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| Citation       | Winslow, Samuel W. et al. “Quantification of a PbClₓ Shell on the Surface of PbS Nanocrystals.” ACS Materials Letters 1, 2, [June 2019]: 209-216 © 2019 American Chemical Society |
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| As Published   | http://dx.doi.org/10.1021/acsmaterialslett.9b00200                                                                                                                                              |
| Publisher      | American Chemical Society (ACS)                                                                                                                                                                 |
| Version        | Final published version                                                                                                                                                                         |
| Citable link   | https://hdl.handle.net/1721.1/123840                                                                                                                                                            |
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Quantification of a PbCl\textsubscript{x} Shell on the Surface of PbS Nanocrystals

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ABSTRACT: Differences between the properties of PbS nanocrystals prepared using a large excess of PbCl\textsubscript{2} and those prepared using other Pb sources have led to speculation that a thin PbCl\textsubscript{x} shell may be present on the surface of PbCl\textsubscript{2}-derived PbS nanocrystals. However, characterization of this chloride layer has proven to be challenging because of the poor contrast provided by electron and X-ray scattering probes. Here, we show that small-angle neutron scattering (SANS) provides the compositional sensitivity needed to unambiguously quantify the PbCl\textsubscript{x} shell that is present on the surface of PbCl\textsubscript{2}-derived PbS nanocrystals. Using a charge-balanced structural model, the scattering contribution of a ~0.3 nm thick surface PbCl\textsubscript{x} layer is parsed separately from ligand carboxylate head groups and PbS in the core. Global fitting of the SANS data across a solvent deuteration series enables unique determination of the spatial distribution of each material. These results are corroborated by quantitative nuclear magnetic resonance (NMR) and energy-dispersive X-ray spectroscopy (EDS). This work resolves a discrepancy in reported sizing curves for PbS nanocrystals prepared by different syntheses and further demonstrates the power of SANS in resolving molecular structure in soft and hybrid nanomaterials.

PbS quantum dots (QDs) have been investigated as the active material in many next-generation optoelectronic devices. The broadly tunable absorbance/emission across the near-infrared spectrum makes PbS particularly exciting for use in photodetector and photovoltaic technologies. At the nanoscale, the high surface-to-volume ratio in these materials means the surface structure and energetics are critical to determining ensemble properties. Indeed, the core surface has a profound effect on energy-level modification and electron-phonon coupling. There are multiple synthetic routes for producing PbS QDs using either PbO or PbCl\textsubscript{2} as the lead precursors. However, there are notable differences in the reported materials from each synthesis. A sizing curve for PbO-based PbS QDs yields smaller nanocrystal sizes for a given first exciton absorption peak as compared to a sizing curve for PbS QDs synthesized with a large excess of PbCl\textsubscript{2}. Additionally, the reported Pb/S ratio in PbCl\textsubscript{2}-based QDs is higher than that for PbO-based QDs, and residual Cl can be detected even after washing.

Circumstantial evidence suggests that PbS QDs prepared from a PbCl\textsubscript{2} precursor may be coated with an insulating PbCl\textsubscript{x} shell. Additional anecdotal evidence supporting the presence of an insulating PbCl\textsubscript{x} shell includes (1) improved resistance of chloride-based PbS QDs to oxidation and prolonged stability, (2) slower charge carrier hopping times for lead halide based lead chalcogenide QDs, and (3) superior triplet sensitization capability of PbO-based QDs. However, direct structural evidence is missing. Transmission electron microscopy (TEM) cannot clearly distinguish between a PbS core and a PbCl\textsubscript{x} shell. This is because electron scattering techniques are dominated by the heavy lead atoms, which are present in both the PbS core and the hypothesized PbCl\textsubscript{x} shell. Small-angle X-ray scattering (SAXS) likewise suffers from this lack of good contrast between PbS and PbCl\textsubscript{x}. Moreover, X-ray powder diffraction (XRD) is of limited value since an epitaxial PbCl\textsubscript{x} shell, by definition, will have the same continuous crystal structure as the PbS core.

Here, we show that small-angle neutron scattering (SANS) provides the elemental contrast needed to quantify the presence of a PbCl\textsubscript{x} shell in olate-capped PbCl\textsubscript{2}-based PbS QDs. Unlike electron and X-ray scattering probes, neutron scattering cross sections do not scale with the atomic number. SANS is well-suited to resolve all components of a colloidal nanocrystal because of significant contrast between core, surface layer, ligand—shell, and solvent resulting from different scattering length densities (SLDs) of each of these components. Additionally, the capability to shift contrast with the solvent through deuteration enhances model fitting.
Our SANS analysis yields a lead chloride surface layer thickness of ~0.3 nm, which is consistent with a monolayer of PbCl₂ epitaxially bound to the PbS core. The difference in sizing curves is attributed to this surface layer. The ligand coverage and atomic ratios measured with SANS agree with nuclear magnetic resonance (NMR) spectroscopy and energy-dispersive X-ray spectroscopy (EDS) measurements on the same QDs. Finally, we propose an atomic surface configuration that is charge neutral and consistent with all experimental measurables.

**QD Structure Determination from Neutron Scattering.** In a SANS experiment, the observed intensity profile \( I(q) \) for a dilute solution of centrosymmetric, monodisperse particles is related to the scattering length density (SLD) of the scattering particle as

\[
I(q) = n \left( 4\pi \int_0^\infty \Delta \rho(r)^2 j_0(qr) \, dr \right)^2
\]

with \( n \) the number density of particles in solution, \( r \) the radial coordinate, \( \Delta \rho(r) \) the excess SLD profile or solvent contrast, and \( j_0 \) the zeroth-order spherical Bessel function of the first kind. For a known \( \rho(r) \) profile, \( I(q) \) may be calculated. We propose a \( \rho(r) \) profile as a linear superposition of the individual profiles of each material comprising the QD: core, surface layer, ligand, and penetrating solvent. The \( \rho(r) \) profiles are calculated from a superposition of radial volume fraction profiles for each component \( \psi_i(r) \) through scaling by the bulk SLD of each material \( \rho_i^{\text{bulk}} \). For the surface layer, the bulk SLD of stoichiometric PbCl₂ is used. Though the near-surface PbCl₂ stoichiometry is unknown, this choice partitions the surface as stoichiometric PbCl₂ for the purposes of atomic ratio quantification. This is discussed later in the context of a proposed surface structure. The model we fit is inspired by the structures resulting from molecular dynamics (MD) simulations, and we leverage a Markov chain Monte Carlo (MCMC) fitting procedure within the framework of Bayesian inference to determine statistically robust structural parameters. The MD results and fitting procedure are described in the Supporting Information. When performing the fit, a ligand consistency constraint is implemented such that the number of olate ligand head groups near the surface is equal to the number of full ligand molecules as measured by integrating the ligand volume fraction profile. The head and tail of the ligand are accounted separately because the carboxylate head has a different SLD than the aliphatic tail.

SANS data for 3 separate batches of PbS QDs were collected at 9 deuteration fractions each, ranging from 17.8% to 100% deuteration, yielding 27 independent \( I(q) \) scattering curves. All 3 batches of QDs were synthesized according to the Weidman et al. method, using PbCl₂ and elemental sulfur in oleylamine as the reactants with a Pb/S ratio of 24:1. Nominal core sizes and polydispersities for each batch as measured by UV–vis spectroscopy are 6.2 (σₚ ≤ 4.1%), 6.8 (σₚ ≤ 4.4%), and 7.7 nm (σₚ ≤ 4.2%). Figure 1a shows the fit of the SLD profile to the experimental data using the MD-inspired composite model. Only a subset of the intensity profiles are shown for clarity. The full fits for all batches are shown in the Supporting Information. The corresponding \( \rho_f(r) \) and \( \rho_c(r) \) profiles are shown in Figure 1b and 1c, respectively. Multiple parameter sets sampled from the fit parameter distributions are plotted as transparencies to visually demonstrate the uncertainty of the fit. Correlations between parameters are minimal and are discussed in the Supporting Information.

Our structural model predicts the intensity profiles well over the full \( q \) range and across all solvent deuteration fractions (Figures 1 and S6). The shift in the first scattering peak near 0.1 Å⁻¹ with changing solvent deuteration fraction arises from solvent penetration into the ligand shell, which is captured in our structural model shown in Figure 1b. The SLD profile for one of the 27 core size/deuteration combinations is shown in Figure 1c. Ligand carboxylate head groups and the proposed PbCl₂ shell both have higher SLDs than PbS, leading to a peak in the composite SLD profile near the PbS surface (black curve, Figure 1c). The ligand tail groups have low SLD, and so, a valley in the SLD profile is observed at higher radial
positions. Solvent penetration into the shell modulates the SLD profile, leading to a substantial radial variation in the SLD outside the PbS core as the deuteration fraction is changed (Figure S6b, f, and j); this variation allows for unique characterization of the solvent penetration into the ligand shell. Because the SLD contribution of the carboxylate ligand head group is constrained by the ligand tail contribution at larger radial positions, we found that varying the solvent deuteration fraction pro-
t be used to quantify each component of the colloidal QD. These profiles correspond to a mass density profile when scaled by the bulk mass density. The mass density profiles may be integrated to obtain the total mass of each material by

$$m_i = \int \rho_i(r) \, dV = \int_0^\infty 4\pi r^2 \rho_i^{bulk} \varphi_i(r) \, dr$$

(2)

with $m_i$ the mass of each material, $\rho_i(r)$ the mass density profile, $\rho_i^{bulk}$ the bulk density of material $i$, and $\varphi_i(r)$ the fit volume fraction profile of each material. The mass can be converted to a number of molecules using the molecular weight. We then use the number of PbS, PbCl2, and ligand molecules to count the number of atoms and calculate atomic ratios. Because we chose the SLD of bulk PbCl2 for scaling the volume fraction profile, the number of molecules calculated are stoichiometric

$$N_{Pb,shell} = N_{PbCl_2}$$

$$N_{Cl,shell} = 2N_{PbCl_2}$$

(3)

(4)

In a stoichiometric PbS core, the sum of the number of Pb and S atoms is twice the number of PbS pairs: $N_{Pb,core} + N_{S,core} = 2N_{PbS}$. However, the PbS core is not stoichiometric and $N_{Pb,core}$ will be greater than $N_{S,core}$. This ratio of lead to sulfur is calculated from a charge balance with the ligands, assuming each ligand and excess lead atom provide a $1^-$ charge and $2^+$ charge, respectively. The combined mass and charge balances yield

$$N_{Pb,core} = N_{PbS} + \frac{N_{ligand}}{4}$$

$$N_{S,core} = N_{PbS} - \frac{N_{ligand}}{4}$$

(5)

(6)

In addition to the number of atoms and atomic ratios, the mass of PbS and PbCl2 may be used to calculate an equivalent core diameter, PbCl2 shell thickness, and total nanocrystal diameter including the PbCl2 shell. The number of ligand molecules is divided by the surface area based on total core diameter to obtain a ligand coverage. In this calculation, the surface area is divided by 0.9212, the maximal sphericity of a truncated octahedron family QD, as the actual surface area is larger than that of a sphere.

Table 1 summarizes our complete SANS characterization and also includes external measurements of the core size by UV–vis spectroscopy,15,14 number of ligands from quantitative nuclear magnetic resonance spectroscopy (qNMR),24 and
elemental ratios determined by energy-dispersive X-ray spectroscopy (EDS). The values given from SANS represent the median of these computed descriptors for 100 samples from the parameter distributions, as well as the central 95% credible region. For qNMR and EDS, the values quoted are the mean of repeat measurements with propagated uncertainty based on the standard deviation.

The measured PbCl$_2$ shell thickness (~0.3 nm, Table 1) is commensurate with a monolayer coverage of PbCl$_2$ on the PbS surface. Previous experimental work studied the structure of PbCl$_2$ growth on PbS and showed that PbCl$_2$ can grow epitaxially on PbS with minimal lattice distortion.\textsuperscript{72,25} The structure of this PbCl$_2$ shell is discussed further in the following section.

The nominal sizes predicted by the Weidman sizing curve (large excess PbCl$_2$) are significantly larger than the PbS core sizes extracted from SANS analysis, but close to the total nanocrystal diameter as measured by SANS (Table 1). The Weidman calibration curve was constructed from a combination of SAXS and TEM measurements, and likely reflects the total diameter of the nanocrystal (both PbS core and PbCl$_2$ shell). However, the SANS PbS core diameter is close to that predicted by the sizing curves of Moreels et al. (PbCl$_2$-based, low excess PbCl$_2$) and Maes et al. (PbO-based), which used TEM and SAXS, respectively, to quantify core size (Figure 2).\textsuperscript{13,26} Deviations of the SANS measurements from the sizing curves are minimal and likely stem from the discretization of the core surface in the model. These comparisons are consistent with SANS measurements on PbO-derived PbS QDs and suggest that neither the PbO route nor the PbCl$_2$ route with low excess PbCl$_2$ lead to a measurable PbCl$_2$ shell.\textsuperscript{18}

Ligand coverage agrees well with previous experimental measurements on PbS and PbSe in the range of 3–5 nm.\textsuperscript{27–29} Although the ligand coverage of the smallest QDs measured is high, it is does not exceed the maximum based on charge balance with excess lead atoms for a representative octahedral core shape. When compared to the values measured by qNMR, the SANS results are both higher and lower across the three batches with an average relative error of 21%. The qNMR results assume accurate knowledge of the concentration or number density of QDs in solution, which incurs more error than is accounted for in the repeat measurement uncertainty quoted. However, the SANS-based ligand coverages are estimated in a self-consistent way with the core size, without assuming knowledge of the concentration.

The core Pb/S ratio matches the range of 1.1–1.3 expected for the truncated octahedron family in this size range.\textsuperscript{60} The total Pb/S ratio estimated by SANS accounting for the PbCl$_2$ surface supports elevated values measured by Weidman et al. using EDS on batches made from the same synthesis.\textsuperscript{14} Though the total Pb/S ratio measured by EDS for the QDs in this study is lower than estimated by SANS, there are wide uncertainty margins on the sulfur and chlorine elemental ratios due to difficulty identifying those materials in the EDS measurement. SANS does not have the same difficulty because of the high SLD of PbCl$_2$. Despite the uncertainty in the EDS measurement, the reported chlorine percentages from both techniques are in agreement.

Although batches of PbCl$_2$-derived QDs are known to evolve shortly after synthesis as PbCl$_2$ precipitates out of solution,\textsuperscript{12,14,16,26} this is not a confounding variable in this study. Additional elemental quantification shows one month is sufficient for any precipitation to occur. Inductively coupled plasma optical emission spectrometry (ICP-OES) and mass spectrometry (ICP-MS) were used to measure atomic ratios on a comparable batch of QDs one month after synthesis. The measured atomic percentages were 45.6 ± 4% lead, 34.8 ± 4% sulfur, and 19.6 ± 4% chlorine. The Pb/S ratio was 1.31 ± 0.19. This chlorine population matches that of the QDs measured with SANS, which was performed over a year after synthesis. These results suggest most of the PbCl$_2$ that will precipitate out of solution after synthesis does so within one month as the measured chlorine percentages are the same one month or one year after synthesis. Following this first month, we observe a negligible blue shift (less than 5 nm change in peak position) between one month and one year after synthesis.

**Proposed PbCl$_2$ Surface Layer Structure.** We complete our near-atomistic characterization with a description of the core shape and surface PbCl$_2$ structure. The core Pb/S ratio can be used with the equivalent volume diameter to map the experimental batches to a model core. Octahedra, truncated octahedra, and cuboctahedra have, respectively, lower Pb/S ratios as the shapes increasingly resemble the bulk cubic structure. For each individual shape, the ratio also decreases as the core size increases. There is a unique combination of atomic ratio to size for each batch. Figure 3 shows these approximate ideal models for each of the 3 batches measured. As the QDs grow in size, the (100) stoichiometric facets become larger. The models resemble the growth pathway previously observed.\textsuperscript{30} The model cores used for MD simulation correspond well with the extracted model cores, and the surfaces of these models are used for further consideration of the PbCl$_2$ shell structure.

We propose that the PbCl$_2$ shell is a near-monolayer of epitaxially bound, near-stoichiometric PbCl$_2$ on both (100) and (111) facets of the QDs (Figure 4). It has been observed previously that PbCl$_2$ can grow on the (100) facets of PbS with minimal lattice strain,\textsuperscript{26} and halides have been introduced post-synthesis to protect the exposed (100) facets from surface oxidation.\textsuperscript{17} Epitaxial growth is consistent with our observation that no separate crystalline PbCl$_2$ peaks are observed in the X-ray diffraction (XRD) pattern after full precipitation of excess PbCl$_2$.\textsuperscript{14} However, the number of chlorine atoms we measure is too high to be solely bound to the (100) facets without

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**Figure 2. Comparison of UV–vis sizing curves with SANS results.** SANS PbS-core-only (filled circles) and total diameter (open circles) are plotted alongside three published sizing curves.\textsuperscript{13,14,26} Error bars are the 95% credible region. Error bars smaller than the size of the marker are not shown.

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DOI: 10.1021/acsmaterialslett.9b00200

ACS Materials Lett. 2019, 1, 209–216
multiple layers. Moreover, the smallest batch of QDs measured is nearly octahedral in shape with minimal exposed (100) surface area—yet this batch still has a comparable chlorine fraction to the others measured. Even for lower Pb/S ratios with more exposed (100) surface area, reasonable core shapes would not present enough binding sites for a monolayer of PbCl\(_2\) with the appropriate number of chlorine atoms. Consequently, we conclude that there must be PbCl\(_2\) bound to the (111) facets as well.

Strain within the PbCl\(_2\) layer on the (111) facet may be the reason that growth of the PbCl\(_2\) shell is limited to one monolayer. When comparing sizing curves in Figure 2, the difference between the Maes et al. and Weidman et al. curves decreases for larger core sizes. This matches the expected trend for a constant-thickness PbCl\(_2\) layer, regardless of the core diameter. Additionally, most of the chloride ions are bound to the (111) facets in this described framework, which reduce in fraction of total surface area as the core size increases.

We also consider ligand binding to the surface layer. Full surface termination in chloride ions would not present any Pb binding sites for the oleate ligands. Likewise, there are not enough lead atoms in the measured PbCl\(_2\) layer to provide full coverage of a Pb-terminated (111) facet on top of a chloride monolayer presenting outwardly for ligand binding. A proposed schematic with Pb-oleate binding on the (111) facets is presented in Figure 4.

The (100) facets are terminated in PbCl\(_2\) “molecules” similar to the proposed PbX\(_2\) adlayer by Woo et al.\(^{17}\) On the (111) facets, a monolayer of chlorine atoms occupies the lattice sites where an additional layer of sulfur would be present if the QD grew larger. These chlorides ions are bound to lead atoms terminating the (111) facets which form the binding sites for oleate ligands. This description means the approximate core models in Figure 3 use a slightly elevated Pb/S ratio as some of the lead atoms attributed to the PbS core must terminate the PbCl\(_2\) layer. Thus, the exact cores might resemble truncated octahedra or cuboctahedra for larger sizes. Despite this precise positioning of individual atoms being beyond the capability of this measurement, the core ratio should still be reasonably accurate as it was derived from a charge balance with the ligands. As such, the proposed models are still accurate as descriptors for the core shape. Importantly, the proposed surface structure shown in Figure 4 is charge neutral and consistent with the dimensions and mass fractions obtained from SANS.

In summary, in this work we have leveraged SANS to quantify the PbCl\(_2\) surface on PbS QDs. This study reconciles differences in reported sizing curves for PbS QDs prepared from different PbO or PbCl\(_2\) precursors with varying excess PbCl\(_2\) ratios. The implications of using a particular synthesis for an application must be considered. PbO-based QDs are ideal for charge transport applications because there is no insulating surface layer, yet these materials are susceptible to surface oxidation. PbCl\(_2\)-based QDs synthesized from a high excess PbCl\(_2\) ratio are well-suited to self-assembly, structural studies, and luminescence applications because of their long-term colloidal stability and excellent monodispersity.

### EXPERIMENTAL SECTION

#### Synthesis.
PbCl\(_2\)-derived PbS quantum dots were synthesized according to a previously published hot-injection method with PbCl\(_2\) (Alfa Aesar, 99.999%) and elemental S (Sigma-Aldrich, ≥99.99%) in oleylamine (Sigma-Aldrich, ≥98% primary amine) as the precursors.\(^{14}\) A Pb/S ratio of 24:1 was used. Oleic acid (Sigma-Aldrich, 90%) was used for initial crashout and ligand exchange. Methanol (Sigma-Aldrich, ≥99.8%) and ethanol (KOPTEC, anhydrous 100%) were used for additional crashouts followed by redispersion in hexanes (ACS, ≥98.5%).

An additional batch of PbO-derived PbS quantum dots were synthesized using a modification of the hot-injection protocols from Hines & Scholes and Colbert et al.\(^{11,31}\) PbO (450 mg (2.0 mmol), Sigma-Aldrich, ≥99%), 14 g of 1-octadecene (Sigma-Aldrich, 90%), and 1.4 g (4.96 mmol) of oleic acid (Sigma-Aldrich, 90%) were used for the lead precursor. The mixture was stirred under vacuum at 120 °C for 3 h, turning the solution clear. The flask was placed under flowing nitrogen gas, and the temperature was raised to 130 °C. Meanwhile, the sulfur precursor was prepared in a second three-neck flask with 4 g of 1-octadecene and 210 μL of hexamethyldisilathiane (HMDS) (Sigma-Aldrich, synthesis grade). Following in-

Figure 3. Shape dependence of the Pb/S ratio. The core Pb/S ratio as a function of size for different core models in the phase space for regular octahedra (black), truncated octahedra (blue), and cuboctahedra (red).

![Figure 3](image_url)

Figure 4. Proposed structure of the PbCl\(_2\) shell. A pristine PbS core (blue) is covered in a monolayer of PbCl\(_2\) (orange) over both (100) and (111) facets. The three-dimensional structure, including oleate ligand bound to the (111) facets, is charge neutral.
ection, the heating mantle was removed after 5 seconds, and the flask was cooled by a room-temperature water bath. The QDs were isolated by precipitation with acetone followed by centrifugation. The product was then cleaned in ambient air by dissolving the precipitated QDs in ~3 mL of hexanes and precipitating once with acetone and twice with methanol. The precipitated QDs were then brought into the glovebox and re-dispersed in anhydrous toluene.

UV-vis Spectrophotometry. Absorption spectra were measured using a Cary 5000 UV-vis-NIR spectrophotometer. For measurement, the QDs were suspended in tetrachloroethylene. The core diameters (dispersity \( \sigma_d \)) for the PbCl2-derived PbS QDs were measured to be 6.22 (\( \sigma_d \leq 4.1\% \)), 6.83 (\( \sigma_d \leq 4.4\% \)), and 7.66 nm (\( \sigma_d \leq 4.2\% \)). For the PbO-based QDs, the core size using the Maes et al. sizing curve was found to be 3.41 nm (\( \sigma_d \leq 4.5\% \)).

SANS Sample Preparation. SANS samples were prepared by evaporating off the hexanes solvent overnight in a vacuum chamber before redispersion in a measured mixture of hydrogen-bearing (ACS, \( \geq 99.5\% \)) and deuterated toluene (Sigma-Aldrich, \( \geq 99.6\% \) C-D3) to an approximate total scatterer volume fraction of 1.0 v/v%. A ligand coverage of 3 ligands/nm² was assumed for this calculation. The true volume scatterer volume fraction is 1.0 v/v%.

SANS Instrument and Data Reduction. SANS experiments were performed on the NG7-SANS instrument at the NIST Center for Neutron Research (NCNR). Three detector distances were used to cover the q range from approximately 0.004 Å⁻¹ to about 0.55 Å⁻¹. The neutron wavelength for all detector configurations was 6 Å with the wavelength spread of 12%. The samples were loaded into demountable titanium cells with quartz windows provided by NCNR. The obtained data were reduced using the SANS data reduction package of NCNR.

Proton Nuclear Magnetic Resonance Spectroscopy. \(^1\)H-NMR was performed on a three-channel Bruker Avance Neo spectrometer operating at 500.34 MHz equipped with a 5 mm liquid-nitrogen cooled Prodigy broad band observe (BBO) cryoprobe. The instrument runs in full-automation off of a SampleXpress 60 sample charger. Known quantities of QDs, measured by absorbance, were dissolved in 650 μL of deuterated toluene containing a known quantity (2 μL) of dibromomethane as an internal quantitative standard. Measurement temperature was 25 °C. The spectra were measured under conditions of full \( T_1 \) relaxation (delay of 45 s). The integrated area under the CH,Br resonance (3.98 ppm) and the bound ligand vinyl proton resonance (5.71ppm) were used to measure the number of ligands per QD. The vinyl proton resonance of bound ligands is shifted downward and broadened from that of free ligands (5.49 ppm), so free and bound ligand populations can be separately quantified. Figure S1 demonstrates that the standard and ligand peaks are well separated from solvent.

Energy Dispersive X-ray Spectroscopy. EDS was conducted on a JEOL JEM 2010FEG Transmission Electron Microscope operating at 200 kV, equipped with an Oxford INCA EDS system. A range of 5–9 measurements were performed for each batch of QDs.

Inductively Coupled Plasma Spectroscopy. Inductively coupled plasma–optical emission spectrometry (ICP-OES) and mass spectrometry (ICP-MS) were performed on a comparable batch of QDs to the three measured by SANS. ICP-OES was used to quantify the lead and sulfur weight percentages. ICP-MS was used to supplement this measurement for chlorine weight percentage as ICP-OES cannot accurately measure the chlorine fraction.

For ICP-OES, a Perkin Elmer Optima 7300 V instrument was used with WinLab32 ICP, version 5.1.3.0550, software. Solution samples were aspirated and converted to an aerosol through a nebulizer (Teflon GemCone) in a spray chamber (Cyclonic) and directed into an argon plasma. Here, the sample was dried, vaporized, atomized, and ionized in the argon plasma, which generated emission spectra. The resulting light emissions were then directed through a series of lenses, where the emitted light was focused onto a detector, measuring the wavelengths characteristics of the elements present. The constituents of an unknown sample could then be identified and quantified. Three replicates were prepared using 50 mg of sample each. The acid digestion media consisted of a combination of trace metals grade nitric acid, hydrogen peroxide, and 18.2 MΩ deionized water. All elements analyzed were calibrated with a minimum calibration coefficient of 0.996. Quality control standards were run at the start and finish of the run with a minimum acceptance criterion of ±15%. Typical uncertainties range from 3% to 5% at the 95% confidence level.

For ICP-MS, a Nexion 350D instrument was used with a Cetac ASX-520 auto sampler. Solution samples were aspirated and converted to an aerosol through a nebulizer (Opalmist) in a spray chamber (Tracey PFA44) and directed into an argon based plasma. Here, the sample was dried, vaporized, atomized, and ionized in the argon plasma. The resulting ions were then directed into a quadrupole mass analyzer where they were then separated and measured according to their mass to charge ratios. Five replicates were performed.

Computational Methods

Molecular Dynamics Simulations. PbS nanocrystals are faceted in shape with exposed \{100\} and \{111\} crystal planes. By specifying the number of atoms along any adjoining planes, we generated core models in the typical truncation sequence from octahedron, through truncated octahedron, to cuboctahedron. Ligands were grafted exclusively onto (111) facets in line with computational and experimental results. Coverage was manually varied as ligand coverage is known to vary in experiment. Electrostatic interactions were excluded from the simulations. The core was prescribed as a rigid body and ligands were bound to individual lead atoms such that no surface rearrangement was allowed; the simulation was purely to probe potential core, surface, and ligand-shell shapes. We used an explicit toluene solvent. Simulation parameters and methodology were the same as reported in Winslow et al. The simulation results were used to generate profiles of the radial volume fraction distribution of each material from the nanocrystal center. A bin width of 4 Å was used for these histograms.

Associated Content

Supporting Information

The following files are available free of charge. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmaterialslett.9b00200. NMR spectra for ligand quantitation, SANS intensity curves and data analysis methodology, additional core
shape MD volume fraction profiles, corner plot for the fit parameters to the data shown in the main text, and full fits to SANS data for PbCl$_2$ and PbO-based QDs (PDF)

Spreadsheet of background-corrected SANS data, including q resolution and scattering intensity, at nine deuteration fractions for the nominally 6.2 nm batch (CSV)

Spreadsheet of background-corrected SANS data, including q resolution and scattering intensity, at nine deuteration fractions for the nominally 6.3 nm batch (CSV)

Spreadsheet of background-corrected SANS data, including q resolution and scattering intensity, at nine deuteration fractions for the nominally 7.7 nm batch (CSV)

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**Notes**

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**ACKNOWLEDGMENTS**

The authors thank Brad Olsen for helpful conversations in interpreting SANS data and Yong Zhang for assistance in performing EDS measurements. The authors also thank Mark Wilson and Philippe Green for first pointing out the sizing curve discrepancy and suggesting the presence of a PbCl$_2$ shell. Y.L. acknowledges support by the Center for High Resolution Neutron Scattering (CHRNS), a partnership between the National Institute of Standards and Technology and the National Science Foundation under Agreement No. DMR-1508249. J.W.S. was supported by the MIT Portugal Seed Fund. W.A.T. was supported by the Camille and Henry Dreyfus Foundation.

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