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# Hydroxylation of the surface of PbS nanocrystals passivated with oleic acid

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## Article

### Abstract

Controlling the structure of colloidal nanocrystals (NCs) is key to the generation of their complex functionality. This requires an understanding of the NC surface at the atomic level. The structure of colloidal PbS-NC passivated with oleic acid has been studied theoretically and experimentally. We show the existence of surface OH- groups, which play a key role in stabilizing the PbS(111) facets, consistent with x-ray photoelectron spectroscopy as well as other spectroscopic and chemical experiments. The role of water in the synthesis process is also revealed. Our model, along with the existing observations of NC surface termination and passivation by ligands, helps to explain and predict the properties of NCs and their assemblies.

The structure of the interior of nanocrystals (NCs) can be determined quite accurately by crystallography, but the structure of their surfaces cannot be obtained from this analysis due to the complexity of organic capping ligands (1–6). However, the NC surface structure controls the growth and solubility, and strongly influences the physical and chemical properties (7–12). We take advantage of improved insights of the mechanisms of nanocrystal growth (3–6), combined with extensive ab initio total energy calculations, to create a testable model for the atomic surface passivation structure of the exposed facets of a PbS-NC. The model makes specific, and at first surprising, predictions about the surface-bound species that were subsequently verified experimentally. PbS is ideal for this study because of the high symmetry of its rocksalt structure and its propensity to form NCs with well-defined (111) and (001) facets (13, 14). PbS-NCs with controlled size and shape can be produced from a PbO lead precursor, hexamethyldisilathiane (TMS<sub>2</sub>S) sulfur precursor, and oleic acid that binds to exposed Pb atoms to stabilize the surface (1–6).

We performed ab initio electronic structure calculations on relevant sub-systems and on the reaction steps involved in the synthetic process, including: studies of immediate

precursors; fate of by-products of the initial decomposition step; NC-ligand interactions; and ligand-ligand and ligand-solvent interactions. Our methods (15) are density functional theory (DFT) in the generalized gradient approximation (GGA). The GGA is not accurate enough to describe the van der Waals (vdW) interactions, and the entropic contributions in the solvent are prohibitively time-consuming at present to be calculated directly. However, we have taken advantage of likely cancellations of these terms when comparing different systems. We found the following features in our theoretically derived model: (1) The Pb:S atomic ratio is roughly 1.2:1 (Pb<sub>excess</sub>:S~0.2:1) for ~5 nm NCs; (2) The ratio between the number of surface oleate molecules and the number of excess Pb atoms is ~1:1; (3) The ligands can be easily removed from the (001) surface; (4) The average (111)/(001) surface to center distance ratio of the truncated octahedral shape is about 0.82:1; (5) OH- groups are present on the NC (111) facet. These features are consistent with prior and current experimental studies including Rutherford backscattering (RBS), TEM (TEM), X-ray photoelectron spectroscopy (XPS), sum frequency generation (SFG) spectroscopy, nuclear magnetic resonance (NMR), and Fourier transform infrared spectroscopy (FTIR) (5, 6, 16–18). The presence of hydroxide groups on the surface predicted in the calculation as by-products of precursor decomposition was verified with XPS and SFG. The existence of water in the precursor was supported with NMR and FTIR measurements.

The colloidal PbS-NCs (4, 5) are synthesized by dissolving PbO in hot oleic acid (15). One of the by-products of the reaction is water, which was proposed to remain as free molecules in the solution (4, 5). Our calculations however show that it is energetically more favorable for water to bind to the Pb-precursor (15). Thus, the first reaction step can be written as:



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(1)

where OAH denotes oleic acid. The DFT optimized structure of the Pb(OA)<sub>2</sub>⋯H<sub>2</sub>O is shown in Fig. 1A. In the experiment, the reaction products were degassed at 110°C under vacuum for 1 hour. To determine whether such degassing removed all of the water in the precursor as previously suggested, we used NMR and FTIR. Although NMR demonstrated the absence of liquid water, it was unable to distinguish water molecules bound to the Pb(OA)<sub>2</sub> complexes (15). Using FTIR measurements and deuterated oleic acid (d1-OA), we distinguished O-H stretching modes associated with water bound to Pb(OA)<sub>2</sub> (15). The d1-OA was prepared so that only the acid H was exchanged for D. A major part of the water remained after degassing in sufficient amounts to provide the required 20% of water in Eq. 1 for the surface passivation described below (Pb<sub>excess</sub>:S = 0.2:1, one OH- per excess Pb). The existence of water is consistent with the observation that the Pb(OA)<sub>2</sub> precursors often form clusters (19). As a further demonstration of the role of water we added acetic anhydride (20), as a drying agent during the reaction of Eq. 1, followed by evacuation to remove acetic acid and excess anhydride (15). The subsequent formation of PbS-NC was much slower and the NCs were of reduced size, from the 8 to 10 nm (for that particular synthesis condition) to 4 nm. Also, the particle shapes became rather irregular with many (001) surfaces (15), consistent with our model.

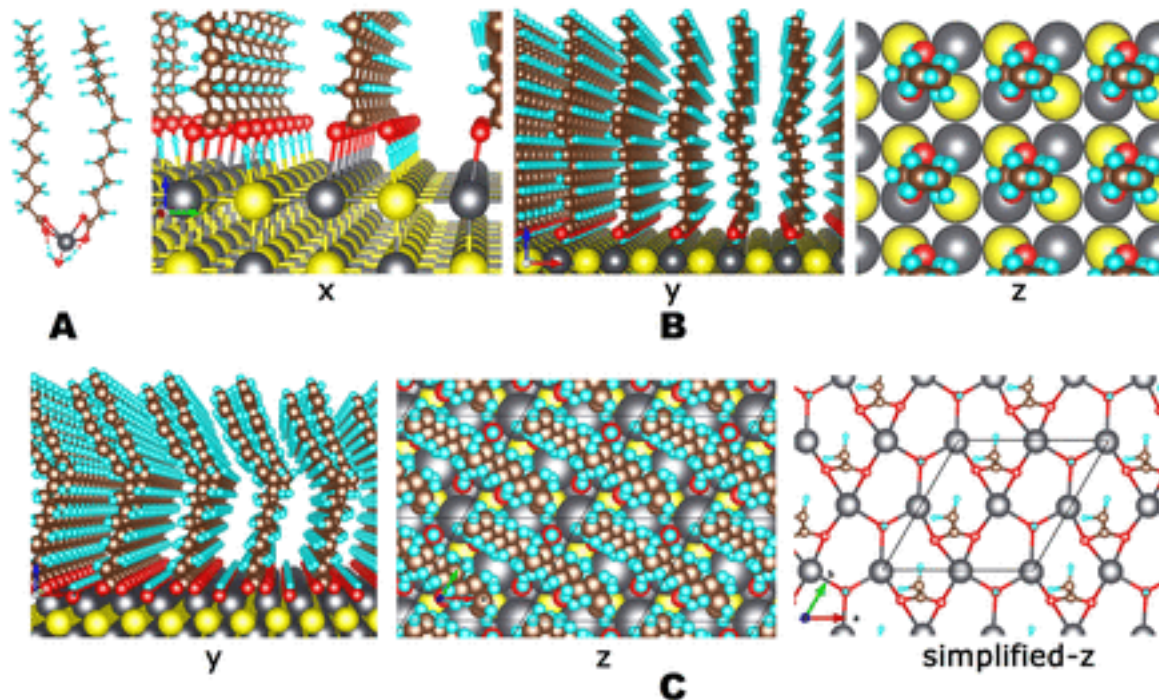
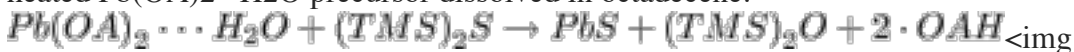


Fig. 1

Optimized molecular configurations.

(A) A water molecule formed during NC synthesis is bound to the  $Pb(OA)_2$  molecule forming a  $Pb(OA)_2 \cdots H_2O$  complex. (B) Relaxed configuration of OAH molecules on the  $PbS(001)$  surface (x,y,z-views). (C) Relaxed lowest energy configuration of  $OA^-$  and  $OH^-$  molecules on the  $PbS(111)$  surface: y- and z-views. On the right a simplified z-view schematic is shown with truncated tail chains. Pb(gray), S(yellow), O(red), H(blue), C(brown).

In the second step,  $TMS_2S$  dissolved in trioctylphosphine (TOP) is injected into the heated  $Pb(OA)_2 \cdots H_2O$  precursor dissolved in octadecene:



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(2)

The calculated  $\Delta G$  of Eq. 2 is -2.13 eV. It was suggested that the end product from oleic acid is (oleyl-CO)<sub>2</sub>O (4, 5). It is also known, and computationally confirmed, that water will react with (oleyl-CO)<sub>2</sub>O to form two oleic acid molecules. Thus, during NC synthesis, oleic acid,  $Pb(OA)_2 \cdots H_2O$  (from excess  $Pb(OA)_2$  precursor),  $(TMS)_2O$ , TOP and octadecene are present in the solution as possible passivants. In the following, we will consider passivations of the (001) and (111) surfaces separately.

Our calculation shows that oleic acid has the strongest binding energy to the (001) surface, because of its -COOH group (15). The (001) surface covered by  $OA^-$  (9) has a much higher energy than when covered by OAH, because the  $OA^-$  can bind with a cation in the solvent, and thus has a much lower chemical potential in the solvent than OAH. On the  $PbS(001)$  surface, the -COOH groups form bidentate bridges between Pb and S

atoms ( $-C=O \cdots Pb$  and  $-COH \cdots S$  bonds; Fig. 1B). This model contains one OAH molecule per two surface PbS-pairs: one pair bound to one OAH, and the other unbound. A high-density packing, with one OAH per PbS-pair, is unfavorable because of steric repulsions between the oleyl tails. The binding energy between oleic acid and the PbS-(001) surface is calculated as:

$$E(bind) = E(mol/surf) - (E(mol) + E(surf))$$

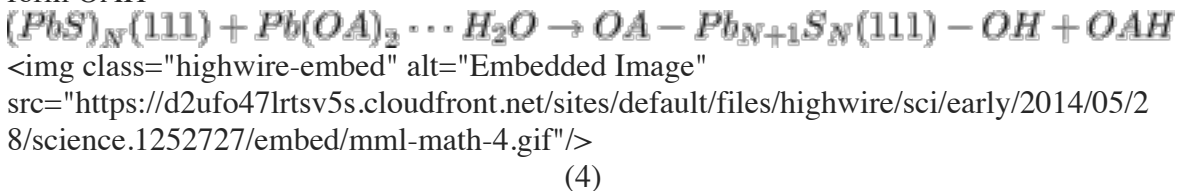
(3)

Here  $E(mol/surf)$  is the energy of the whole system,  $E(surf)$  is the energy of the unpassivated nonpolar PbS(001) surface after atomic relaxation, and  $E(mol)$  is the free energy of the passivating molecule in the solvent including solvent binding effects. There are two types of solvent binding effects, hydrogen-bonding (H-bonding) between functional groups and vdW interactions between alkane chains; of these, only H-bonding can be described accurately by the GGA method. For the vdW interaction, we have removed the GGA vdW alkyl chain-chain interaction energy from the  $E(mol/surf)$  term in Eq. 3 because the chain-chain vdW interaction will approximately cancel each other between the  $E(mol/surf)$  term and  $E(mol)$  term (15). For  $E(mol)$ , we included the  $-0.83$  eV binding energy of the H-bonded OAH-OAH dimer. We also ignored the entropy change of the ligand molecules, which we deem to be small (15). The final calculated (001) binding energy is  $-0.16$  eV per oleic acid (Table 1).

Table 1

Surface and ligand binding energies for the (001) and (111) surfaces of PbS-NC. The (001) and (111) surface areas per OAH (OA-) molecule are  $35.2 \text{ \AA}^2$  and  $30.5 \text{ \AA}^2$  respectively.

Assessing the energetics of capping the polar (111) facets is more complicated because of the need for charge compensation (21, 22) to satisfy the electron counting rule (23–25). The NCs formed in Eq. (2) have equal number of Pb and S, with stoichiometric nonpolar (111) facets with only half of the terminal Pb atoms (22, 26). We then considered whether the  $Pb(OA)_2 \cdots H_2O$  group in the solvent can fill-in the surface vacancies (missing Pb atoms). We found that, in agreement with Bealing *et al.* (9), it is sterically impossible to fill every missing Pb atom of the (111) surface with one  $Pb(OA)_2$ , but one OA- per missing Pb is possible. Hence an anionic species is needed for charge balance. This species is OH-, provided by the dissociation of bound H<sub>2</sub>O, while the H<sup>+</sup> is used to form OAH



Here  $(PbS)_N(111)$  denotes the reconstructed nonpolar (111) surface and  $Pb_{N+1}S_N(111)$  denotes the full Pb-terminated polar surface (Fig. 2, A to D). The binding energy of this passivation, which equals to the  $\Delta G$  of the reaction (4), is  $-0.52$  eV per oleate (Table 1), which is much larger than the (001) surface binding energy. The minimum energy

configuration (15) of OA-PbN+1SN(111)-OH is shown in Fig. 1C, where the OA<sup>-</sup> group stabilizes the Pb ions via  $\mu$ 2-bidentate bridging bonds and the OH<sup>-</sup> group stabilizes the Pb ions via  $\mu$ 3-Pb3-OH bonds. In the calculation of  $\Delta G$  we included the OAH-OAH dimer interaction of  $-0.83$  eV, and removed the alkyl chain-chain vdW interaction at the surface like in the (001) surface case. Although we have considered other possible passivation stoichiometries and configurations (15), none was found to be as stable as the ones considered above (Table 2).

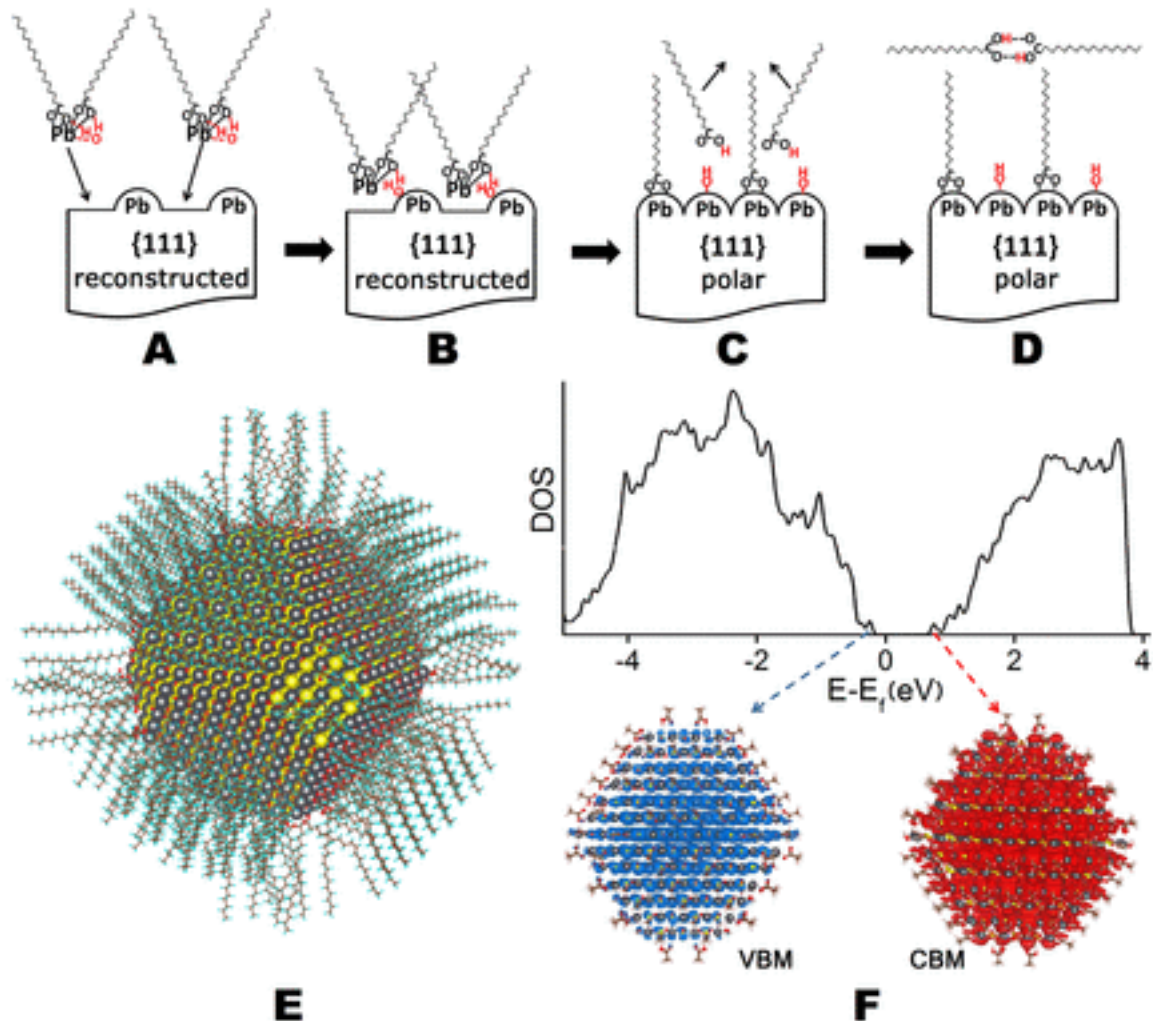


Fig. 2  
 Model of PbS-NC in colloidal solution. (A-D) Multistep process for building up the (111) facets of PbS-NC: (A) Pb(OA)<sub>2</sub>·H<sub>2</sub>O precursors approach the nonpolar and stoichiometric (111) facets. (B) Pb ions bind to surface vacancies. (C) One of the two OA<sup>-</sup> in each Pb(OA)<sub>2</sub>·H<sub>2</sub>O complex is removed due to steric effects, and the water molecule dissociates to provide an OH<sup>-</sup> group to the surface, and H<sup>+</sup> for desorbing OA<sup>-</sup>. (D) The desorbed OAH molecules dimerize in the solvent. (E) Calculated atomic structure of a 5nm diameter NC passivated with OA<sup>-</sup> and OH<sup>-</sup> ligands [coordinates in (15)]. (F) Electron density of states, showing the valence band maximum (VBM) and conduction band minimum (CBM) levels, of a NC passivated with truncated oleic acid alkyl chains [coordinates in (15)].

Table 2 Ligand patterns binding energies (eV) on the (111) PbS-NC surface for a 4 Pb atoms area.

For Pb(OA)<sub>2</sub> cases, the binding energy of H<sub>2</sub>O with Pb(OA)<sub>2</sub> and the binding of liquid water (after Pb(OA)<sub>2</sub> is bound to the surface) are taken into account. The “2OA-, 2OH-“ (current model) value is twice that shown in Table 1 because the surface area is twice as large here. The “2OA-, O2- “ corresponds to the case where 2OH- form one O2- on the surface and one H<sub>2</sub>O leaving the surface.

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In order to predict the shape of the PbS-NC, we calculated the surface energies of the (001) and (111) surfaces, which are equal to the unpassivated surface energies (nonpolar for (111)) plus the binding energies calculated above. The unpassivated surface energies were calculated from the energies of the slabs minus the corresponding bulk values. The resulting energies (Table 1) were used in a Wulff construction model (27–29) to determine the equilibrium NV shape. We obtain a (001) to (111) Wulff ratio of 0.82, in excellent agreement with the average 0.82 value derived from TEM images (Fig. 3). With this procedure we constructed a model NC with all the surface passivation features (15) and with OH- groups placed at the edges to determine if it provides good passivation of edges and corners. To simplify the calculation we truncated the alkyl chains of the oleic acids to the shorter acetic acid, which is not expected to change NC surface electronic structure. We subsequently relaxed the atomic structure of the 2325 atoms, 4 nm diameter NC in the DFT/GGA (15). The final system shows perfect surface passivation, with a clean band gap, without impurity or defect induced states (Fig. 2F), and with good edge and corner passivation. Thus, we propose that the 3D bulk structure determines the 2D surface passivation structure, which in turn determines the 1D edge passivation. For a 5 nm NC, our model (15) also provides the ratio between excess-Pb and S atoms of 0.19:1, and between excess-Pb and surface OA molecules of 1.18:1 respectively, which agree closely with experimentally observed values of 0.21:1 (measured by RBS) and 0.97:1 reported in (6). In our model the ligand binding energy on the (001) surface is much smaller than that on the (111) surface, consistent with the images in Fig. 3, where all NC are standing up on (001) facets, with some in direct contact via (001) facets. Both observations indicate that it is easy to remove the ligand molecules from the (001) facets.

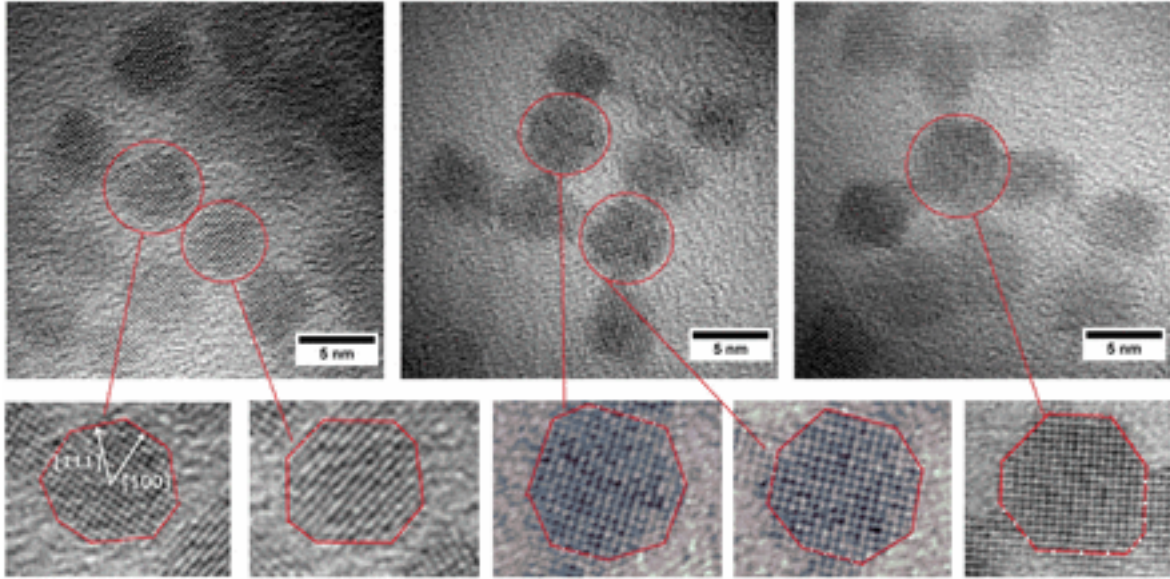


Fig. 3

TEM images of PbS-NCs.

High-resolution TEM images of the synthesized PbS-NC with enlarged views of selected NC shown below. The (111)/(001) Wulff ratios of center-to-surface distances of NCs are 0.820, 0.762, 0.866, 0.847, 0.792 from left to right, respectively, with an average ratio of 0.817, in good agreement with the calculated value.

One of the most interesting features of our passivation model is the existence of the OH- groups on the (111) facet. Water readily dissociates into OH- and H+ on transition metal or oxide surfaces (30–33), and the binding of H<sub>2</sub>O to Pb(OA)<sub>2</sub> in the solvent provides a natural kinetic pathway for this reaction (Fig. 2, A to D). The presence of small size anions is also required to establish charge neutrality over the entire quantum dot that could not be achieved by the sterically hindered OA- molecules alone. The co-existence of sterically demanding ligands, like OA-, and small anions to fill the gaps and fulfill the electron counting rule, could apply to other metal chalcogenide systems as well. To probe the existence of OH-, two NC samples were synthesized, one as described above (denoted as PbS-OH), and another following the procedure developed by Moreels *et al.* (17) that uses Cl- and no water during synthesis [denoted as PbS-Cl (15)]. In the PbS-Cl sample, the Cl- anion has effectively replaced OH-. Both samples were spin coated on freshly cleaved graphite, followed by thorough washing with acetone to remove unbound ligands, to form a sub-monolayer film. The XPS data including those for the two control samples, graphite and Pb(OH)<sub>2</sub> powder, are shown in Fig. 4. Although the graphite is freshly cleaved in an Ar glove box (with less than 1 ppm oxygen concentration), it is slightly oxidized (34, 35), showing an O 1s peak at 534.0 eV. Because of the incomplete surface coverage (15), this substrate peak is also present in the PbS-Cl and PbS-OH NC samples. After subtracting this peak, the PbS-Cl shows only one additional peak at 532.1 eV, likely from the oleate species. The PbS-OH sample contains three peaks at 534.0 eV, 532.1 eV, and 531.2 eV. The new peak at 531.2 eV is assigned to OH-, in agreement with the Pb(OH)<sub>2</sub> powder single peak at 531.2 eV, and with reported values for other metal-OH groups XPS peaks (36, 37). In the PbS-Cl sample, this feature is absent while the chlorine species produced a peak in the XPS (15). We note



that the 534.0 eV and 532.1 eV peaks have the same widths in different samples in Fig. 4. The SFG measurement also indicates the existence of OH<sup>-</sup> in the sample (15). While the present work applies to PbS-NC, we expect the general applicability of this approach to other colloidal NCs.

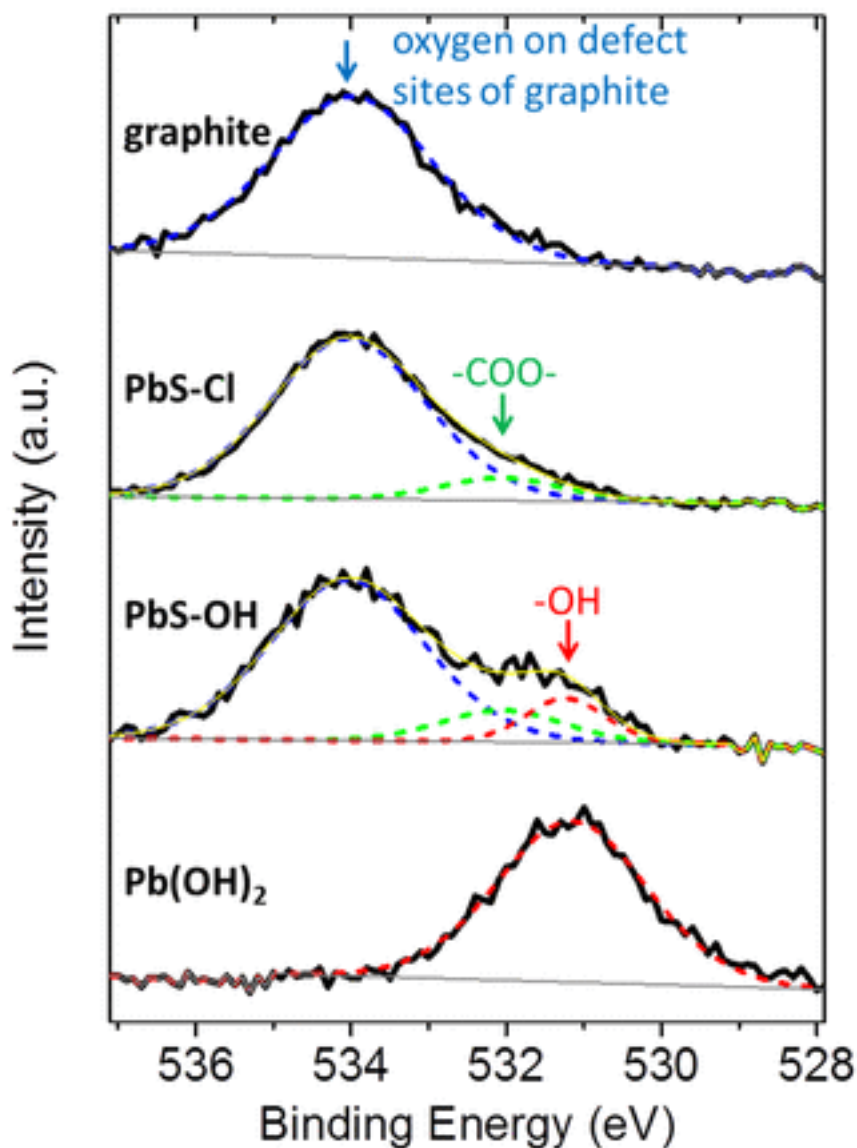


Fig. 4  
The XPS spectra of PbS-NCs.  
O 1s XPS showing peaks at 531.2eV (red) from oxygen in OH<sup>-</sup> groups, and at 532.1eV (green) from oxygen in carboxyl groups. The peak at 534 eV is due to substrate O bound to graphite.

Supplementary Materials

[www.sciencemag.org/cgi/content/full/science.1252727/DC1](http://www.sciencemag.org/cgi/content/full/science.1252727/DC1)

Materials and Methods

Supplementary Text

Figs. S1 to S19

Tables S1 to S3

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Databases S1 and S2

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