The Passivating Effect of Cadmium in PbS/CdS Colloidal Quantum Dots Probed by nm-Scale Depth Profiling – Supplementary Information.

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Ligand Exchange Procedures

All chemicals were purchased from Sigma Aldrich and used without further modification unless stated; 99.5% butylamine, 90% trioctylphosphine (TOP), 25% tetramethylammonium hydroxide in methanol (TMAH), methanol (anhydrous), hexane (anhydrous), chloroform (anhydrous), 3-mercaptopropionic acid (3-MPA).

Butylamine ligand exchange used a modified method from Fairclough et al.¹

1 ml of PbSCdS solution in octane was placed in a phial with 0.2 ml of butylamine (anhydrous) and stirred overnight at 40 °C in a nitrogen atmosphere. The solution was transferred to a centrifuge tube under an inert atmosphere. The CQDs were precipitated from solution with excess methanol followed by centrifugation for 5 minutes at 4000 rpm. The supernatant was discarded and the CQD pellet redispersed in hexane. This procedure was repeated and the CQDs finally dispersed in 0.5 ml chloroform.

3-MPA ligand exchange used a modified method from Zhang et al.²

To facilitate 3-MPA ligand exchange the CQDs first required a ligand exchange to TOP, where 0.2 ml PbS/CdS solution in octane was added to 0.2 ml TOP in a glovebox and stirred overnight. The CQDs were then cleaned by precipitating the CQDs by adding excess anhydrous acetone followed by centrifugation at 5000 rpm for 5 minutes. The supernatant was discarded and the CQD pellet dispersed in 5 ml anhydrous chloroform and stored under nitrogen.

Under nitrogen, a 3-MPA stock solution was made by adding 0.5 ml MPA to 5 ml anhydrous methanol. A further 5.5 ml TMAH was added to the 3-MPA solution until the pH was greater than 12. 0.5 ml of 3-MPA-MeOH-TMAH stock solution was added to the PbSCdS-TOP chloroform solution and stirred for 30 minutes. A further 5 ml degassed deionised water was added and stirred for 20 min. The CQD-water phase was extracted. This solution was cleaned with excess acetone ~5.0-8.0 ml and centrifuged for 5 minutes at 4000 rpm. The supernatant was discarded and the CQD pellet dispersed in 0.4 ml methanol. The solution was subsequently cleaned by adding excess chloroform and

centrifuged at 4000 rpm for 5 minutes. The final CQD pellet was dispersed in 0.2 ml methanol and stored under nitrogen.

Calibration of the X-ray photoelectron (XPS) spectra.

Recording the data at different photon energies presents a challenge for accurate calibration of the binding energy (BE) scale, as the photon energy calibration of the beamline is not accurate to fractions of an eV, and the requirement to maintain the sample position over the whole experiment meant that the Fermi level of a reference material could not be measured at every photon energy. The S 2p spectra were calibrated to a bulk PbS S $2p_{3/2}$ component at 160.7 eV.^{3,4} This allowed the calibration of the Pb 4f spectra, as they were recorded at the same photon energy. From this the Pb 4d and Pb 5d spectra were calibrated, using the binding energy differences between them and Pb 4f.⁵ The Pb 4d signals were measured with Cd 3d and N 1s at the same photon energy, so they were also effectively calibrated from the S $2p_{3/2}$ position. The resulting BE of the Cd $3d_{5/2}$ peak obtained via this route (405.4 eV) is in good agreement with the literature for CdS.⁶

Elemental Ratios from XPS

XPS spectra for the following orbitals were measured in sets of constant kinetic energy (and hence sampling depth); Pb 4d, Cd 3d, N 1s, S 2p, Pb 4f, C 1s. These were then fitted with sum Gaussian-Lorentzian peaks⁷ using CASA XPS.⁸ The binding energies of all components measured in the PbS/CdS CQD samples are listed in Table S 2. An example of the fit to the Cd 3d (at 405.4 eV) and Pb 4d (at 413 eV) region at three sampling depths for the 0.34 nm shell PbS/CdS sample is shown in Figure S 1. The areas were then extracted and corrected for photoionization cross sections and asymmetry factors.⁹ Elemental ratios were then calculated for each sampling depth.



Figure S 1. XPS spectra of the Pb 4d and Cd 3d regions at three of the measured photoelectron kinetic energies/sampling depths normalized to the Pb $4d_{5/2}$ area at that energy. These have not been corrected for photoionization cross sections and asymmetry; the corrected ratios are displayed in Table S 1.

The effect of beam damage was checked for by repeating measurements of sets of data during the data accumulation, and no effect on the elemental ratios was found. To investigate the possibility of some initial beam damage from the high intensity synchrotron radiation (SR) at the start of our measurements, we compared ratios calculated from synchrotron data with the photon energy set to 1486.7 eV with data taken in parallel using an Al K α (1486.7 eV) X-ray source from the same sample, using identical preparation and air exposure conditions. The resulting ratios (for the fresh sample with a 0.14 nm thick CdS shell), displayed in Table 1, are in agreement. We conclude that any synchrotron beam damage is small and does not significantly affect our results. Nevertheless in a small number of cases a small metallic Pb component was observed, and a density of states at the Fermi level was observed in the valence band spectra. Although this component does not increase in intensity with irradiation time, we cannot rule out a small amount of rapid initial decomposition under the SR beam leaving elemental Pb.¹⁰

X-ray Source	Cd 3d:Pb 4d	Pb 4f: S 2p
Synchrotron	0.27	0.9
	± 0.06	± 0.2
ΑΙ Κα	0.29	0.82
	± 0.05	± 0.07

Table 1. Elemental ratios from the fresh PbS/CdS sample with a 0.14 nm thick CdS shell taken with Al K α and synchrotron sources, both with photon energy 1486.7 eV.

Sampling Depth and Shell Thickness Calculations

The sampling depth was calculated from the inelastic mean free path (IMFP) of PbS. The IMFP was calculated from the TPP-2M formula ^{11–13} using band gaps calculated from the absorbance spectra (Figure 1, main text). The sampling depth was defined as the depth that 95% of the photoelectron signal originates from, and calculated in the nanoscopic spherical particle regime.¹⁴ This is used because the attenuation length of the photoelectrons is comparable to the size of the CQD. This gives a more realistic sampling depth for small CQDs than that obtained by taking the sampling depth is smaller in CQDs than in a flat surface due to the larger number of atoms in the surface layer of a CQD than the subsequent layers.

Shell thicknesses were calculated in two ways, both developed by Shard: the first method was used to generate the expected variation in the ratios of shell and core elements for different photoelectron kinetic energies for a set core diameter and shell thickness.¹⁴ Because we used synchrotron radiation to excite our samples we were able to measure signals from both core and shell elements at the same kinetic energies (and hence constant sampling depth). The predicted variation was then compared to the ratios extracted from our depth profiling XPS data. The results from this method are presented in Figure 3 in the main text and Figure S 2. This method gave a shell thickness with an error of between ±0.02 and ±0.04 nm, depending on the signal-to-noise ratio in the experimental data.



Figure S 2. Plots showing [Cd]/[Pb] ratios measured with XPS at different photoelectron kinetic energies, compared with the variation calculated using the core-shell model of Shard *et al.*¹⁴ for a series of different CdS shell thicknesses on (A) a 3.1 nm diameter PbS core, (B) a 2.8 nm diameter PbS core and (C) a 3nm diameter PbS core, as determined from absorption¹⁵. The CQDs in (A) was found to have an effective shell thickness of 0.04±0.02 nm, in (B) 0.14±0.02 nm, and in (C) 0.15±0.02 nm.

A second method was used separately to calculate shell thicknesses for each depth at which core and shell ratios were measured, for a set core size.¹⁶ As an example, the [Cd]/[Pb] ratios calculated from XPS of Cd 3d and Pb 4d (corrected for photoionization cross section and asymmetry⁹) and the shell thickness calculated at this depth are shown in Table S 1 for the 4.9 nm diameter PbS/CdS CQD sample. The average shell thickness for this sample from this method was calculated to be 0.10 ± 0.01 nm. There is good agreement across the sampling depths for the shell thickness in this sample, and this method also agrees with the first method, which was presented in the main text in Figure 3, giving a shell thickness of 0.10 ± 0.02 nm.

Table S 1. [Cd]/[Pb] ratios calculated from XPS at different sampling depths and the corresponding shell thicknesses calculated from a method by A. Shard¹⁶ for a 4.9 nm diameter core PbS/CdS CQD sample.

Sampling depth (nm)	1.34	1.63	1.86	2.06	2.30	2.46	2.55	2.65
[Cd]/[Pb] from XPS	0.41	0.28	0.24	0.22	0.23	0.18	0.19	0.18
	± 0.07	± 0.08	±0.07	±0.06	±0.07	±0.05	±0.03	±0.04
Calculated Thickness								
(nm)	0.12	0.10	0.10	0.10	0.11	0.09	0.10	0.10

XPS vs Absorption for Determining Shell Thickness



Figure S 3. The shell thicknesses for 5 samples as calculated from XPS and as calculated from the 1S 'absorption-difference' method. The shell thicknesses are plotted against the difference in 1S absorption energies before and after the shell was formed, divided by the initial energy.

In general, the shell thickness as calculated by us using XPS does not agree well with the shell thickness calculated from the difference in the 1S absorption energy before and after cation exchange, using an empirical relationship.¹⁵ The errors shown in the shell thicknesses calculated from absorption in Figure S3 are purely experimental; the overall errors including those from fitting to the Moreels relationship¹⁵ are more substantial. Figure S 3 shows that a range of CdS shell thicknesses were found by XPS for samples which all had approximately the same shell thickness when calculated by absorption. As both the extent of surface oxidation and the electronic structure at the VBM correlate very well with the XPS shell thickness, we conclude that the shell thickness estimates from XPS are more reliable for the CQDs as used in our experiments. We cannot rule out a change to the effective thickness during the ligand-exchange process (although we would normally expect this to decrease, rather than increase the shell thickness).¹⁷ Nevertheless, our results suggest that the 'absorption-difference' method alone is not a sufficiently discriminating method for determining the shell thickness.

Ligands in Unbound and Bound States Found using XPS

In two of the samples, the amount of ligands was significantly higher than seen in the other samples, as shown in Figure 2. This is because of insufficient washing after ligand exchange. In the N 1s photoelectron peak shown in Figure S 2A two species were identified, assigned to bound and unbound oleylamine ligands. In Figure S 2B signals from bound and unbound 3-MPA species were found, as well as PbS and Pb_xCd_{1-x}S. In the N 1s signal shown in Figure S 2D three N components are present. The lowest binding energy signal was identified as due to butylamine ligands bound the CQD surface, while the second largest component is assigned to unbound butylamine. The remaining N 1s component corresponds to tetramethyl ammonium left over from the synthesis procedure. The binding energies of these states are detailed in Table S 2.



Figure S 4. XP spectra of various regions showing the signals from the unbound ligands in the PbS/CdS quantum dot samples at a sampling depth of 1.3 nm. (A-C) are from the 0.15 nm CdS shell sample and (D) is from the 0.04 nm thick shell sample. The 0.15 nm shell sample was synthesized using oleylamine ligands which were exchanged for 3-MPA; the same process, with exchange for butylamine was used for the 0.04 nm shell sample. A) shows the Pb $4d_{5/2}$ component, Cd 3d, and N 1s. B) shows the S 2p region. C) is a schematic drawing showing the ligands attached to the 0.15 nm CdS shell PbS sample, with ligands present in the amounts found in XPS. D) shows the Pb $4d_{5/2}$ component, Cd 3d, and N 1s signals for a sample which was ligand exchanged to have butylamine.

Effect of aging in air on the Pb 4f signal

The changes in the S 2p spectrum as a function of air exposure were discussed in the main text (Figure 4). The corresponding Pb 4f spectra taken at the same time are presented here. The chemical shift for each peak component is displayed in Table S 2. The amount of oxidation products increases with age, and PbSO₄ appears only after significant air exposure. Slightly more Pb-containing oxidation products are present (as given by the signals in the Pb 4f spectrum of the fresh sample) than are found from the corresponding S 2p spectrum. This is most probably due to initial formation of Pb(OH)₂ (which has the same binding energy as PbSO₃, see Table S 2), as small CQD surfaces show Pb-rich (111) facets.¹⁸ Pb(OH)₂ has previously been seen to appear first in the aging of PbS nanoparticles.^{10,19}



Figure S5. Effect of surface aging time in air on the Pb 4f photoelectron spectra for a 3 nm diameter PbS quantum dot with an effective Cd shell thickness of 0.14 nm. The fresh sample was measured after a maximum of half an hour of air exposure. The sampling depth was 1.17 nm in each case, achieved with a photon energy of 390 eV.

Core level	Component	Literature Binding	Observed Binding	Spin Orbit	
		Energy (eV)	Energy (eV)	Splitting (eV)	
S 2p _{3/2}	PbS	160.7 ^{3,4}	160.7±0.1	1.2	
	-SO/S-C/-SH	161.6 ²⁰ / 161.8 ²¹ /	163.6±0.2		
		161.9 ²²			
	-SO ₂	163.15 ^{20,23}			
	PbSO ₃	166.45 ^{20,23}			
	PbSO ₄	168.1 ²⁰			
	Pb _x Cd _{1-x} S	161 to 161.7 ²⁴			
	CdSO ₄	168.8 ²⁵			
	Bound 3-MPA (bound	161.7 ⁴	161.7±0.1	1	
	via S end)				
	Unbound 3-MPA	163.4 to 163.6 ^{26,27}	163.6±0.2		
Cd 3d _{5/2}	Pb _x Cd _{1-x} S	405.4 ⁶ (CdS)	405.4±0.1	6.7	
Pb 4d _{5/2}	PbS	413 ⁵	413.0±0.2	22.1	
	Pb	412.3 ⁵	412.4±0.2		
	PbSO ₃ / Pb(OH) ₂	-	414.3±0.2		
N 1s	Bound butylamine	-	399.1±0.1	-	
	Unbound butylamine	-	400.5±0.2		
	Bound oleylamine	-	399.2±0.2		
	Unbound oleylamine	-	400.4±0.1		
	Tetramethylammonium	403.9 ²⁸	403.5±0.3		
	ion (reaction precursor)				
Pb 4f _{7/2}	PbS	137.8 ^{5,21}	137.8±0.1	4.8	
	PbSO ₃ / Pb(OH) ₂	138.4 ²¹	138.4±0.1		
	PbSO ₄	139 ²¹	139±0.1		
	Pb	136.629	136.6±0.1]	

Table S 2 Binding Energies of chemical species identified in different PbS/CdS CQD samples from XPS.

Shell Thickness and Oxidation

To display the passivating effect of cadmium on the PbS CQD surface, Table S 3 shows which (if any) oxide species were found at the CQD surfaces for samples with a maximum of 30 minutes air exposure. Figure S 6 shows the ratio of oxide species (PbSO_x) to PbS for different effective cadmium shell thicknesses. For effective cadmium shell thicknesses greater than 0.1 nm, the CQDs were well passivated and no oxidation was observed.

Table S 3 Calculated shell thicknesses of CdS, and the corresponding oxide species found at the surface, for PbS/CdS CQDs after 30 minutes maximum air exposure.

CQD	Core size (nm)	Effective Shell Thickness (nm)	PbSO ₃ present?	PbSO₄ present?
PbS	3	0	Yes	Yes
PbS/CdS	3	0.04	Yes	Small amount
PbS/CdS	5	0.10	Yes	Small amount
PbS/CdS	3	0.14	No	No
PbS/CdS	3	0.15	No	No
PbS/CdS	3	0.34	No	No



Figure S 6. Ratio of amounts of $(PbSO_3 + PbSO_4)$ to PbS measured in XPS for fresh samples (maximum 30 minutes air exposure) as a function of effective CdS shell thickness.

Valence Band Photoemission

Valence band photoemission spectra were recorded at a photon energy of 370 eV, chosen to be as low as possible consistent with maintaining viable flux from the beamline. The reasons for choosing a low photon energy are twofold; firstly, to maximize the signal from the surface of the CQDs, but more importantly to strongly enhance the cross section for photoemission from the anion (sulfur) orbitals relative to the cations (Pb, Cd). The features at lowest BE (Figure 6, main text) are of mainly S 3p character,³⁰ and their weak intensity in conventional XPS (typically using Al K α X-rays of energy 1486.6 eV) can lead to a significant error in determining the VBM, as noted by Miller *et al.*³¹

In cases where a signal was present from the underlying ITO substrate, the ITO valence band spectrum (recorded separately) was subtracted from the ITO+CQDs spectrum before the valence band maximum was determined. Before subtraction, the ITO valence band was aligned and normalized with the ITO+CQDs spectrum at the In 4d peak. In a small number of cases, metallic Pb was present (possibly due to decomposition under the SR beam, commented on above), and in these cases, the resulting Fermi edge feature was used to determine the zero of binding energy. Otherwise valence bands were aligned to the Pb 5d_{5/2} BE, which was effectively calibrated to a literature value for S 2p_{3/2} (as described previously), giving a Pb 5d_{5/2} BE for PbS at 19.1 eV, also consistent with literature values.⁵ Examples of the procedure used to estimate the position of the valence band maximum are given in Figure S 7 for the 0.34 nm sample, and the 0.14 nm sample when fresh and after it was aged in air for 8 months. In the case of the aged sample, the main feature of the valence band is due to oxidation products on the surface of the CQDs, but the intrinsic VBM from the underlying CQD can still be determined.



Figure S 7. Photoemission spectra of the valence band of (A) PbS/CdS CQDs with an effective shell thickness of 0.34 nm and (B) PbS/CdS CQDs with an effective shell thickness of 0.14 nm when fresh and after 8 months of aging in air. All valence bands were measured at 370 eV photon energy. The estimated positions of the valence band maxima are shown. In the case of (A) no contributions from ITO were present, as determined from core level XPS, whereas in (B) the ITO valence band has been subtracted from the data, as shown in Figure 6 B and C (main text).

The parameters used to construct Figure 8 (main text)

The band alignment uses the offset between the VBM and E_F estimated from the valence band photoemission (main text Figure 6, and Figure S 7). The position of the trap states was taken from work by Konstantatos *et al.*³² For the 8-month-aged 0.14 nm shell sample, the shell barrier is assumed to be sulfate, taken to have a band gap of 3.44 eV.³³ The VBM and E_F offset of the sulfate was also determined from our valence band photoemission. For the fresh 0.34 nm sample, an alloyed shell with varying band gap is assumed, as discussed in section 4.1, main text. The band gap is assumed to vary between that of the PbS core and that of an alloyed Pb_xCd_{1-x}S shell, with $x\approx 0.3$ (estimated from Figure 2, main text), with the band gap at the edge of the shell estimated from work on Pb-Cd alloyed nanowires.³⁴ The VBM and E_F offset for the shell edge were taken from our valence band photoemission for this sample, while for the core, the offset of a reduced core radius was used, as indicated by TEM results for this sample (Section 3.2, main text).³¹ The schematic diagram of the CQD structures was drawn using Jmol,³⁵ using the experimental XPS ratios of Cd:Pb and oxidation products:Pb to estimate the chemical appearance of the CQD surface.

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