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Influence of multi-step surface passivation on the performance of PbS colloidal quantum dot solar cells

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ABSTRACT: The performance of devices containing colloidal quantum dot (CQD) films is strongly dependent on the surface chemistry of the CQDs they contain. Multi-step surface treatments, which combine two or more strategies, are important for creating films with high carrier mobility that are well passivated against trap states and oxidation. Here we examine the effect of a number of these surface treatments on PbS CQD films, including cation exchange to form PbS/CdS core/shell CQDs, and solid-state ligand exchange treatments with Cl, Br, I, and EDT (1,2-ethanedithiol) ligands. Using lab-based and synchrotron-radiation-excited XPS, we examine the compositions of the surface layer before and after treatment, and correlate this with performance data and stability in air. We find that halide ion treatments may etch the CQD surfaces, with detrimental effects on the air stability and solar cell device performance caused by a reduction in the proportion of passivated surface sites. We show that films made up of PbS/CdS CQDs are particularly prone to this, suggesting Cd is more easily etched from the surface than Pb. However, by choosing a less aggressive ligand treatment, a good coverage of passivators on the surface can be achieved. We show that halide anions bind preferentially to surface Pb (rather than Cd). By isolating the part of XPS signal originating from the topmost surface layer of the CQD, we show that air stability is correlated with the total number of passivating agents (halide + EDT + Cd) at the surface.

1. INTRODUCTION

Lead sulfide (PbS) colloidal quantum dots (CQDs) have been successfully used as the light absorbing component in solar cell devices, achieving near-record CQD solar cell efficiencies.¹ One of the outstanding problems in achieving commercially viable CQD-based solar cells is their poor stability in ambient conditions. There has been a large effort worldwide to improve the air stability of PbS CQDs. One strategy is to reduce the CQD size to increase the proportion of the surface formed from Pb-rich (111) ligand-passivated facets which are more air stable than the stoichiometric (100) facets.^{2,3} However the requirement to keep the size below a certain threshold restricts the freedom to tune the band gap through quantum confinement, which is one of the benefits of using CQDs.⁴ Other strategies for achieving good air stability include chemically adjusting the surface with cation exchange,⁵ or inorganic ligand exchange/halide ion passivation, both of which eliminate surface trap states and protect the surface from oxidation.^{6–10} Multi-step passivation treatments, where the above strategies (and often short organic ligand exchange) are combined, have produced improved power conversion efficiencies (PCE) over single passivation treatments in solar cells. Passivation strategies have mostly focused on hybrid ligand exchanges, where halides are used in combination with short organic ligands for increased charge transport between CQDs.^{11,12} Neo *et al.*

used a multi-step treatment, with a hybrid ligand exchange using bromide and 1,2-ethanedithiol (EDT) ligands on cation-exchanged PbS/CdS CQDs.¹³ By combining a sub-monolayer CdS shell and atomic halide ligand treatment, they achieved a good passivation of surface trap states while reducing the barrier to charge transport created by the CdS shell.¹⁴ The improved charge transport achieved by combining Cd- and Cl-passivation has also been observed by Tang *et al.*⁶ Although multi-step passivation strategies offer many advantages, care should be taken to optimize the surface chemistry. This is particularly important as some ligand exchanges have been found to etch the CQD surface. This has been observed when using short chain thiols and alcohols,^{15,16} and for molecular chlorine and halide salt treatments if the treatment is too aggressive.^{11,17–21} The solvent used for solid state ligand exchanges has also been found to affect the performance of CQD solids.²² Here we investigate the potential causes for surface etching of PbS and PbS/CdS core/shell quantum dots, and the effect of etching on air stability and device performance.

PbS CQDs passivated with iodide have achieved higher PCEs and air stability than those treated with other halides.^{1,6,23,24} The reason for this is thought to be due to the size of iodide, since a larger halide can sterically inhibit oxidative attacks.⁷ Here, we show that iodide treatment produces an increased surface coverage of halide compared with chloride and

bromide treatments. Despite this, successful passivation by combining Cd and halides on PbS CQD surfaces has been limited to Cl and Br.^{6,13} We hypothesize that this is related to the way the different halides bind to the PbS/CdS surface, which we probe here.

Previously we have used X-ray photoelectron spectroscopy (XPS) to show how cadmium localized on the outside of PbS CQDs is effective in reducing the rate of oxidation in air.⁵ Now we present an in-depth study showing how halide ion treatment affects the PbS and PbS/CdS surface, how the halides bind to the CQD surface and which multi-step passivation strategies are the most effective for preventing oxidation. In order to enable this analysis, information about the composition of the topmost surface layer of the CQDs is extracted from the XPS data. We examine the relationship between the number of passivators in this layer and the resulting air stability and device performance. We find that devices incorporating halide-treated PbS/CdS CQDs show a worse performance than identical devices with halide-treated PbS-only CQDs. We suggest this is because Cd on the surface is more easily removed through etching than Pb. We find that aggressive halide treatment etches the surface without providing additional halide passivation, so the best passivation is achieved by limiting the number of halide treatment cycles.

2. EXPERIMENTAL SECTION

2.1 PbS/CdS Core/Shell CQD Synthesis.

3 nm (1.3 eV) PbS CQD cores were synthesized by a procedure adapted from Hines and Scholes.²⁵ The CdS shells were grown by cation exchange, in the procedure developed by M. S. Neo *et al.*²⁶ The details of this synthesis have been described previously.¹³ The ligand attached to the CQDs after the synthesis is oleic acid (OA).

Reference 3 nm CdS core-only CQDs were synthesized by a procedure adapted from Yu and Peng.²⁷ Details are given in the supporting information.

2.2 Film preparation, solid state ligand exchange and device preparation.

CQD films were deposited in an ambient atmosphere. They were deposited on pre-patterned ITO-coated glass, with a 50 nm overlayer of PEDOT:PSS spin coated at 5000 rpm and annealed at 150 °C for at least 5 minutes. Layer-by-layer spin coating was employed to build up the CQD films, full details of which have been reported previously.^{13,28} Solid state ligand exchange was performed *in situ* on each layer after deposition using one of/a combination of: tetrabutylammonium chloride (TBAC) for the chlorine (Cl) source, tetrabutylammonium bromide (TBAB) or cetyltrimethylammonium bromide (CTAB) for the bromine (Br) source, tetrabutylammonium iodide (TBAI) for the iodine (I) source and a bifunctional linker molecule, 1,2-ethanedithiol (EDT). Approximately 50 nm-thick films were made this way.

For the halide treatments, the surface of the film was covered with 10 mg/mL halide ligands in a methanol solution for 1 minute. The film was then spun dry at 2000 rpm before washing off excess ligands by adding 3 drops of methanol. This procedure was repeated 3 times for each layer of the film.

For ligand exchange to EDT, the sample was spun at 2000 rpm while two drops of 1% v/v EDT in methanol were dropped onto surface, followed by 3 drops of methanol and 3 drops of toluene to wash off unbound ligands.

For the hybrid ligand exchange, where CTAB and EDT were both used, the halide flooding procedure was carried out only once before two drops of 1% v/v EDT in methanol was added.

The films were characterized by XPS and optical absorption spectroscopy after this stage.

For fabrication of a solar cell device, two final steps were performed. First an *n*-type layer was deposited by spin coating a colloidal solution of ZnO at 1000 rpm on top of the CQD film to form a 100 nm-thick ZnO layer. Then a 100 nm-thick aluminum top electrode was deposited thermal evaporation in an Edwards 306 evaporator at 1×10^{-6} torr, with an evaporation rate of 0.1 nm s⁻¹. Devices made in this way were stable for around 5 days with the instability likely to be attributable to the interface between the aluminium top electrode and the ZnO nanoparticles. For this reason devices were stored under N₂ and *I-V* measurements were taken immediately after fabrication.

2.3 Characterization.

Optical absorption spectroscopy of the CQD films was measured using a PerkinElmer Lambda 1050 UV-vis-NIR spectrophotometer.

XPS was performed on SPECS PHOIBOS 150 and Kratos Axis Ultra spectrometers, both with excitation from focused monochromated Al K α (1486.6 eV) X-rays and using an electron flood gun for charge neutralization. Peaks were recorded with a pass energy of 30 eV (SPECS) or 40 eV (Kratos) and total instrumental resolutions of 0.8 eV and 1.1 eV at these pass energies respectively.

Synchrotron radiation excited XPS (SR-XPS) was performed using the BACH beamline ($45 < h\nu < 1650$ eV), equipped with a Scienta R3000 hemispherical analyzer at the Elettra synchrotron in Trieste, Italy. XP spectra were recorded at room temperature at an angle of 60° between incident X-rays and analyzed photoelectrons, using light linearly polarized in the scattering plane. The total instrumental resolution ranged from 170 meV (at 250 eV photon energy) to 1.26 eV (at 1400 eV photon energy). Data were collected in sets of spectra at the same photoelectron KE, between 225 eV and 900 eV KE. As the inelastic mean free path (IMFP) of photoelectrons emitted from the sample is dependent on their KE, the depth probed increases with KE.²⁹ All XPS spectra were fitted with CasaXPS.³⁰ The areas of XPS peaks were corrected for photon flux and photoionization cross section.³¹ Binding energies were calibrated to the literature values for PbS in Pb 4f.^{5,11,32}

2.4 Device Characterization

To minimize degradation, devices were loaded into a sealed testing chamber flushed with N₂ and continuously purged with N₂ throughout testing. A Keithley 2400 source meter was used for current-voltage (*I-V*) measurements. A Newport solar simulator fitted with an AM1.5 filter produced AM1.5 solar spectrum illumination, with the power density of the light source calibrated by a Thorlabs D3MM thermal sensor. The voltage was swept from -0.4 to 1 V in 0.025 V steps.

3. RESULTS

3.1 Depth Profiling – locating the passivating atoms

A number of films were studied using SR-XPS to check if the passivating atoms are located on the outer surface of the CQDs. Figure 1 shows the variation in the Br/Pb and Cd/Pb ratios in a PbS/CdS TBAB film as a function of sampling depth. Both the amounts of Br and Cd decrease relative to Pb as the sampling depth increases and more of the core is probed, demonstrating that both Br and Cd are located on the outside of the PbS core. The Br/Pb ratio is much larger than the Cd/Pb ratio, indicating that there is more Br on the surface than Cd (Br/Cd is 17:1 at the lowest sampling depth). The ratio of Cd/Pb suggests that there is still Pb present on the surface.⁵ This is explored further in section 3.3.

Figure 1 C shows the depth sensitivity of the concentrations of Br, Cd, and N relative to Pb. The depth sensitivity was calculated by normalizing each elemental ratio to the respective ratio observed at the lowest sampling depth. This shows that Br and Cd have the same depth sensitivity, and so are localized in the same layer, meanwhile N (present from residual TBA left from the solid state ligand exchange) is more sensitive to change in depth, so is located further from the Pb core, outside the CQD surface. The variation of the Br/S ratio as a function of sampling depth was also investigated (supporting information) and also suggests that Br is concentrated on the surface outside of the PbS core. The knowledge that Br and Cd are located in the outer layer of the PbS CQDs allows us to calculate the composition of the topmost surface layer of the CQDs from XPS (section 3.3).

Figure 1. Elemental ratios as a function of sampling depth for (A) [Br]/[Pb], and (B) [Cd]/[Pb], as calculated from synchrotron-excited X-ray photoelectron spectroscopy, for

the PbS/CdS TBAB sample. (C) Depth sensitivity plot: XPS-determined ratios of [Cd], [Br], and [N] (from TBA) to [Pb], each normalized to their ratio at the lowest sampling depth.

3.2 Halide binding to the surface

In addition to preventing oxidation, a further benefit of incorporating halide ions onto PbS CQD surfaces is to passivate trap states at under-coordinated surface atom sites. For PbS/CdS CQDs, with a sub-monolayer of Cd on the surface, the halides could bind to either Pb or Cd. The two possible surface chemistries could have an effect on device performance. A change in the surface chemistry may change the CQD film properties, such as work function, carrier mobility, and charge transport barriers.^{13,33–36} The XPS binding energy (BE) of the halide core levels gives information about the chemical environment of the element. Here, we use XPS to determine whether the halide in halide-passivated core/shell PbS/CdS CQDs binds to Cd or Pb. Figure 2 shows the XPS spectra of the Cl 2p, Br 3d, and I 4d regions for PbS/CdS CQD films treated with chlorine, bromine, and iodine respectively. For reference, signals from halide-treated PbS- and CdS-only CQDs are shown at the top and bottom of Figure 2 respectively. The BEs of the XPS signals and their assignments are displayed in Table 1. The BE values found for the Cl 2p signal of Cl bound to Pb, and the corresponding Br 3d Pb-Br, and I 4d Pb-I BEs agree with those found in the literature.^{9,37,38} No suitable references could be found for Cd bound to Br and I, but higher binding energies relative to Pb are expected due to the lower electronegativity of Cd.³⁹

Table 1. XPS peak assignments for halides bound to Pb and Cd.

Core level	Assignment	Literature Binding Energy	Observed Binding Energy (eV)	Spin Orbit Splitting (eV)
Cl 2p	Pb-Cl	198.0 ³⁷	198.0±0.1	1.6
	Cd-Cl	198.8 ⁴⁰	198.7±0.1	
Br 3d	Pb-Br	68.2 ⁹	68.1±0.1	1.1
	Cd-Br	-	68.9±0.1	
I 4d	Pb-I	49.1 ³⁸	49.0±0.1	1.7
	Cd-I	-	49.7±0.1	

For each of the PbS core-only CQDs, only a single component could be fitted to the XPS spectra in Figure 2, so each halide is bound to Pb only. The binding energy positions of Pb-X (X=halide) are marked in Figure 2 with dashed lines indicating the lower BE component of the doublet. For the CdS core-only CQDs, the BE positions of the halide peaks are higher than those from the PbS core-only CQDs. In these cases, the halides are bound to Cd only. Next, we examine the photoemission spectra from the PbS/CdS CQDs which have both Cd and Pb present on the surface. In the case of Cl- and Br-passivated PbS/CdS CQDs, single components could be fitted which have BEs corresponding to Cl bound to Pb, and Br bound to Pb respectively, as can be seen in Figure 2. This indicates that Cl and Br are bound only to Pb on the surface of PbS/CdS CQDs. However for I, two components were required to achieve a suitable fit. In this

case the larger component corresponds to Pb-I, but a smaller peak is present from Cd-I. In this case two dashed lines are marked in Figure 2 to show the agreement with these two components and the binding energy positions found for the reference PbS- and CdS-only CQDs. We rationalize the observation that, of the halides, only I binds to cadmium by noting that the bond dissociation energy of the Pb-X bond is larger than that of the Cd-X bond, but that the difference decreases substantially in the sequence X=Cl,Br,I (supporting information). This is also supported by comparing the Cd 3d

XPS spectra for the PbS/CdS samples (supporting information), where a higher binding energy component is present for the PbS/CdS TBAl sample, corresponding to Cd bound to iodide. In the case of Cl and Br, a much stronger bond is made when the ligand binds to Pb than to Cd, and we find that the halide is bound only to Pb. In the case of I, where there is an enhanced affinity between Cd and I as soft acid/soft base⁴¹, the difference in bond strength between Pb-I and Cd-I has decreased to a point where some halide is binds to Cd.

Figure 2. XPS spectra of the Cl 2p, Br 3d, I 4d signals for PbS, CdS, and PbS/CdS (core/shell) CQD films passivated with different halide treatments. Dashed lines have been added to aid the eye when comparing the peak positions, using the lower BE components of the doublets. Differences in the FWHMs of the signals between samples are due to measurements being taken with two different spectrometers with different instrumental resolutions. Spectra from all CdS samples, PbS/CdS TBAl and PbS TBAC samples were recorded using the Kratos Axis Ultra spectrometer. All other spectra were measured with the SPECS Phoibos spectrometer.

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3.3 Surface Composition

By using pathlength arguments, we estimate that 45% of the XPS signal at the Al K α energy originates from the top monolayer of the 3 nm-diameter CQDs (see supporting information). As shown in section 3.1, SR-XPS shows that the halide and cadmium are localized on the surface of the CQDs. Using this knowledge we can calculate the composition of the topmost surface layer of the CQDs for

multiple samples measured with lab-based XPS. The procedure used is described in the supporting information. The surface compositions of the CQD samples obtained in this way are shown in Figure 3.

In the initial cation-exchanged state, before any halide or ligand treatment (PbS/CdS OA), approximately 45% of surface Pb is exchanged for Cd, as seen in Figure 3. The remaining amount of Cd after the further solid-state ligand exchange processes is a useful indicator of whether the surface is etched by the treatment. When the OA is

exchanged for EDT (PbS/CdS EDT), the amount of Cd on the surface is unchanged, so the EDT ligand exchange process does not etch the surface. However, all the PbS/CdS halide-exchanged samples show a decrease in Cd surface occupancy to approximately 10-20% of the available sites. This suggests the halide treatment etches Cd from the surface. Similar etching of CQD surfaces has been reported after ligand exchanges to short chain alcohol ligands and amines^{15,16,42,43}, with molecular chlorine,^{18,20} propyl trichlorosilane on CdSe/CdS core/shell nanocrystals,²¹ and with ammonium chloride on CdSe nanocrystals.¹⁹ In contrast, the hybrid ligand exchange (PbS/CdS CTAB+EDT, Figure 3) results in the same amount of halide on the CQD surfaces as other halide-passivated PbS/CdS samples, but the Cd surface occupancy is approximately 40%, close to the original PbS/CdS OA CQDs. As described in section 2.2 the hybrid ligand exchange treatment used only one third of the number of cycles of the full halide treatment, but produced a similar coverage of halide on the surface, without etching away cadmium. This indicates that halide can be added to the PbS/CdS CQD surface without significantly removing Cd from the surface, and highlights the importance of checking the surface composition after different surface treatments to find the optimum treatment.

Figure 3. Composition of the surface (top monolayer) of PbS and PbS/CdS CQDs with various surface passivation strategies as measured by X-ray Photoelectron Spectroscopy. The blue bars represent the percentage of the surface Pb cation exchanged for Cd, red represents halide bound to Pb (X=Cl,Br,I), green represents a thiol from EDT ligands bound to the surface, and purple represents the percentage of the available surface sites that remains as PbS (non-stoichiometric).

3.4 Air stability

To investigate the stability in air of CQD films prepared using the different treatments, the XPS S 2p spectra were compared after the films were stored in dark, ambient conditions for 30 days. The S 2p region is useful for diagnosing surface oxidation because of the large chemical shifts between oxidation products from PbS.⁵ In lab-based XPS, there is typically a large background from the Pb 4f

peaks, preventing accurate fitting. Nevertheless, the presence or absence of oxidation products is clear.

First we examine the effect of the surface coverage of passivators after multi-step treatments on oxidation. The S 2p spectra for PbS/CdS CTAB, PbS/CdS EDT, and PbS/CdS CTAB+EDT CQD films are shown in Figure 4 A. CQD films treated with only EDT ligands are known to be unstable in air.⁸ In both the EDT- and CTAB-treated films evidence of some oxidation is present in the region of 166-170 eV BE where S 2p signals from sulfites and sulfates are found.^{5,44,45} However, the PbS/CdS CTAB+EDT sample shows no sign of these oxidation products having formed after 30 days, suggesting this film is more air stable. The reason for superior air stability is likely to be related to the surface chemistry. Since both the PbS/CdS CTAB and PbS/CdS CTAB+EDT samples have the same coverage of Br on the surface (approximately 35%, Figure 3) this cannot explain the difference in air stability. The amount of exposed PbS on the surface is different however, with PbS/CdS CTAB+EDT showing the least PbS remaining on the surface, and so the most surface sites are passivated of any sample studied here (Figure 3). Etching of the surface by the halide treatment, as determined in section 3.3, is responsible for the greater amount of PbS exposed on the PbS/CdS CTAB sample. In this case we found that the surface of the PbS/CdS CTAB sample was etched more than the PbS/CdS CTAB+EDT film, probably due to the larger number of repetitions of the halide treatment. This etching has left surface Pb and S sites open to oxidation. This is supported by the O 1s spectra of these films (supporting information) where the component related to Pb(OH)₂ and PbSO₃ species is larger in the PbS/CdS CTAB CQD film than in the corresponding hybrid ligand exchanged film (PbS/CdS CTAB+EDT).

CQD solar cells including PbS CQD films passivated with iodide have been shown to maintain relatively high efficiencies in ambient conditions over several months.²⁴ Figure 4 B shows the S 2p spectra for PbS TBAI and PbS/CdS TBAI films after 30 days of air exposure. We observe that in the case of the PbS/CdS TBAI films some oxidation products are formed. For PbS TBAI no oxidation products can be discerned. It seems that here, the combination of Cd and I passivators on the surface has resulted in a less air-stable film. To explain this, we can again use our understanding of the surface composition. 75 % of the Cd was removed from the surface in the halide treatment of PbS/CdS TBAI (compare PbS/CdS OA, Figure 3), and only approximately 25% of the surface is covered in I (bound to Pb) compared with 60% on the PbS TBAI film (Figure 3). The total amount of passivants on the surface of the PbS/CdS TBAI CQDs is less than for PbS TBAI and the air stability is reduced.

Overall, for a range of samples, our XPS results suggest that air stability is correlated with the total number of passivating agents (halide + EDT + Cd) at the surface. Optical absorption spectroscopy is also useful for studying the effect of aging in CQDs. A blue shift in the *iS* peak has been attributed to surface oxidation as the effective size of the core shrinks.^{3,46-49} Broadening of the excitonic peak has been noted as another effect of oxidation, caused by different CQDs within the film oxidizing by different amounts.⁴⁸ Figure 5 shows the optical absorbance spectra of a series of CQD films, measured over several months. The samples were first measured after 5 days' storage in air. It is possible that some

changes in the optical absorbance had already occurred before the first absorption measurement, although Zhang *et al.* observed minimal shifts in PbSe CQD films treated with bromide after 5 days of air storage.⁴⁸ The 1S peak shows a blue shift in all films in Figure 5 after 5 months' ageing, but the shift is difficult to quantify due to the peak broadening also observed. Figure 5A compares the behavior of halide- and hybrid ligand exchanged CQD films. The 1S peak of both films can be seen to broaden during ageing. Clearly the excitonic peak of the CTAB-treated film is broader at all ages than the CTAB+EDT film, suggesting that at every stage the CTAB is more oxidized than CTAB+EDT, consistent with the XPS results (Figure 4), and the lower number of surface passivators (Figure 3). Broadening of the excitonic peak is also a sign of ligand etching,⁵⁰ which could contribute to the larger initial width of the PbS/CdS CTAB film absorption.

Figure 4. Comparison of the extent of surface aging from the S 2p Al K α X-ray photoelectron spectra of PbS colloidal quantum dots with different surface treatments after 30 days air storage: A) PbS/CdS CQD films treated with CTAB, CTAB+EDT, and EDT, B) PbS and PbS/CdS CQD films treated with TBAI. The BE positions of different possible components are indicated. The BE position of S bound to Cd is omitted as the binding energy depends on the amount of Cd on the surface, but it is within +1 eV of PbS.⁵

Broadening is also evident for the films shown in Figure 5B, where CQD films treated with TBAI, with and without Cd are compared. At each stage the excitonic peak is broader for the PbS/CdS TBAI film than PbS TBAI. This supports the XPS evidence in Figure 4B suggesting that the PbS/CdS TBAI film is more prone to oxidation than PbS TBAI, and consistent with the poorer overall passivation (Figure 3).

Before being deposited into a film, the positions of the 1S peak for PbS and PbS/CdS passivated with oleic acid were 990 nm and 960 nm (see supporting information). The shift between these peaks is due to the reduction in the PbS core size after cation exchange to form a sub-monolayer CdS shell.^{5,13} The 1S absorption energies displayed in Figure 5 are clearly significantly red shifted from these values. This is attributed to the reduction of interdot distance in the solid-state ligand-exchanged films, and hence reduced confinement.^{6,12,13,51–55}

Figure 5. Effect of aging over 5 months on the absorbance spectra of A) PbS/CdS CQD films treated with CTAB (black) and with CTAB+EDT (red), and B) PbS (black, offset) and PbS/CdS (red) CQD films treated with TBAI.

3.5 Effects of passivation on device performance

To investigate the effect of a sub-monolayer of CdS on halide-passivated devices, the PbS and PbS/CdS films with TBAC, TBAB and TBAI were incorporated into a heterojunction device as the p-type layer and tested under AM 1.5 illumination after fabrication. The *JV* curves for the champion devices are displayed in Figure 6 and the V_{oc} , J_{sc} ,

fill factor (FF) and PCEs are displayed in Table 2. The current density-voltage (J - V) characteristic curves in Figure 6 show that in all cases the PbS/CdS devices showed poorer performances (lower PCE) than those with PbS. The PbS/CdS TBAI device, however, (Figure 6C) performed considerably worse than the PbS TBAI device, showing a very significantly

Table 2. Device performances for PbS and PbS/CdS CQD devices treated with TBAC, TBAB, and TBAI. The performance of the champion device is quoted in brackets.

	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
PbS TBAC	6.69 ± 0.70 (7.30)	0.46 ± 0.01 (0.46)	0.43 ± 0.05 (0.48)	1.32 ± 0.29 (1.60)
PbS/CdS TBAC	3.57 ± 0.50 (4.10)	0.46 ± 0.02 (0.44)	0.40 ± 0.01 (0.40)	0.65 ± 0.07 (0.72)
PbS TBAB	20.3 ± 0.5 (20.6)	0.51 ± 0.01 (0.50)	0.45 ± 0.03 (0.48)	4.62 ± 0.38 (5.00)
PbS/CdS TBAB	16.9 ± 0.8 (17.7)	0.49 ± 0.01 (0.50)	0.43 ± 0.01 (0.43)	3.58 ± 0.26 (3.84)
PbS TBAI	18.4 ± 0.8 (19.2)	0.54 ± 0.01 (0.53)	0.39 ± 0.01 (0.40)	3.88 ± 0.19 (4.07)
PbS/CdS TBAI	5.71 ± 0.43 (6.1)	0.48 ± 0.02 (0.50)	0.43 ± 0.01 (0.43)	1.18 ± 0.14 (1.31)

Figure 6. Current density vs. voltage performance of the champion devices incorporating 50-nm-thick PbS and PbS/CdS CQD films treated with TBAI, TBAB, and TBAC, tested under AM1.5 illumination conditions.

lower J_{sc} . While the PbS/CdS TBAC and TBAB devices also performed worse than their PbS equivalents, the difference in performances is not so great compared with the TBAI-passivated devices. These observations are discussed in terms of the surface chemistry in the next section.

4. DISCUSSION

A comparison of the surface compositions before and after various treatments reveals strong evidence for etching during halide treatments. Using the percentage surface coverage of Cd in PbS/CdS CQDs as an indicator (given that Cd is known to be located primarily at the surface (Figure 1)), we see that this can decrease to as little as 20% of the original value (PbS/CdS OA) following halide treatments for PbS/CdS TBAC, TBAB, CTAB, and TBAI (Figure 3). Etching of Pb cannot be quantified, since Pb is present throughout the CQDs. However, it is rational to assume that less Pb is removed than Cd, since the bond energy of the Cd-S bond (208.5 kJ/mol)⁵⁶ is approximately half that of the Pb-S bond (398 kJ/mol), i.e. Pb is more strongly bound to S, and is expected to be harder to remove by etching.⁵⁶ The only case where negligible Cd was removed from the surface after halide treatments was in the preparation of the PbS/CdS CTAB+EDT film (Figure 3). In this case a less intense halide treatment was used (1 iteration), yet the percentage of halide on the surface is the same as for the PbS/CdS CTAB film (3 iterations). Thus it is possible to perform a halide ligand exchange without significantly etching the CQD surfaces.

Comparing the films which have been subjected to 3 iterations of halide treatment, we note that the PbS/CdS CTAB film shows roughly twice as much Cd remaining at the CQD surfaces than PbS/CdS TBAX (X=Cl, Br, I). This suggests the treatment involving CTAB is less aggressive in etching the CQD surface than TBAX, and the counterion could be responsible. Balazs *et al.* have previously shown the choice of counterion can affect the reactivity during ligand exchange, controlling carrier transport in the CQD films produced.⁵⁷ Oh *et al.* found that the coordination strength of oleate to its counterion controls the rate of etching on CdS nanorods during synthesis.⁵⁸ However in this case the counterions were monoatomic ions rather than the quaternary ammonium ions used here. Further study is required to know exactly how etching during halide ligand exchange depends on the counterion.

The amount of halide bound to Pb on the surface is in the range 35-45 % for all halide-passivated samples except PbS TBAI where approximately 60% of the surface is covered by

iodide, and PbS/CdS TBAI where only 25% of the surface is covered. The greater coverage of the surface by iodide on the PbS TBAI surface, leaving fewer Pb and S surface sites exposed, is likely to be a factor in the high PCEs and air stability achieved using iodide-passivated PbS CQDs.^{1,8,24,59}

The diversity in the surface chemistry of the studied films can be used to understand the differences in air stability and device performance. The air stability of the PbS TBAI and PbS/CdS TBAI films have been compared here using XPS of the S 2p region (Figure 4B) and optical absorbance (Figure 5B). In this case the PbS TBAI film was found to be more air stable than the PbS/CdS TBAI film. The addition of Cd to the surface would be expected to improve the air stability,⁵ but evidently the opposite has happened. We attribute this to the lower total number of surface passivators at the CQD surfaces in the case of the PbS/CdS TBAI film, with a larger amount of PbS remaining on the surface after the ligand exchange (Figure 3). In this case both films underwent the same halide treatment, but etching is expected to have been more severe in the PbS/CdS case since Cd bound to S is easier to remove than Pb. This reasoning can also explain the greatly reduced performance observed in the PbS/CdS TBAI solar cell device compared to PbS TBAI (Figure 6 and Table 2). Approximately 20% more of the surface of the PbS/CdS TBAI CQDs is unpassivated (corresponding to Pb and S at the surface) than the PbS TBAI CQDs after the ligand exchange. The remaining unpassivated Pb and S sites create more trap states on the surface, reducing the performance significantly.¹¹ We believe the poorer performance in the PbS/CdS TBAI device could also be related to how the iodide bonds to the surface. As shown in Figure 2, iodide bonds to both Cd and Pb on the PbS/CdS surface, in contrast to chloride and bromide which only bind to Pb. It has been shown that, surface S atoms adjacent to cation-exchanged Cd atoms are more stable than those next to Pb and are fully bonded, so do not produce trapping defects.^{5,13,60} Therefore substituting S atoms that are bound to Cd for I is less effective in increasing passivation than substituting for those bound to Pb atoms which have unpassivated dangling bonds causing trap states.^{6,11} The I which binds to Cd is not passivating these trap states, and does not contribute to improving the performance of the device.

The air stability of the PbS/CdS CTAB and CTAB+EDT films was also compared (Figure 4A and 6A). Both measurements showed that the CTAB film oxidized more rapidly than the CTAB+EDT film. As shown in Figure 3, the surface of the CQDs in the CTAB film have more unpassivated PbS present, due to etching of Cd from the surface during the halide treatment. This comparison highlights the importance of avoiding excessive halide surface treatments as the potential damage could be critical to device performance and air stability. Etching can produce unpassivated surface sites.²¹ Unpassivated Pb sites on (111) facets and Pb and S sites on (100) facets are unstable,^{3,61} and result in defects within the band gap of the CQD.^{43,55,62} It is possible that etching CQD surfaces can also create new unpassivated sites that are more vulnerable to oxidation than those on these facets.⁸

The results from the PbS/CdS CTAB and CTAB+EDT films also help explain the results seen by Neo *et al.*,¹³ for devices incorporating PbS/CdS CTAB+EDT and PbS/CdS CTAB CQD films produced by the same methods as presented here. The film with CTAB+EDT was found to outperform one with only

CTAB. The improvements to both J_{sc} and V_{oc} are likely to be due to the superior passivation of the CTAB+EDT CQD surfaces, in addition to the improvement in charge transport due to a reduced interdot distance after ligand exchange with EDT.^{13,54,55}

5. CONCLUSIONS

SR-XPS was used to depth profile multi-step-treated CQDs and to show that both Cd and halides are located on the CQD surfaces after cation exchange and halide ion exchange treatments. This knowledge was used to extract the percentage compositions of the topmost surface layer of the CQD surfaces for 10 different surface treatments. This showed that etching occurs during a standard halide ligand exchange process, resulting in a marked reduction of surface Cd concentration in PbS/CdS CQDs. However etching does not occur when a reduced, less aggressive halide treatment is used, but the same halide surface coverage as the standard treatment is achieved. We also find evidence suggesting that the counterion used in the halide treatment affects the amount of etching that occurs on the CQD surface.

We have examined how different halides bind to the surface of PbS/CdS cation-exchanged CQDs, using the binding energy positions of the halide peaks. In the case of Cl and Br, the halides bind exclusively to Pb. Iodide however is found to bind to Cd as well as to Pb. This, compounded with etching by halides, contributes to the lack of improvement we find in the performance of a device incorporating PbS CQDs treated with a Cd cation exchange and TBAI ligand exchange, compared to one without cation exchange.

The air stability and device performances of CQD films with different surface treatments have been compared. The films with better air stability and device performances can be explained by the differences in surface chemistry. We find that device performance and air stability are inversely related to the amount of PbS remaining on the CQD surface after treatments. In particular, PbS TBAI CQDs have a higher percentage of their surface covered with halide (and therefore less unpassivated PbS on the surface) than PbS TBAB and PbS TBAC, which helps explain the success of this treatment. We also show that surface etching from halide treatments can have detrimental effects on air stability and device performance in PbS CQD films, leaving unpassivated sites open, forming trap states and being prone to oxidation. This study highlights the importance of considering the depth dependence of XPS data (to isolate the part of XPS signal originating from the topmost surface layer of the CQD alone) in establishing the effect of different treatments on the CQD surface.

ASSOCIATED CONTENT

Supporting Information.

Details of CdS CQD synthesis, Br/S depth profiling, examination of a Cd-I bond in Cd 3d, bond dissociation energies comparisons, further details of surface composition calculations, O 1s XPS spectra of PbS/CdS CTAB+EDT and PbS/CdS CTAB, absorbance spectra of PbS and PbS/CdS in solution with OA.

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ABBREVIATIONS

BE, binding energy; CBM, conduction band minimum, CQD, colloidal quantum dot; CTAB, cetyltrimethylammonium bromide; EDT, 1,2-ethanedithiol; IMFP, inelastic mean free path; ITO, indium tin oxide; KE, kinetic energy; SR, synchrotron radiation; TBAB, tetrabutylammonium bromide; TBAC, tetrabutylammonium chloride; TBAI, tetrabutylammonium iodide; VBM, valence band maximum; XPS, X-ray photoelectron spectroscopy.

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