [4], and multiple exciton generation [5]. Yet, despite these beneficial optical properties, the performance of QD-PVs is still limited by the low electron and hole mobilities of the QD thin films, in the range of 10^{-4} to $0.1 \text{ cm}^2/\text{V s}$ [6], due mostly to the high trap state density [1] in the film. A wide variety of surface ligands have been employed as passivating agents in an attempt to remove such trap states [7,8]; however, only limited improvement has been demonstrated thus far, primarily due to the fact that a fundamental understanding regarding the origin of trap states is lacking in these materials.

In contrast to the effects of QD shape and size on key opto-electronic properties, which have been investigated extensively [9,10], relatively little attention has been given to an additional critical feature in such materials, namely, their stoichiometry. Control over the QD surface stoichiometry in experiments has been considered extremely challenging, although a number of approaches to

achieving tunability are possible; recent experiments have demonstrated that QD stoichiometry control is feasible simply by altering ligand types [11]. Given the potential for stoichiometry to become a QD attribute as tunable as size and shape, and given the need to improve the electronic properties of QD films for enhancing device efficiencies, a detailed, atomic-scale picture of the impact of stoichiometry on the electronic structure of QDs is highly desirable.

In this Letter, using *ab initio* density functional theory (DFT) calculations, we elucidate the influence of QD stoichiometry (S/Pb ratio, defined as R) on the electronic structure of both bare and passivated PbS QDs. For bare PbS QDs, our results reveal that: (i) perfectly stoichiometric QDs ($R = 1$) possess semiconducting electronic behavior with no midgap states and independent of QD shape, (ii) off stoichiometry ($R \neq 1$) is the major origin of midgap (trap) states within the band gap that have been observed in several QD experiments [12,13], and (iii) stoichiometry control enables QDs to transition between semiconducting and “metallic” behavior. Using 1,2-ethanedithiol (EDT) molecules as passivating agents, we demonstrate that the above observations can further be expanded to the case of ligand passivated QDs. In particular, we show that there exists an *optimal* number of QD-attached ligands that fully heals the originally undesirable electronic structure of off-stoichiometric QDs. We demonstrate that when the role of ligand attachment is viewed within the framework of stoichiometry change, both the optimal number of ligands as

well as their structural orientation play crucial roles regarding the overall electronic structure.

The traditional view on surface traps and ligand passivation of QDs is that each surface atom with at least one dangling bond is responsible for trap states and, thus, needs to be completely passivated for trap-free electronic structure. In this work, however, we consider the ligand passivation as a change in overall QD stoichiometry, rather than elimination of surface dangling bonds. According to our findings, as long as the QD is kept effectively stoichiometric, trap-free band gaps are produced even with numerous dangling bonds remaining on the surface.

We carried out *ab initio* DFT calculations using the plane wave basis VASP code [14] and employed the generalized gradient approximations (GGA) of Perdew-Burke-Ernzerhof [15] for the exchange correlation functional. The projector-augmented-wave method [16] was adopted to describe the core electrons. An energy cutoff of 500 eV was used, and a vacuum spacing of 20 Å was used to prevent spurious interactions between QDs. We sampled k points via a $1 \times 1 \times 1$ Monkhorst-Pack scheme. Spin-orbit coupling was included in all DFT calculations since its importance in PbS systems was confirmed by previous work and ourselves [17–19].

In order to justify our particular choice of GGA functional, we performed *ab initio* DFT calculations on representative QDs with the HSE06 hybrid functional [20] for comparisons and confirmed that all relevant phenomena related to QD stoichiometry variations were completely preserved. Thus, the band gap issue associated with standard DFT functional does not change the results presented here [19].

First, we explore the case of bare PbS QDs. We are particularly interested in cube- or faceted-cube-shaped QDs since these are the most commonly observed PbX ($X = S, Se, Te$) QD shapes [21,22] in experiments. The $\{100\}$ and $\{111\}$ crystalline planes are well-known to be the dominant facets in PbS QDs although other crystalline planes including $\{110\}$ and $\{311\}$ are often observed from x-ray diffraction studies [23,24]. In this work we have explored QD shapes of perfect cubes and truncated octahedra with 8- $\{111\}$ faces.

In Fig. 1, PbS QDs are classified into four different types (referred to as types A, B, C, and D) by QD shape and stoichiometry for simple reference throughout the rest of this Letter. Types A and C are cube-shaped QDs with $\{100\}$ surface planes exposed whereas types B and D have faceted cube shapes with both $\{100\}$ and $\{111\}$ surface planes exposed. Each type of QD has a different stoichiometry: types A and B QDs are Pb_nS_n , type C QDs are either $Pb_{n+1}S_n$ or Pb_nS_{n+1} , and type D QDs are Pb_nS_m with $|n - m| \geq 7$ due to the richness of either lead or sulfur atoms at faceted $\{111\}$ surfaces. By exploring these four different types of QDs, we are able to identify the roles

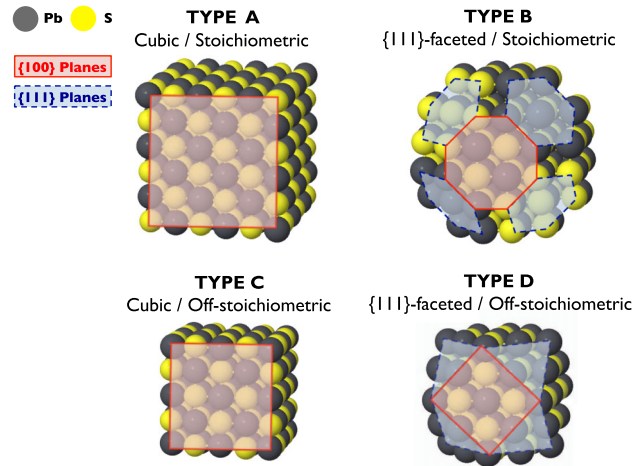


FIG. 1 (color online). Classification of PbS QDs into four different types (A, B, C, and D).

played on the electronic structures of a wide range of QD shapes and stoichiometries.

We first compute the properties of purely stoichiometric QDs; since R is fixed as unity for both types A and B QDs, the comparison between these two types of QDs allows for a comparison of shape on the electronic structure. Both type A and B stoichiometric QD systems have shown semiconducting electronic behavior with no defect states in the gap. Yet, even though types A and B QDs behave qualitatively similar in terms of their electronic structure, in our calculations the band gap trends with size are somewhat different: faceted-cube shapes result in lower gaps than purely cubic shapes for a given total number of atoms [19]. This difference suggests that for a given number of atoms, charges in the faceted cubes will be less quantum confined compared with charges in the perfect-cube case.

Next, we examine the case of off-stoichiometric QDs. In Fig. 2, the projected density of states (PDOS) is shown for a representative QD of each of the four types considered in this work. In Figs. 2(a) and 2(b), in addition to the ideal gaps described above, one can see that the contribution to the conduction bands for type A and B QDs arises mainly from Pb states whereas the valence band states arise predominantly from S. The type C QD shown in Fig. 2(c) is only just off stoichiometry (for this case, $Pb_{63}S_{62}$, $R = 0.98$), yet as a result midgap states have emerged. We have computed the properties of a number of type C QDs with different sizes (up to a total of 343 atoms) and find that regardless of the system size, such midgap states are present. Upon examination of the wave function distribution, we find that these states can be attributed mostly to surface atoms. In this particular example, the wave function is highly localized on the corner Pb atoms, which have the most number of dangling bonds [19]; in S-rich type C QDs (Pb_nS_{n+1}) the wave function is mostly localized on surface S atoms.

The existence of midgap states in QD films has been verified experimentally, and the role played by such states

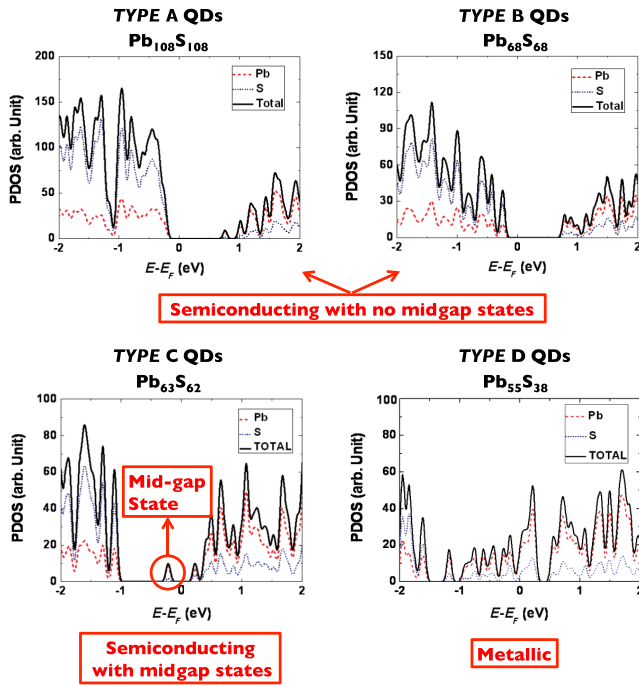


FIG. 2 (color online). PDOS as a function of energy for an example of each type of QD considered here.

in the charge transport has been shown to be crucial [12]. Yet, despite such high importance the origin of midgap states is not well understood apart from the fact that they can be attributed to surface atoms of the QDs [25], which we have also confirmed in our calculations. However, a critically important additional point is that, in the case of bare QDs, these midgap states emerge only when QDs are off stoichiometric. Furthermore, experiments have revealed that the midgap states in PbS QDs are weakly conductive in terms of charge transport [12], which is in good agreement with the charge localization on surface atoms for the midgap states in the DFT calculations.

The effect of off stoichiometry becomes even greater when {111} facets are introduced at the corners of type C QDs, which form type D off-stoichiometric QDs, an example of which ($\text{Pb}_{55}\text{S}_{38}$, $R = 0.69$) is shown in Fig. 2(d). Unlike the other three types of QDs, type D QDs show metallic-like electronic behavior, with a dense number of energy states near the Fermi level. Such cases are expected to play a negative role in PV: the inclusion of a large portion of type D metallic QDs in the PV active layer could short out the device.

On the basis of only these four specific cases, our calculations demonstrate the strong influence of QD stoichiometry on the electronic structure, and as such we have carried out a more comprehensive stoichiometry analysis. DFT Kohn-Sham energy levels for a number of QDs with R varying from 0.46 to 2.17 are shown in Fig. 3. Types A and B stoichiometric QDs ($R = 1.0$) show clear semiconducting electronic behavior. The type C

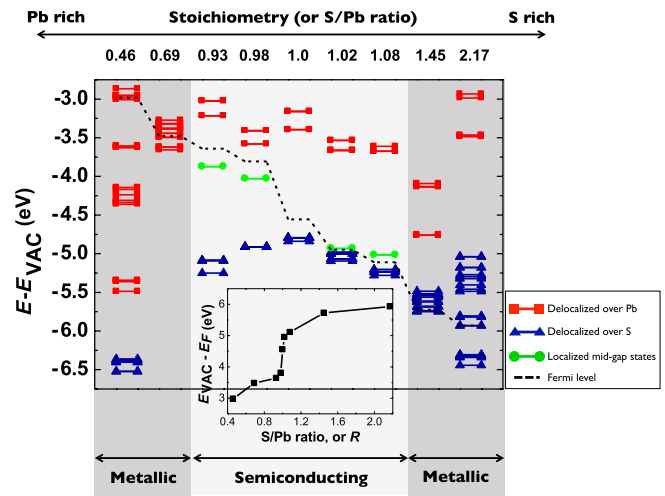


FIG. 3 (color online). Kohn-Sham energy levels, shifted with respect to the vacuum level, for QDs with a range of different stoichiometry. Electronic states in red are mostly delocalized over Pb atoms whereas ones in blue are mostly delocalized over S atoms, and the states in green refer to localized mid-gap states. States below the black dashed line are occupied while the other states are not occupied in the ground state. The inset describes “ $E_{\text{VAC}} - E_F$ ” as a function of QD stoichiometry.

off-stoichiometric QDs shown in Fig. 3 ($R = 0.93, 0.98, 1.02, 1.08$) possess midgap states between the band edges. By examining off stoichiometry both above and below unity, we observe that the midgap states are occupied in the Pb-rich type C QDs whereas in the S-rich type C QDs the states are unoccupied. For type D QDs ($R = 0.46, 0.69, 1.45, 2.17$ in Fig. 3), metallic-like electronic behavior is observed.

Another notable point is that the energy difference between the vacuum and the Fermi levels ($E_{\text{VAC}} - E_F$, the work function for metals) monotonically increases from 2.98 to 5.93 eV as a function of the S/Pb ratio (Fig. 3). Considering that the ionization potential of a S atom is much higher than that of a Pb atom, it makes sense that S-rich QDs exhibit greater $E_{\text{VAC}} - E_F$ values than Pb-rich QDs. In PbS QD-based heterojunction PV devices, the QD film and electron accepting layer form an interface where excitons are separated into free charge carriers [6]. Thus, the fact that $E_{\text{VAC}} - E_F$ is highly sensitive to the QD stoichiometry suggests that caution be applied when controlling QD stoichiometry for favorable band alignments.

Thus far, we have established a framework for understanding the electronic structure of bare QDs in relation to their stoichiometry. In QD materials and devices, however, ligands are typically present on the QD surface as they are used in the synthesis of the dots as a means to prevent clumping. Here, we show that the same framework of stoichiometry can be applied to ligand passivated QDs and that the ligand passivation itself can be thought of as a change in the QD surface stoichiometry. For example, EDT molecules that are commonly used as passivating

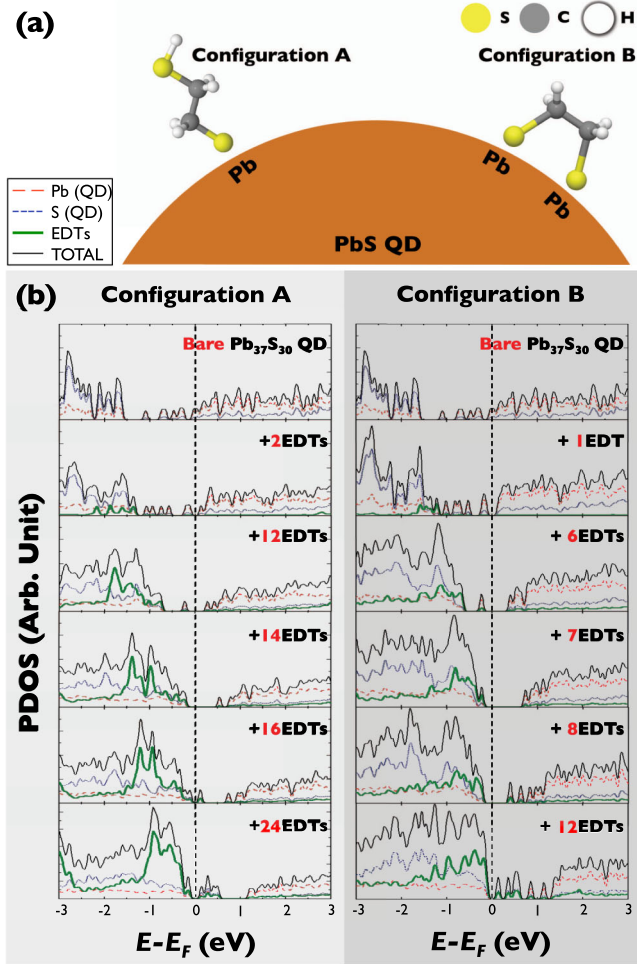


FIG. 4 (color online). (a) Schematic of two different EDT binding configurations on the PbS QD surface (referred to as configurations A and B). (b) PDOS as a function of the number of QD-attached EDT ligands for both configurations.

agents attach to the QD via a sulfur atom in the ligand covalently bonding to a surface lead atom in the QD, which of course changes the QD surface stoichiometry.

In Fig. 4(a), we examine the effects of two different possible binding configurations [7,26]: one with only one sulfur in EDT attached to a lead atom on the QD surface, and another with both sulfur atoms of EDT attached to neighboring lead atoms. Our calculations show that, for each case, EDT passivation effectively changes the overall QD stoichiometry although by a different amount per ligand. In configuration A, EDT alters the overall stoichiometry by an amount equivalent to 1/2 of a S atom whereas in configuration B, EDT changes the overall stoichiometry in the same manner as a full sulfur atom. Each S atom in EDT carries 1/2 of the stoichiometry value of a regular QD S atom due to the fact that it is already bound to neighboring atoms within the ligand. We define Δ , effective stoichiometry imbalance, as

$$\Delta = -N_{\text{Pb(QD)}} + N_{\text{S(QD)}} + fN_{\text{EDT}},$$

where $N_{\text{Pb(QD)}}$ and $N_{\text{S(QD)}}$ are the numbers of lead and sulfur atoms in the QD, respectively, and N_{EDT} is the number of QD-attached EDT ligands. Furthermore, f is the weight factor that determines the overall stoichiometry contribution from a single EDT ligand, which is 0.5 for EDT in configuration A and 1.0 for EDT in configuration B.

Taking the $\text{Pb}_{37}\text{S}_{30}$ type D QD with metallic characteristics as an example [Fig. 4(b)], we compute the electronic structure as a function of N_{EDT} for each binding configuration. In order to make Δ zero, i.e., make the QD/ligands system effectively stoichiometric, either 14 ligands in configuration A or 7 ligands in configuration B should attach to the QD surface. According to our picture of the role of stoichiometry, such passivation will convert the QD from the metallic-like electronic properties in the bare $\text{Pb}_{37}\text{S}_{30}$ QD to semiconducting electronic ones with no defect states in the passivated QD. As can be seen in Fig. 4(b), this is exactly what our calculations illustrate. For passivation that results in near but not perfect stoichiometry, when Δ is small but nonzero, we expect the QD to possess type C behavior. As shown in Fig. 4(b), for the case of $|\Delta| = 1$ (corresponding to 12 or 16 ligands in configuration A and 6 or 8 ligands in configuration B), we predict semiconducting electronic behavior with localized midgap states within the band gap. When $|\Delta| \gg 1$, for example, in the case of 2 or 24 EDTs in configuration A and 1 or 12 EDTs in configuration B, a large number of defect states forms in the gap, leading to metallic-like electronic properties. Additionally, we confirmed that our stoichiometry framework holds even in the mixed configuration A/B case. Our calculations show that, for example, the attachment of 6 ligands in configuration A and 4 ligands in configuration B, together resulting in $\Delta = 0$, completely eliminate midgap states.

On the basis of these observations, emphasis should be placed on the fact that the full passivation of the QD surface is not necessarily desirable for favorable electronic structure in QD-based optoelectronic applications. Rather, there exists an *optimal* number of QD-attached ligands such that the whole QD/ligands system becomes effectively stoichiometric, or $\Delta = 0$. Furthermore, the greater $|\Delta|$ value means the greater density of localized midgap states and finally makes the system possess metallic characteristics. Importantly, we find that the same ligand can alter the stoichiometry differently depending on its binding configuration, and thus the *optimal* number of attached ligands can also vary depending on how each ligand is bound on the QD surface.

In summary, we used first-principles calculations to predict the impact of QD stoichiometry on the electronic structure of both bare and EDT passivated PbS QDs. Beginning with bare QDs, we showed that regardless of the QD shape, stoichiometric QDs exhibit semiconducting behavior with no midgap states. Yet, when we introduce slight off stoichiometry, midgap states start to emerge, and heavily off-stoichiometric PbS QDs finally end up losing

their semiconducting behavior. The stoichiometry framework established in bare PbS QDs can be equally applied to ligand passivated QDs by considering the attachment of ligand molecules as stoichiometry variations. We demonstrate that there exists an *optimal* number of attached ligands that makes the QD/ligands system effectively stoichiometric, resulting in a semiconducting behavior with no trap states. The amount of stoichiometry contribution from a single EDT molecule could be different depending on its binding configuration.

The authors acknowledge Prof. Vladimir Bulovic, Dr. Giuseppe Romano, Dr. David Strubbe, Sangjin Lee, Priyank Kumar, Patrick Brown, and Darcy Wagner at MIT and Dr. Su Kyung Suh at SAIT for insightful discussions. We wish to thank TeraGrid for computing resources. D. K. is grateful to Yeseul Oh at the Rhode Island School of Design (RISD) for helping to illustrate figures in the Letter. In addition, D. K. thanks the Samsung Scholarship Foundation for funding during his graduate studies.

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