Letter

Embedding PbS QDs in Pb-halide perovskite matrices: QD Surface chemistry and antisolvent effects on QD dispersion and confinement properties

Ashley Gaulding, Xihan Chen, Ye Yang, Steven P. Harvey, Bobby To, Young-Hoon Kim, Matthew C. Beard, Peter C. Sercel, and Joseph M. Luther

ACS Materials Lett., **Just Accepted Manuscript** • Publication Date (Web): 22 Sep 2020

Downloaded from pubs.acs.org on September 22, 2020

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

Embedding PbS QDs in Pb-halide perovskite matrices: QD Surface chemistry and antisolvent effects on QD dispersion and confinement properties

E. Ashley Gaulding,^{1,2*} Xihan Chen,^{1,2} Ye Yang,^{1,2} Steven P. Harvey,² Bobby To,² Young-Hoon Kim,^{1,2} Matthew C. Beard,^{1,2} Peter C. Sercel,^{1,3*} Joseph M. Luther^{1,2*}

¹ Center for Hybrid Organic Inorganic Semiconductors for Energy (CHOISE)

² National Renewable Energy Laboratory, Golden, CO USA

³ Department of Applied Physics and Materials Science, California Institute of Technology, Pasadena, CA USA

* Corresponding authors

TOC Graphic

Abstract

Hybrid materials of metal chalcogenide colloidal quantum dots (QDs) embedded in metal halide perovskites (MHPs) have led to composites with synergistic properties. Here, we investigate how QD size, surface chemistry, and MHP film formation methods affect the resulting optoelectronic properties of QD/MHP “dot-in-matrix” systems. We monitor the QD absorption and photoluminescence throughout synthesis, ligand exchange and transfer into the MHP ink, and characterize the final QD/MHP films via electron microscopy, and transient absorption. Additionally, we are the first to globally map how PbS QDs are distributed on the micron scale within these dot-in matrix systems using 3D tomography time-of-flight secondary ion mass spectrometry. The surface chemistry imparted during synthesis directly affects the optical properties of the dot-in-matrix composites. Pb-halide passivation leads to QD/MHP dot-in-matrix samples with optical properties that are well-described by a theoretical model based on a Type-I finite barrier heterostructure between the PbS QD and the MHP matrix. Samples without Pb-halide passivation show complicated size-dependent behavior, indicating a transition from a Type-I heterostructure between the PbS QD wells and MHP barriers for small sized QDs to PbS QDs that are electronically decoupled from the MHP matrix for larger QDs. Furthermore, the choice in perovskite antisolvent crystallization method leads to a difference in the spatial QD distribution within the perovskite matrix, differences in carrier lifetime, and photoluminescence shifts of up to 180 meV for PbS in methylammonium lead iodide. This work establishes an understanding of such emerging synergistic systems relevant for technologies such as photovoltaics, IR-emitters and detectors, and other unexplored technological applications.

Heterojunctions and heterostructures in semiconductor systems are used to control energy flow, enhance charge separation or radiative recombination, confine carriers, form superlattices and so forth.^{1–13} Here, we examine an emerging heterostructure system between metal halide perovskite (MHP) and colloidal quantum dots (QDs). MHPs have fascinating properties and are heavily studied because of their ability to form high quality crystalline films via solution processing. Likewise, QDs have tunable properties and are also cast into films using solution deposition methods. In QDs, subtle differences in the surface chemistry can affect many properties.¹⁴ Pb-halide passivation^{15–20} on Pb-chalcogenides, for example, improves charge transport in arrays over those that have purely organic passivation. Pb-halide passivated surfaces lead to lower trap densities than incumbent short organic molecules such as 1,2-ethanedithiol, mercaptopropionic acid, hydrazine, etc.^{15–20} Complimentary processing techniques used for these materials have naturally led to their co-integration into interesting heterostructures whereby MHP salts offer passivating ligand chemistries,^{18,21} core-shell structures,^{22,23} and “dot-in-matrix” geometries²⁴ for Pb-chalcogenide QD films. The initial research challenge in producing these multicomponent structures involves the discrepant solvents used to handle colloidal QDs versus those used for MHPs. Typically, nonpolar organic solvents interact with aliphatic surface ligands to suspend the QDs, whereas polar aprotic solvents are used to solubilize precursor salts which form the MHPs. For QDs to be mixed into the MHP precursor ink, the native surface ligands on the QDs must be replaced with ionic or polar ligands which allow the QDs to be stabilized in polar aprotic solvents such as dimethylformamide (DMF).^{18,21,25}

Similar lattice constants and cubic crystal structures between PbS and MHPs enable crystalline 3D heterostructures with structural coherency. In particular, Pb-chalcogenide QDs and MHPs are reported to form epitaxial interfaces creating unique heterostructures.^{24,26} PbS NCs were embedded in MAPbX₃ (MA = methylammonium and X = I, Br, or Cl) and show efficient NIR emission suggestive of a Type-I band alignment.^{24,27–30} PbS QDs alter the crystallization of the precursor solution by nucleating apparent MHP grains ~4X larger than the ≤100 nm pure perovskite grains.^{25,31} Mora-Seró and co-workers observed a tunable exciplex emission from QD – MHPs for designing intermediate-band photovoltaics and NIR LEDs and detectors.^{32–35} More recently, epitaxial seeding of PbS QDs in MHPs has enabled “lattice anchoring” to strain and stabilize a thermodynamically unstable phase of CsPbI_{3-x}Br_x in ambient.²⁶ Additionally, PbS QDs in MHP single crystals have shown promise for use in resistive switching.³⁶ In all of these cases, the effects of QD size²⁷ (particularly for small diameters), QD synthesis, and MHP crystallization methods have not been extensively investigated. Yet these parameters play an important role in the final synergistic optoelectronic properties.

In this work we not only explore the size-dependence of the PbS QDs embedded within MAPbI₃, but also how QD surface chemistry influences the QD/MHP interface, and how film processing using various antisolvent approaches, used heavily in MHP photovoltaics, influences the coupling between the QDs and MHP. We measured the optical properties, and additionally characterize the final QD/MHP films via scanning electron microscopy (SEM), transient

absorption (TA), and 3D tomography time-of-flight secondary ion mass spectrometry (TOF-SIMS). Investigating these three parameters: QD size, synthesis methods (namely the QD surface chemistry), and MHP crystallization (antisolvent methods), addresses critical questions to further tune and control the symbiosis of QD/MHP heterostructures.

Experimental Section

Dot-in-matrix heterostructure formation is accomplished via a stepwise process schematically illustrated in Fig. 1. QDs are synthesized using conventional routes: either via hot-injection with PbO as the lead precursor where bis(trimethylsilyl)sulfide ($\text{TMS}_2\text{-S}$) is injected at an elevated temperature,³⁷ or a heat ramp method³⁸ using PbCl_2 and $\text{TMS}_2\text{-S}$ is introduced at a lower temperature and heated to control nucleation and QD growth (Fig. 1a). This produces similar QDs, but with different surface chemistries that impact the resulting optoelectronic properties of the films. A ligand exchange is performed using the MHP precursor salts (MAI and PbI_2) to replace oleate ligands in both cases and transfer the QDs from hexane to dimethylformamide (DMF) (Fig. 1b). The ligand-exchanged QDs are isolated via precipitation and the purified PbS QD pellet is redispersed into the MAPbI_3 precursor ink (Fig. 1c).^{18,25} The composite ink is then cast and crystallized using the antisolvent method³⁹ where chlorobenzene (CB), methyl acetate (MeOAc), or anisole (AN) removes excess solvent and forms chemical adducts, which affect crystallization^{39–44} (Fig. 1d). Finally, the film is annealed to crystallize the MHP with embedded PbS QDs (Fig. 1e). Details are described in the Supplementary Information (SI).

Fig. 1. Synthetic route to PbS/MAPbI₃ heterostructured films: a) Synthesis using either PbO or PbCl₂ as the precursor, b) MAI/PbI₂ ligand exchange of PbS from hexane to DMF phase, c) PbS precipitation using centrifugation and redispersion in concentrated MAPbI₃ precursor solution, d) one-step spin-coating film deposition using different antisolvents showing approximate colors of the intermediate phase before annealing, e) Schematic showing proposed distribution of PbS throughout the film.

In Fig. 2, the absorption of the QD solutions and the photoluminescence of completed films are shown versus QD size using the two PbS QD preparation routes. For reference, Fig. 2a shows the absorption of pure MHP precursor solution without QDs, and Fig. 2b shows the photoluminescence of pure MAPbI₃ film. First we will describe the QDs synthesized using the hot-injection synthesis.³⁷ Fig. 2c shows absorption of OA-capped QDs synthesized using PbO (notated PbS_{PbO}) and those same QDs after the MAI/PbI₂ ligand exchange in solution for sizes spanning 1.9 to 4.8 nm. The ligand exchange does not affect the size of the QDs.¹⁸ However, after exchange and phase transfer, the PbS_{PbO} QD exciton peak redshifts for QD diameters ranging from 4.8 – 2.8 nm, consistent with previous reports.¹⁸ For smaller PbS_{PbO} QDs (diameters below 2.5 nm) when the exciton approaches the bandgap of MAPbI₃ (~800 nm), we observe a more dramatic redshift and broadening of the peak, resulting in a break from a monotonic trend. This is consistent with the observation of a more dramatic redshift for smaller PbS in PL measurements of MAI/PbI₂ exchanged QDs.²⁵ Interestingly, the redshift is smaller when the same PbS QDs are exchanged with MABr/PbBr₂ and redispersed in a MAPbBr₃ precursor solution (Fig. S1). Previous work hypothesized that a MHP shell forms on the QD post ligand exchange.²¹ Formation of this shell likely results in some degree of wavefunction spillage outside the PbS core and into the shell for wider bandgap QDs, resulting in some loss of confinement. Since MAPbBr₃ has a wider bandgap than MAPbI₃, one would expect a higher

electronic barrier at the PbS/MHP in the Br system, resulting in less redshift of the exciton adding evidence to that hypothesis.

Solution PL measurements were taken before and after QD ligand exchange (Fig. S2, S3). Interestingly, while dispersed in the MHP precursor ink, the QDs are dark, yet cast within the MHP matrix, the QD PL re-emerges. The fact that polar solutions are dark could be due to the strong desorption of anions in DMF (a strong Lewis acid) leading to a dynamic, trap-riddled surface which is repaired upon MHP crystallization and removal of DMF after drying.¹⁸ Yet it is worth noting that a previous report of PbS/CdS core/shell QDs exchanged using a similar process show PL emission while in the MAPbI₃ precursor solution, and that the PL energy is essentially unchanged once crystallized into a MAPbI₃ film.²⁵ This suggests the CdS shell in the core/shell structure prevents the QD exciton from coupling to defect states, though the morphological integrity of the QD is maintained in both cases. We further confirmed that the PbS QDs indeed remain morphologically unchanged once crystallized into a MHP film by measuring the absorption of the PbS/MHP precursor solution beforehand, crystallizing the ink into a PbS/MAPbI₃ film, then re-dissolving the film in DMF and remeasuring the absorption (Fig. S4). The measurements show little change in the QD exciton absorption, suggesting the QDs remain discrete.

The PL trends from the PbS_{PbO}/MAPbI₃ matrix films (Fig. 2d) are reflective of the absorbance features for the ligand exchanged PbS_{PbO} QDs in solution noted above, including the curious behavior of a break in the monotonic size dependent trend, which will be further discussed below. We also observe almost complete quenching of the 800 nm PL arising from the band edge emission of MAPbI₃. The degree of MHP quenching depends upon the QD loading. Higher QD concentrations lead to more PL quenching of the MHP if charges can be captured by the QD.²⁴ In the aforementioned PbS/CdS core/shell in MAPbI₃ system, this quenching does not occur, perhaps due to a barrier from the CdS shell.^{25,33}

Fig. 2. Size dependent optical spectroscopy of PbS QDs. a) Absorption of MHP precursor solution only, b) PL of MAPbI₃ film. PbO synthesized PbS_{PbO} c) absorption pre (OA-capped in hexane, solid line) and post (in precursor solution, dashed line) ligand exchange and d) PL of PbS_{PbO} in MAPbI₃ crystallized with CB. PbCl₂ synthesized PbS_{PbCl₂} e) absorption pre (OA-capped in hexane, solid line) and post (in precursor solution, dashed line) ligand exchange and f) PL emission from PbS_{PbCl₂} in MAPbI₃ crystallized with CB. Gray shading shows where absorption of MAI/PbI₂ precursor or PL of the crystallized MAPbI₃ is expected. Data is normalized and offset for clarity.

Surface or interface states may explain the peculiar non-monotonic absorption and PL versus QD size observed in the PbS_{PbO}/MAPbI₃ system. To test this theory, we investigated other methods to synthesize PbS QDs. Cl-terminated surfaces demonstrate improved passivation and PL quantum yield.^{11,17,38,45,46} One method to impart Cl passivation involves using PbCl₂ rather than PbO as the Pb source. Thus, we synthesized Cl-passivated QDs to test incorporation into the MHP matrix without interface states hypothesized to be involved in the non-monotonic trends observed in Fig. 2(c,d). We repeated the PbS/MAPbI₃ procedures as described above but

synthesizing the QDs using the diffusion-controlled, temperature ramp method.³⁸ The analogous optical data of the $\text{PbS}_{\text{PbCl}_2}$ QDs is shown in Fig. 2(e,f). There is still a more significant redshift in the exciton upon ligand exchange of small QD, but the abrupt discontinuity in the trend of the optical data for diameters ≤ 2.4 nm in the PbS_{PbO} QDs is not observed for the $\text{PbS}_{\text{PbCl}_2}$ QDs and the PL is more monotonic with respect to the starting QD properties. This result shows that surface chemistry of the QDs influences their incorporation in the MAPbI_3 matrix.

In addition to surface chemistry, another variable likely influencing the heterostructure optoelectronic properties is the perovskite crystallization. Varying concentrations, solvent systems, additives, and antisolvents are used to crystallize MAPbI_3 . In the case of MAPbI_3 , most antisolvent treatments result in a $\text{CH}_3\text{NH}_3\text{I}-\text{PbI}_2$ -DMSO adduct intermediate phase, but the amount of this phase pre-annealing depends on the antisolvent used. For example, the intermediate phase using a toluene drip has a high DMSO content, resulting in a clear intermediate film with little crystallization,³⁹ whereas methyl acetate has a low DMSO content, resulting in a darker film that is already partially crystallized.⁴⁰ Here, we compared three antisolvent crystallization methods of the heterostructures. We use a chlorobenzene drip (CB), methyl acetate drip (MeOAc), and anisole *dip* (AN) (methods described in the SI). For pure MAPbI_3 , the emission properties for different antisolvents show little difference (Fig. S5). However, the effects on the optical properties of the $\text{PbS}_{\text{PbCl}_2}$ in MAPbI_3 are quite dramatic (Fig. 3a, and S6), most notably in the PL for a given QD size depending on the antisolvent (Fig. 3a). First, we compare the large (4.0 nm) $\text{PbS}_{\text{PbCl}_2}$ QDs. The 4.0 nm $\text{PbS}_{\text{PbCl}_2}$ QDs emit at 1250 nm using CB vs. 1500 nm using AN. This corresponds to a 180 meV shift between films employing the same QDs yet crystallized differently. Fig. 3b shows the PL energy vs. the reciprocal of the square of the QD radius for the different antisolvents. The slope of the lines for each of antisolvent is different, with CB exhibiting the smallest slope and AN the largest.

To complement the optical properties, we evaluated the carrier dynamics by monitoring the MAPbI_3 optical bleach within $\text{PbS}/\text{MAPbI}_3$ films using transient absorption (TA). As expected, all films with added QDs show shorter carrier lifetimes within the MAPbI_3 relative to MAPbI_3 only films. We observe an increase in the photoexcited carrier lifetime of the MAPbI_3 from CB (~ 30 ps) to MeOAc (~ 50 ps) to AN (~ 100 ps) (Fig. 3c). Faster carrier dynamics could imply a higher QD concentration, smaller grains, or higher surface trap density at the dot-matrix interface.^{24,47,48} To answer these questions, film morphology and PbS distribution in the film should be examined.

Fig. 3: The effects of MAPbI₃ crystallization antisolvent on a) PbS emission in PbS/MAPbI₃ films, and b) PL emission energies of PbS in MAPbI₃ using different antisolvents, in reference to a film of as-synthesized PbS capped with OA. The gray band in a) indicates where MAPbI₃-only films emit, demonstrating strong quenching. c) Transient kinetics probed near 750 nm (photogenerated carriers in MAPbI₃) of 3.5 nm PbS/MAPbI₃ and MAPbI₃ only films fabricated with different antisolvents.

Unlike homogeneous pure QD films, the PbS/MAPbI₃ dot-in-matrix solids have different film morphologies influenced by the QD inclusions and the antisolvent. There could be differences in the distribution of the QDs within the film. When conducting SEM, we observe that the PbS_{PbCl₂} QDs at relatively high concentrations does change the nucleation dynamics of the MHP, resulting in smaller apparent grain size for PbS QDs-in-MAPbI₃ relative to pure MAPbI₃ films (Fig. 4). This observation contradicts previous reports showing QDs *increase* apparent MHP grains, however, the starting grain morphology of these previous reports was smaller (≤ 100 nm) than here. Comparing CB and MeOAc, little difference is seen in the film morphology (Fig. 4a,c and b,d). AN results in comparatively smaller apparent grains for pure MAPbI₃ (Fig. 4e) and even smaller grains with QDs (Fig. 4f). This suggests that the MAPbI₃ nucleation is affected by both the antisolvent method (i.e. drip vs. dip) and by the QDs. However, the TA data shows longer lifetimes for the AN method despite the smaller apparent grain size shown via SEM suggests that the TA lifetime dynamics are not dominated by grain size.

Fig. 4: SEM images showing the effects of different antisolvent crystallization methods of pure MAPbI₃ (top row) and PbS/MAPbI₃ (bottom row) for CB (a, b), MeOAc (c, d), and AN (e, f).

SEM does not provide full insight into the QD distribution within the matrix. Work by Gong *et al.* showed QDs are distributed differently on the mm scale within single MAPbBr₃ crystals depending on the MHP crystallization method.⁴⁹ Currently, there are no reports on how PbS is globally distributed in dot-in-matrix systems on the micron scale or less. To help fill in this gap in the field and gain a better understanding of our results, we used TOF-SIMS 3D tomography to map elements including sulfur (Fig. 5a,b) and evaluate differences in how **PbS_{PbCl₂}** QDs are distributed within the film between the antisolvent treatments.^{50–52} The sulfur-iodide signal (denoted as SI-) was used here to characterize the sulfur distribution because the main sulfur peak suffers from a mass interference with the O²⁻ signal for tomography imaging. Here, we find all films exhibit some gradient of PbS through the film thickness, and that the overall concentration of PbS retained in the films varies, with CB yielding the lowest and AN the highest (Fig. 5a). The in-plane tomography reveals that the **PbS_{PbCl₂}** QDs are clumped together for the CB and MeOAc cases (perhaps at grain boundaries), and are more homogeneously distributed in-plane for AN (Fig. 5b). This is interesting considering the TA data in Fig. 3c, which shows that AN has longest lifetime for carriers within the MAPbI₃, despite the higher density of QDs. We therefore propose that for CB and MeOAc, the crystallization is initiated at the substrate, leading to aggregation of the **PbS_{PbCl₂}** QDs within the film at grain boundaries. Whereas for AN, the MAPbI₃ crystallization occurs at the QD surface. Although this results in

the smaller domain sizes as seen in SEM due to each QD acting as a nucleation point it also results in a more uniform QD distribution, better coupling of the QDs to the semiconductor matrix, and fewer interface recombination centers.

Fig. 5: TOF-SIMS a) depth profile and b) 3D renderings of the SI- signal (reflective of sulfur) of PbS in MAPbI₃ crystallized using different antisolvent methods (scale: 25μm x 25μm x film thickness), c) schematic of PbS distributed in MAPbI₃ for various antisolvent treatments.

One hypothesis for the emission energy redshift dependence on antisolvent could be coupling between QDs as the net QD concentration varies either overall or in local aggregates, as it has been shown in previous publications that the PL emission energy redshifts and PL quantum yield (PLQY) decreases with increasing QD concentration.^{24,27} We therefore measured the PL of a series of films with increasing PbS QD concentrations, and analyzed the data of previously published results.²⁴ However, comparable sizes hit a maximum PL redshift only on the order of 60 – 80 meV (see Fig. S7). Thus, such a redshift shown in Fig. 3a, red, orange and green between CB and AN is unlikely exclusively due to PbS-PbS QD coupling within the MAPbI₃.

We propose a theory to explain the observed properties using a coupled band Kane model,⁵³ assuming an epitaxial interface between the PbS and MAPbI₃ as shown in Fig. 6 (see SI for Table S5). The model has only one free parameter, the Kane energy of PbS, which is determined by fitting to the *colloidal* PbS QDs (Tables S1,S2); the MAPbI₃ bandgap is calculated from absorption of a pure MAPbI₃ film, and other parameters are taken from literature. For a film of as-synthesized, PbS-OA colloids, using either PbO or PbCl₂ as the precursor, the size dependent behavior of the exciton energy is well described within a spherical QD/infinite barrier approximation, with no coupling between QDs (**Error! Reference source not found.**). The PL data shows a significant size-dependent Stokes shift,^{54–56} which we attribute to emission occurring on a transition from a trap state ~250 meV above the bulk conduction band edge to the confined hole state, similar to models previously proposed for the PL emission in colloidal PbS QDs and shown schematically in Fig. S11.^{54,55}

Fig. 6: Band diagram of PbS in MAPbI₃ used for calculations. a) PbS confined states (dashed lines) are derived from colloidal optical data. b) As synthesized PbS_{PbO} and PbS_{PbCl₂} colloids with native OA ligands overlaid on the infinite barrier model curves, c) PbS_{PbO}/MAPbI₃ films overlaid on infinite and finite barrier models, d) PbS_{PbCl₂}/MAPbI₃ films overlaid on the finite barrier model, e) PbS_{PbCl₂}/MAPbI₃ films crystallized using different antisolvent methods overlaid on the various models. Parameters used in the model calculations are described in the text and summarized in Table S5.

Therefore, the emissive state near the conduction band becomes pinned for small QDs while only the movement of the valence band confined hole level influences the shift in PL emission, leading to the observed Stokes shift. It should be noted that all model calculations of the PL energies in **Error! Reference source not found.** are made using the same parameters as used in the absorption calculations (see Table S5) with just one additional parameter, the trap energy, which was determined by fitting the PL of the *colloidal* PbS QDs shown in **Error! Reference source not found.** For the PbS QDs contained within MAPbI₃, the confined states are described within a coupled band Kane model, but in contrast to the colloidal QDs, the QD surface is described within a finite barrier model for the PbS/MAPbI₃ interface.^{53,57} This model, described in the SI, accounts for the effect of strain due to the lattice mismatch between PbS and MAPbI₃ within deformation potential theory, using strain fields calculated within Eshelby inclusion theory and shown in Fig. S9.⁵⁸ The strain in the PbS QDs due to the lattice parameter mismatch with the barrier is found to be purely hydrostatic, leading to a bandgap increase of 70 meV, while the strain of the MAPbI₃ matrix is pure biaxial with no hydrostatic component or band gap change. The band offsets, shown in Fig. 6a, are determined using the measured ionization potentials for bulk PbS⁵⁹ and MAPbI₃,⁶⁰ and assumes that the band edges of the PbS shift equally under hydrostatic strain, resulting in a Type-I band alignment that transitions to a Quasi Type-II alignment for the smallest QD sizes of radius below ~0.9 nm, for which the

confined hole states become unbound (Fig. 6a). As with the model for colloidal PbS-OA, the lowest exciton absorption energy in the PbS/MAPbI₃ system is assigned to the transition between the lowest energy confined states of the conduction and valence bands, while the PL emission is assigned to the transition from the electron trap ~250 meV above the bulk unstrained conduction band edge to the confined hole state. Despite having comparable optical properties for the as synthesized PbS-OA QDs whether synthesized with PbO or PbCl₂, the presence of Cl makes a difference once the PbS QDs are exchanged and crystallized into MAPbI₃ using the same CB method, as first described above in Fig. 2. A simple model cannot explain the non-monotonic behavior observed for the optical properties of PbS_{PbO} in MAPbI₃. To bring some understanding to this unexpected behavior, we plotted the exciton absorption and PL emission energies versus size for both infinite and finite barrier models with emission from a CB trap state at 250 meV above the bulk unstrained PbS band edge, respectively (**Error! Reference source not found.c**), using the same material parameters as in the calculation shown in **Error! Reference source not found.** For the PbS_{PbO}/MAPbI₃ films, the larger sized QDs align well with the infinite barrier model, then snap down the lines representing the finite barrier model. For this system, the small QDs electronically couple better to the MAPbI₃ matrix than do the large QDs. In the case of the **PbS_{PbCl₂}**/MAPbI₃ films crystallized with the same CB method, the system follows the finite barrier model over a wider range of sizes (**Error! Reference source not found.**). This further supports the hypothesis that PbS QDs synthesized via PbCl₂ provide a better electronically coupled interface within the dot-in-matrix system.

Finally, we compare our models to the **PbS_{PbCl₂}**/MAPbI₃ films crystallized using different antisolvent methods. The smaller QD sizes fall neatly on the finite barrier model curve, with the larger QDs generally falling somewhere in between (**Error! Reference source not found.e**). The PL data for the smaller QD sizes for all antisolvents collapse neatly onto the finite barrier model, with the larger sizes having a larger spread on either side depending on the antisolvent method. Evaluation of a PbS QD in a MAPbI₃ matrix using the Eshelby inclusion theory suggests significant biaxial strain within the MAPbI₃ (see SI), which can be expected to result in interface dislocations for larger QDs. This would cause shifts in the absorption energy due to variation in the strain due to relaxation via dislocation formation and would potentially affect PL by introduction of new interface states. The number of dislocations at the PbS/MAPbI₃ interface is highly sensitive to the antisolvent used, hence resulting in a different distribution of optically active states contributing to the PL spread in emission energies despite the same QDs in all films.

In conclusion, we study the effects of PbS QD surface chemistry, QD size, and perovskite antisolvents on the emission and morphological properties of PbS/MAPbI₃ films. Each step within the film preparation process affects the final properties of the heterostructured film including the quality of the heterostructure interface, the distribution of QDs within the MAPbI₃ matrix, and ultimately the energy of the PbS QD emission. PbO synthesized QDs show non-monotonic size dependent optical properties, due to transition from an infinite barrier

heterostructure for larger QDs, to a finite barrier for smaller QDs. PbCl₂ synthesized QDs improve the PbS/MAPbI₃ interface and the system reflects a finite barrier model across a larger QD size range. Furthermore, different antisolvents affect the carrier lifetime, QD spatial distribution, and interface dislocations within the heterostructure, which affect the PbS optical properties with the same QDs embedded in all films. Our findings emphasize factors that need close attention when designing future QD-in-perovskite systems for optoelectronic applications.

Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Information. Additional data related to this paper may be requested from the authors.

Supporting Information: Materials, Experimental Details, Additional Figures (S1-S11), plus details on calculations and modeling.

Acknowledgement

This work is supported by the Center for Hybrid Organic Inorganic Semiconductors for Energy (CHOISE), an Energy Frontier Research Center funded by the Office of Science, Office of Basic Energy Sciences within the U.S. Department of Energy. EAG acknowledges support from the Director's Fellowship within NREL's Laboratory Directed Research and Development (LDRD) program. Part of this work was authored by Alliance for Sustainable Energy, Limited Liability Company, the manager and operator of the National Renewable Energy Laboratory under Contract No. DE-AC36-08GO28308. The views expressed in the article do not necessarily represent the views of the Department of Energy or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

References:

- (1) Lee, J.-S.; Shevchenko, E. V.; Talapin, D. V. Au–PbS Core–Shell Nanocrystals: Plasmonic Absorption Enhancement and Electrical Doping via Intra-Particle Charge Transfer. *J. Am. Chem. Soc.* **2008**, *130*, 9673–9675. <https://doi.org/10.1021/ja802890f>.
- (2) Pietryga, J. M.; Werder, D. J.; Williams, D. J.; Casson, J. L.; Schaller, R. D.; Klimov, V. I.; Hollingsworth, J. a. Utilizing the Lability of Lead Selenide to Produce Heterostructured Nanocrystals with Bright, Stable Infrared Emission. *J. Am. Chem. Soc.* **2008**, *130*, 4879–4885. <https://doi.org/10.1021/ja710437r>.
- (3) Ngo, T. T.; Mora-Seró, I. Interaction between Colloidal Quantum Dots and Halide Perovskites: Looking for Constructive Synergies. *J. Phys. Chem. Lett.* **2019**, *10*, 1099–1108. <https://doi.org/10.1021/acs.jpcclett.8b03657>.
- (4) Selinsky, R. S.; Ding, Q.; Faber, M. S.; Wright, J. C.; Jin, S. Quantum Dot Nanoscale Heterostructures for Solar Energy Conversion. *Chem. Soc. Rev.* **2013**, *42*, 2963–2985. <https://doi.org/10.1039/C2CS35374A>.
- (5) Cargnello, M.; Johnston-Peck, A. C.; Diroll, B. T.; Wong, E.; Datta, B.; Damodhar, D.; Doan-Nguyen, V. V. T.; Herzing, A. A.; Kagan, C. R.; Murray, C. B. Substitutional Doping in

- Nanocrystal Superlattices. *Nature* **2015**, *524*, 450–453. <https://doi.org/10.1038/nature14872>.
- (6) Reiss, P.; Protière, M.; Li, L. Core/Shell Semiconductor Nanocrystals. *Small* **2009**, *5*, 154–168. <https://doi.org/10.1002/sml.200800841>.
- (7) Yanover, D.; Čapek, R. K.; Rubin-Brusilovski, A.; Vaxenburg, R.; Grumbach, N.; Maikov, G. I.; Solomeshch, O.; Sashchiuk, A.; Lifshitz, E. Small-Sized PbSe/PbS Core/Shell Colloidal Quantum Dots. *Chem. Mater.* **2012**, *24*, 4417–4423. <https://doi.org/10.1021/cm302793k>.
- (8) Justo, Y.; Goris, B.; Kamal, J. S.; Geiregat, P.; Bals, S.; Hens, Z. Multiple Dot-in-Rod PbS/CdS Heterostructures with High Photoluminescence Quantum Yield in the Near-Infrared. *J. Am. Chem. Soc.* **2012**, *134*, 5484–5487. <https://doi.org/10.1021/ja300337d>.
- (9) Crisp, R. W.; Schrauben, J. N.; Beard, M. C.; Luther, J. M.; Johnson, J. C. Coherent Exciton Delocalization in Strongly Coupled Quantum Dot Arrays. *Nano Lett.* **2013**, *13*, 4862–4869. <https://doi.org/10.1021/nl402725m>.
- (10) Moroz, P.; Kholmicheva, N.; Mellott, B.; Liyanage, G.; Rijal, U.; Bastola, E.; Huband, K.; Khon, E.; McBride, K.; Zamkov, M. Suppressed Carrier Scattering in CdS-Encapsulated PbS Nanocrystal Films. *ACS Nano* **2013**, *7*, 6964–6977. <https://doi.org/10.1021/nn402844m>.
- (11) Oh, S. J.; Berry, N. E.; Choi, J.-H.; Gaulding, E. A.; Lin, H.; Paik, T.; Diroll, B. T.; Muramoto, S.; Murray, C. B.; Kagan, C. R. Designing High-Performance PbS and PbSe Nanocrystal Electronic Devices through Stepwise, Post-Synthesis, Colloidal Atomic Layer Deposition. *Nano Lett.* **2014**, *14*, 1559–1566. <https://doi.org/10.1021/nl404818z>.
- (12) Kroupa, D. M.; Pach, G. F.; Vörös, M.; Giberti, F.; Chernomordik, B. D.; Crisp, R. W.; Nozik, A. J.; Johnson, J. C.; Singh, R.; Klimov, V. I.; et al. Enhanced Multiple Exciton Generation in PbS/CdS Janus-like Heterostructured Nanocrystals. *ACS Nano* **2018**, *12*, 10084–10094. <https://doi.org/10.1021/acsnano.8b04850>.
- (13) Zhao, Q.; Hazarika, A.; Chen, X.; Harvey, S. P.; Larson, B. W.; Teeter, G. R.; Liu, J.; Song, T.; Xiao, C.; Shaw, L.; et al. High Efficiency Perovskite Quantum Dot Solar Cells with Charge Separating Heterostructure. *Nat. Commun.* **2019**, *10*, 2842. <https://doi.org/10.1038/s41467-019-10856-z>.
- (14) Hughes, B. K.; Luther, J. M.; Beard, M. C. The Subtle Chemistry of Colloidal, Quantum-Confined Semiconductor Nanostructures. *ACS Nano* **2012**, *6*, 4573–4579. <https://doi.org/10.1021/nn302286w>.
- (15) Ip, A. H.; Thon, S. M.; Hoogland, S.; Voznyy, O.; Zhitomirsky, D.; Debnath, R.; Levina, L.; Rollny, L. R.; Carey, G. H.; Fischer, A.; et al. Hybrid Passivated Colloidal Quantum Dot Solids. *Nat. Nanotechnol.* **2012**, *7*, 577–582. <https://doi.org/10.1038/nnano.2012.127>.
- (16) Ning, Z.; Ren, Y.; Hoogland, S.; Voznyy, O.; Levina, L.; Stadler, P.; Lan, X.; Zhitomirsky, D.; Sargent, E. H. All-Inorganic Colloidal Quantum Dot Photovoltaics - Supp Info. *Adv. Mater.* **2012**, *24*, 6295–6299. <https://doi.org/10.1002/adma.201202942>.
- (17) Tang, J.; Kemp, K. W.; Hoogland, S.; Jeong, K. S.; Liu, H.; Levina, L.; Furukawa, M.; Wang, X.; Debnath, R.; Cha, D.; et al. Colloidal-Quantum-Dot Photovoltaics Using Atomic-Ligand Passivation. *Nat. Mater.* **2011**, *10*, 765–771. <https://doi.org/10.1038/nmat3118>.
- (18) Dirin, D. N.; Dreyfuss, S.; Bodnarchuk, M. I.; Nedelcu, G.; Papagiorgis, P.; Itskos, G.; Kovalenko,

- M. V. Lead Halide Perovskites and Other Metal Halide Complexes As Inorganic Capping Ligands for Colloidal Nanocrystals. *J. Am. Chem. Soc.* **2014**, *136*, 6550–6553. <https://doi.org/10.1021/ja5006288>.
- (19) Crisp, R. W.; Kroupa, D. M.; Marshall, A. R.; Miller, E. M.; Zhang, J.; Beard, M. C.; Luther, J. M. Metal Halide Solid-State Surface Treatment for High Efficiency PbS and PbSe QD Solar Cells. *Sci. Rep.* **2015**, *5*, 9945. <https://doi.org/10.1038/srep09945>.
- (20) Zhang, J.; Gao, J.; Church, C. P.; Miller, E. M.; Luther, J. M.; Klimov, V. I.; Beard, M. C. PbSe Quantum Dot Solar Cells with More than 6% Efficiency Fabricated in Ambient Atmosphere. *Nano Lett.* **2014**, *14*, 6010–6015. <https://doi.org/10.1021/nl503085v>.
- (21) Sytnyk, M.; Yakunin, S.; Schöfberger, W.; Lechner, R. T.; Burian, M.; Ludescher, L.; Killilea, N. A.; YousefiAmin, A.; Kriegner, D.; Stangl, J.; et al. Quasi-Epitaxial Metal-Halide Perovskite Ligand Shells on PbS Nanocrystals. *ACS Nano* **2017**, *11*, 1246–1256. <https://doi.org/10.1021/acsnano.6b04721>.
- (22) Zhang, X.; Lu, M.; Zhang, Y.; Wu, H.; Shen, X.; Zhang, W.; Zheng, W.; Colvin, V. L.; Yu, W. W. PbS Capped CsPbI₃ Nanocrystals for Efficient and Stable Light-Emitting Devices Using p-i-n Structures. *ACS Cent. Sci.* **2018**, *4*, 1352–1359. <https://doi.org/10.1021/acscentsci.8b00386>.
- (23) Quintero-Bermudez, R.; Sabatini, R. P.; Lejay, M.; Voznyy, O.; Sargent, E. H. Small-Band-Offset Perovskite Shells Increase Auger Lifetime in Quantum Dot Solids. *ACS Nano* **2017**, *11*, 12378–12384. <https://doi.org/10.1021/acsnano.7b06363>.
- (24) Ning, Z.; Gong, X.; Comin, R.; Walters, G.; Fan, F.; Voznyy, O.; Yassitepe, E.; Buin, A.; Hoogland, S.; Sargent, E. H. Quantum-Dot-in-Perovskite Solids. *Nature* **2015**, *523*, 324–328. <https://doi.org/10.1038/nature14563>.
- (25) Ngo, T. T.; Suarez, I.; Sanchez, R. S.; Martinez-Pastor, J. P.; Mora-Sero, I. Single Step Deposition of an Interacting Layer of a Perovskite Matrix with Embedded Quantum Dots. *Nanoscale* **2016**, *8*, 14379–14383. <https://doi.org/10.1039/C6NR04082A>.
- (26) Liu, M.; Chen, Y.; Tan, C.-S.; Quintero-Bermudez, R.; Proppe, A. H.; Munir, R.; Tan, H.; Voznyy, O.; Scheffel, B.; Walters, G.; et al. Lattice Anchoring Stabilizes Solution-Processed Semiconductors. *Nature* **2019**, *570*, 96–101. <https://doi.org/10.1038/s41586-019-1239-7>.
- (27) Gong, X.; Yang, Z.; Walters, G.; Comin, R.; Ning, Z.; Beauregard, E.; Adinolfi, V.; Voznyy, O.; Sargent, E. H. Highly Efficient Quantum Dot Near-Infrared Light-Emitting Diodes. *Nat. Photonics* **2016**, *10*, 253–257. <https://doi.org/10.1038/nphoton.2016.11>.
- (28) García de Arquer, F. P.; Gong, X.; Sabatini, R. P.; Liu, M.; Kim, G.-H.; Sutherland, B. R.; Voznyy, O.; Xu, J.; Pang, Y.; Hoogland, S.; et al. Field-Emission from Quantum-Dot-in-Perovskite Solids. *Nat. Commun.* **2017**, *8*, 14757. <https://doi.org/10.1038/ncomms14757>.
- (29) Yang, Z.; Yassitepe, E.; Voznyy, O.; Janmohamed, A.; Lan, X.; Levina, L.; Comin, R.; Sargent, E. H. Self-Assembled PbSe Nanowire/Perovskite Hybrids. *J. Am. Chem. Soc.* **2015**, *137*, 14869–14872. <https://doi.org/10.1021/jacs.5b10641>.
- (30) Wang, R.; Wang, F.; Zhou, W.; Fan, J. Z.; García de Arquer, F. P.; Xu, K.; Sargent, E. H.; Ning, Z. Colloidal-Quantum-Dot-in-Perovskite Nanowires. *Infrared Phys. Technol.* **2019**, *98*, 16–22. <https://doi.org/10.1016/j.infrared.2019.02.004>.

- (31) Han, J.; Luo, S.; Yin, X.; Zhou, Y.; Nan, H.; Li, J.; Li, X.; Oron, D.; Shen, H.; Lin, H. Hybrid PbS Quantum-Dot-in-Perovskite for High-Efficiency Perovskite Solar Cell. *Small* **2018**, *14*, 1801016. <https://doi.org/10.1002/sml.201801016>.
- (32) Hosokawa, H.; Tamaki, R.; Sawada, T.; Okonogi, A.; Sato, H.; Ogomi, Y.; Hayase, S.; Okada, Y.; Yano, T. Solution-Processed Intermediate-Band Solar Cells with Lead Sulfide Quantum Dots and Lead Halide Perovskites. *Nat. Commun.* **2019**, *10*, 43. <https://doi.org/10.1038/s41467-018-07655-3>.
- (33) Sanchez, R. S.; de la Fuente, M. S.; Suarez, I.; Muñoz-Matutano, G.; Martinez-Pastor, J. P.; Mora-Sero, I. Tunable Light Emission by Exciplex State Formation between Hybrid Halide Perovskite and Core/Shell Quantum Dots: Implications in Advanced LEDs and Photovoltaics. *Sci. Adv.* **2016**, *2*, e1501104. <https://doi.org/10.1126/sciadv.1501104>.
- (34) Gao, L.; Quan, L. N.; García de Arquer, F. P.; Zhao, Y.; Munir, R.; Proppe, A.; Quintero-Bermudez, R.; Zou, C.; Yang, Z.; Saidaminov, M. I.; et al. Efficient Near-Infrared Light-Emitting Diodes Based on Quantum Dots in Layered Perovskite. *Nat. Photonics* **2020**, *14*, 227–233. <https://doi.org/10.1038/s41566-019-0577-1>.
- (35) YousefiAmin, A.; Killilea, N. A.; Sytnyk, M.; Maisch, P.; Tam, K. C.; Egelhaaf, H.-J.; Langner, S.; Stubhan, T.; Brabec, C. J.; Rejek, T.; et al. Fully Printed Infrared Photodetectors from PbS Nanocrystals with Perovskite Ligands. *ACS Nano* **2019**, *13*, 2389–2397. <https://doi.org/10.1021/acsnano.8b09223>.
- (36) Younis, A.; Hu, L.; Sharma, P.; Lin, C.; Mi, Y.; Guan, X.; Zhang, D.; Wang, Y.; He, T.; Liu, X.; et al. Enhancing Resistive Switching Performance and Ambient Stability of Hybrid Perovskite Single Crystals via Embedding Colloidal Quantum Dots. *Adv. Funct. Mater.* **2020**, *30*, 2002948. <https://doi.org/10.1002/adfm.202002948>.
- (37) Hines, M. A.; Scholes, G. D. Colloidal PbS Nanocrystals with Size-Tunable Near-Infrared Emission: Observation of Post-Synthesis Self-Narrowing of the Particle Size Distribution. *Adv. Mater.* **2003**, *15*, 1844–1849. <https://doi.org/10.1002/adma.200305395>.
- (38) Zhang, J.; Gao, J.; Miller, E. M.; Luther, J. M.; Beard, M. C. Diffusion-Controlled Synthesis of PbS and PbSe Quantum Dots with in Situ Halide Passivation for Quantum Dot Solar Cells. *ACS Nano* **2014**, *8*, 614–622. <https://doi.org/10.1021/nn405236k>.
- (39) Jeon, N. J.; Noh, J. H.; Kim, Y. C.; Yang, W. S.; Ryu, S.; Seok, S. Il. Solvent Engineering for High-Performance Inorganic–Organic Hybrid Perovskite Solar Cells. *Nat. Mater.* **2014**, *13*, 897–903. <https://doi.org/10.1038/nmat4014>.
- (40) Yang, F.; Kapil, G.; Zhang, P.; Hu, Z.; Kamarudin, M. A.; Ma, T.; Hayase, S. Dependence of Acetate-Based Antisolvents for High Humidity Fabrication of CH₃NH₃PbI₃ Perovskite Devices in Ambient Atmosphere. *ACS Appl. Mater. Interfaces* **2018**, *10*, 16482–16489. <https://doi.org/10.1021/acsami.8b02554>.
- (41) Ahn, N.; Son, D. Y.; Jang, I. H.; Kang, S. M.; Choi, M.; Park, N. G. Highly Reproducible Perovskite Solar Cells with Average Efficiency of 18.3% and Best Efficiency of 19.7% Fabricated via Lewis Base Adduct of Lead(II) Iodide. *J. Am. Chem. Soc.* **2015**, *137*, 8696–8699. <https://doi.org/10.1021/jacs.5b04930>.
- (42) Lee, J.-W.; Kim, H.-S.; Park, N.-G. Lewis Acid–Base Adduct Approach for High Efficiency Perovskite Solar Cells. *Acc. Chem. Res.* **2016**, *49*, 311–319.

- <https://doi.org/10.1021/acs.accounts.5b00440>.
- (43) Yavari, M.; Mazloum-Ardakani, M.; Gholipour, S.; Tavakoli, M. M.; Turren-Cruz, S.-H.; Taghavinia, N.; Grätzel, M.; Hagfeldt, A.; Saliba, M. Greener, Nonhalogenated Solvent Systems for Highly Efficient Perovskite Solar Cells. *Adv. Energy Mater.* **2018**, *8*, 1800177. <https://doi.org/10.1002/aenm.201800177>.
- (44) Moot, T.; Marshall, A. R.; Wheeler, L. M.; Habisreutinger, S. N.; Schloemer, T. H.; Boyd, C. C.; Dikova, D. R.; Pach, G. F.; Hazarika, A.; McGehee, M. D.; et al. CsI-Antisolvent Adduct Formation in All-Inorganic Metal Halide Perovskites. *Adv. Energy Mater.* **2020**, *10*, 1903365. <https://doi.org/10.1002/aenm.201903365>.
- (45) Bae, W. K.; Joo, J.; Padilha, L. A.; Won, J.; Lee, D. C.; Lin, Q.; Koh, W.; Luo, H.; Klimov, V. I.; Pietryga, J. M. Highly Effective Surface Passivation of PbSe Quantum Dots through Reaction with Molecular Chlorine. *J. Am. Chem. Soc.* **2012**, *134*, 20160–20168. <https://doi.org/10.1021/ja309783v>.
- (46) Goodwin, E. D.; Straus, D. B.; Gauding, E. A.; Murray, C. B.; Kagan, C. R. The Effects of Inorganic Surface Treatments on Photogenerated Carrier Mobility and Lifetime in PbSe Quantum Dot Thin Films. *Chem. Phys.* **2016**, *471*, 81–88. <https://doi.org/10.1016/j.chemphys.2015.07.031>.
- (47) Xing, G.; Wu, B.; Wu, X.; Li, M.; Du, B.; Wei, Q.; Guo, J.; Yeow, E. K. L.; Sum, T. C.; Huang, W. Transcending the Slow Bimolecular Recombination in Lead-Halide Perovskites for Electroluminescence. *Nat. Commun.* **2017**, *8*, 1–9. <https://doi.org/10.1038/ncomms14558>.
- (48) Saari, J. I.; Dias, E. a; Reifsnnyder, D.; Krause, M. M.; Walsh, B. R.; Murray, C. B.; Kambhampati, P. Ultrafast Electron Trapping at the Surface of Semiconductor Nanocrystals: Excitonic and Biexcitonic Processes. *J. Phys. Chem. B* **2013**, *117*, 4412–4421. <https://doi.org/10.1021/jp307668g>.
- (49) Gong, X.; Huang, Z.; Sabatini, R.; Tan, C.-S.; Bappi, G.; Walters, G.; Proppe, A.; Saidaminov, M. I.; Voznyy, O.; Kelley, S. O.; et al. Contactless Measurements of Photocarrier Transport Properties in Perovskite Single Crystals. *Nat. Commun.* **2019**, *10*, 1591. <https://doi.org/10.1038/s41467-019-09538-7>.
- (50) Harvey, S. P.; Messinger, J.; Zhu, K.; Luther, J. M.; Berry, J. J. Investigating the Effects of Chemical Gradients on Performance and Reliability within Perovskite Solar Cells with TOF-SIMS. *Adv. Energy Mater.* **2020**, *1903674*, 1903674. <https://doi.org/10.1002/aenm.201903674>.
- (51) Harvey, S. P.; Zhang, F.; Palmstrom, A.; Luther, J. M.; Zhu, K.; Berry, J. J. Mitigating Measurement Artifacts in TOF-SIMS Analysis of Perovskite Solar Cells. *ACS Appl. Mater. Interfaces* **2019**, *11*, 30911–30918. <https://doi.org/10.1021/acsami.9b09445>.
- (52) Baikie, T.; Fang, Y.; Kadro, J. M.; Schreyer, M.; Wei, F.; Mhaisalkar, S. G.; Graetzel, M.; White, T. J. Synthesis and Crystal Chemistry of the Hybrid Perovskite (CH₃NH₃)PbI₃ for Solid-State Sensitised Solar Cell Applications. *J. Mater. Chem. A* **2013**, *1*, 5628. <https://doi.org/10.1039/c3ta10518k>.
- (53) Sercel, P. C.; Lyons, J. L.; Bernstein, N.; Efros, A. L. Quasicubic Model for Metal Halide Perovskite Nanocrystals. *J. Chem. Phys.* **2019**, *151*, 234106. <https://doi.org/10.1063/1.5127528>.
- (54) Fernée, M. J.; Thomsen, E.; Jensen, P.; Rubinsztein-Dunlop, H. Highly Efficient Luminescence from a Hybrid State Found in Strongly Quantum Confined PbS Nanocrystals. *Nanotechnology*

- 2006, 17, 956–962. <https://doi.org/10.1088/0957-4484/17/4/020>.
- (55) Ushakova, E. V.; Litvin, A. P.; Parfenov, P. S.; Fedorov, A. V.; Artemyev, M.; Prudnikau, A. V.; Rukhlenko, I. D.; Baranov, A. V. Anomalous Size-Dependent Decay of Low-Energy Luminescence from PbS Quantum Dots in Colloidal Solution. *ACS Nano* **2012**, 6, 8913–8921. <https://doi.org/10.1021/nn3029106>.
- (56) Han, N.; Liu, C.; Zhao, Z.; Zhang, J.; Xie, J.; Han, J.; Zhao, X.; Jiang, Y. Quantum Dots in Glasses: Size-Dependent Stokes Shift by Lead Chalcogenide. *Int. J. Appl. Glas. Sci.* **2015**, 6, 339–344. <https://doi.org/10.1111/ijag.12138>.
- (57) Sercel, P. C.; Vahala, K. J. Analytical Formalism for Determining Quantum-Wire and Quantum-Dot Band Structure in the Multiband Envelope-Function Approximation. *Phys. Rev. B* **1990**, 42, 3690–3710. <https://doi.org/10.1103/PhysRevB.42.3690>.
- (58) Yang, M.; Sturm, J. C.; Prevost, J. Calculation of Band Alignments and Quantum Confinement Effects in Zero- and One-Dimensional Pseudomorphic Structures. *Phys. Rev. B* **1997**, 56, 1973–1980. <https://doi.org/10.1103/PhysRevB.56.1973>.
- (59) McDonald, S. A.; Konstantatos, G.; Zhang, S.; Cyr, P. W.; Klem, E. J. D.; Levina, L.; Sargent, E. H. Solution-Processed PbS Quantum Dot Infrared Photodetectors and Photovoltaics. *Nat. Mater.* **2005**, 4, 138–142. <https://doi.org/10.1038/nmat1299>.
- (60) Kim, H.-S.; Lee, C.-R.; Im, J.-H.; Lee, K.-B.; Moehl, T.; Marchioro, A.; Moon, S.-J.; Humphry-Baker, R.; Yum, J.-H.; Moser, J. E.; et al. Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%. *Sci. Rep.* **2012**, 2, 591. <https://doi.org/10.1038/srep00591>.