

# Colloidal Quantum Dot Photovoltaics Enhanced by Perovskite Shelling

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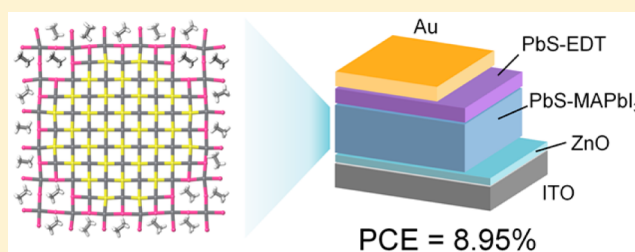
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## S Supporting Information

**ABSTRACT:** Solution-processed quantum dots are a promising material for large-scale, low-cost solar cell applications. New device architectures and improved passivation have been instrumental in increasing the performance of quantum dot photovoltaic devices. Here we report photovoltaic devices based on inks of quantum dot on which we grow thin perovskite shells in solid-state films. Passivation using the perovskite was achieved using a facile solution ligand exchange followed by postannealing. The resulting hybrid nanostructure created a more intrinsic CQD film, which, when incorporated into a photovoltaic device with graded bandstructure, achieved a record solar cell performance for single-step-deposited CQD films, exhibiting an AM1.5 solar power conversion efficiency of 8.95%.

**KEYWORDS:** Colloidal quantum dots, solar cells, perovskites, ligand exchange, surface passivation



Colloidal quantum dots (CQDs) show promise as solar harvesting materials in view of their size-tunable bandgap, facile synthesis, high monodispersity, and solution processability.<sup>1–5</sup> Advances in managing quantum dots' surface chemistry, as well as progress in device architecture, have recently led to certified AM1.5 solar power conversion efficiencies (PCEs)<sup>6–9</sup> of 9.9%.<sup>1,7,10–14</sup>

Colloidal quantum dots capped with suitable ligands can be redispersed in a range of solvents,<sup>15–22</sup> enabling fabrication ranging from layer-by-layer (LBL) spin-casting<sup>23–25</sup> to spray-coating,<sup>26,27</sup> inkjet printing,<sup>28,29</sup> and dip coating.<sup>30–32</sup> These multilayer approaches involve repeated quantum dot deposition, solid-state ligand exchanges, and rinse steps, resulting both in low quantum dot utilization and high solvent consumption.<sup>33</sup>

With the limitations of layer-by-layer methods in mind, researchers have recently focused on fabricating CQD solar cells based on pre-exchanged CQD inks. These can be directly deposited, simplifying the manufacturing, and using materials and solvents more efficiently.<sup>33–35</sup> Unfortunately, the highest-performing devices reported to date based on this approach have been limited to PCEs of 6%, considerably below the best layer-by-layer CQD devices.

Liganding CQDs using methylammonium iodide (MAI) was recently shown to offer the possibility of short-ligand-exchanged CQDs that could be directly deposited from a polar solvent.<sup>20</sup> Very recently, it was reported that PbS quantum dots and methylammonium lead triiodide perovskites

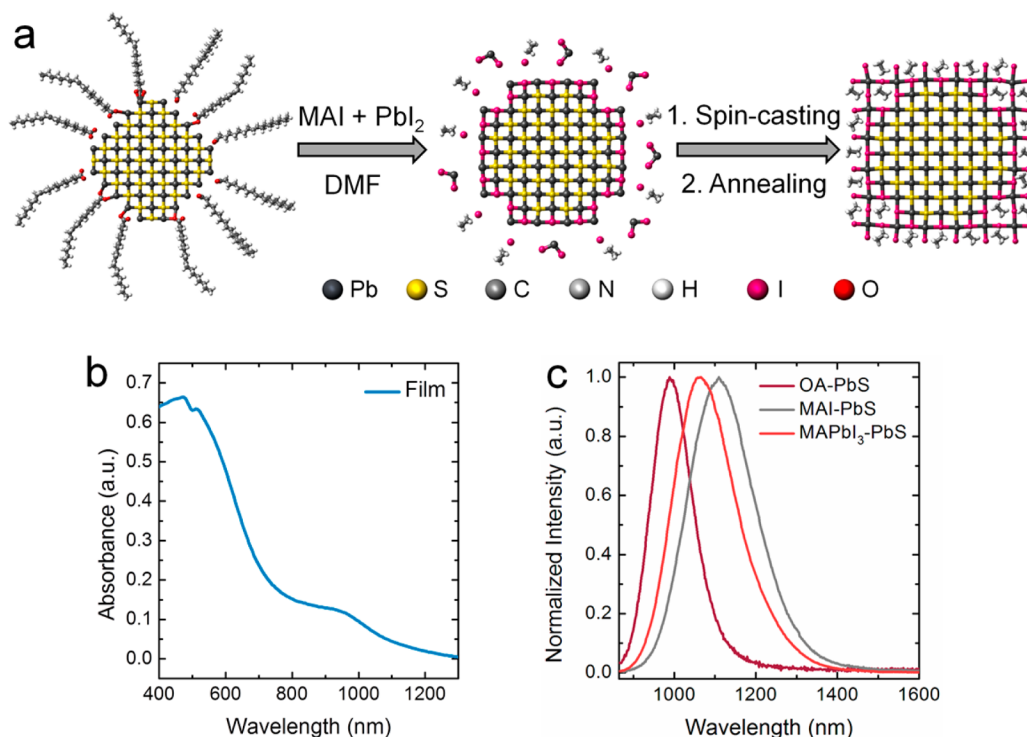
(MAPbI<sub>3</sub>) can exhibit coherence in their lattice fringes owing to their minimal lattice mismatch.<sup>36</sup>

Here we investigate the fabrication of solar cells that employ PbS colloidal quantum dots that, once formed into solid-state films, are passivated using a thin matrix of MAPbI<sub>3</sub>. Inspired by previous investigations of CQD-embedded perovskite solids,<sup>36</sup> we prepared concentrated CQD inks that were prepared to enable subsequent perovskite shelling once formed into films. We find that the films of perovskite-shelled CQDs exhibit a depletion region depth of ~120 nm, indicating a notably lower doping level than in the best prior CQD photovoltaic films. We fabricate CQD solar cells based on the directly deposited composite active medium, and these reach PCEs of 8.95%, a 1.45× improvement over the previous champion CQD-ink-based device.<sup>35</sup>

PbS CQDs were synthesized and purified using an established hot-injection approach and antisolvent method, respectively.<sup>11</sup> Solution ligand exchange was achieved by mixing the CQD octane solution (~20 mg/mL) and dimethylformamide (DMF) solution containing MAPbI<sub>3</sub> perovskite precursors (MAI and PbI<sub>2</sub>, 0.3 mol/L). The MAPbI<sub>3</sub> ligand passivation renders CQDs soluble in DMF that can then be reprecipitated upon addition of toluene. This solvent/

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**Figure 1.** PbS CQDs passivated using ligands that supply the chemical precursors to lead methylammonium perovskites: optical properties and processing. (a) Schematic of solution ligand exchange with perovskite precursors and corresponding CQD film preparation. (b) Absorption spectrum of MAPbI<sub>3</sub>-capped PbS CQD film showing CQD absorption peak at 940 nm. (c) Solution photoluminescence (PL) spectra of PbS CQDs passivated using various ligands. The reduced peak shift and peak broadening after exchange using MAPbI<sub>3</sub> precursors suggests a lesser degree of aggregation than in the MAI case.

antisolvent purification process was repeated twice to remove the residual oleic acid (OA), and the purified CQDs were finally redispersed in dry butylamine to yield a concentrated ink in a solvent with a low boiling point (Figure 1a).

Compared to the absorption spectrum of OA-capped CQDs in solution, the MAPbI<sub>3</sub>-passivated CQD films are red-shifted from 870 to 940 nm (Figure 1b), comparable to conventional films solid-state exchanged with tetrabutylammonium iodide ligand. A 75 nm redshift was seen in photoluminescence spectra of MAPbI<sub>3</sub>-capped dots in solution compared to their OA-capped counterparts (Figure 1c). We note that both the shift and broadening of the PL spectrum are smaller than in prior reports of CQDs passivated using MAI alone.<sup>35</sup> This suggests better surface coverage and less CQD aggregation when both PbI<sub>2</sub> and MAI were employed as ligands. The photoluminescent quantum yield of spin-cast MAPbI<sub>3</sub>-capped CQD film is around 2%, which is comparable to the report values of inorganic shell passivated CQD films.<sup>36,37</sup> X-ray diffraction (XRD) of annealed films and powders are dominated by PbS signals (Figure 2d); i.e., XRD does not resolve the perovskite crystal phase, a finding that we attribute to the perovskite's low concentration and the limits of XRD signal-to-background.

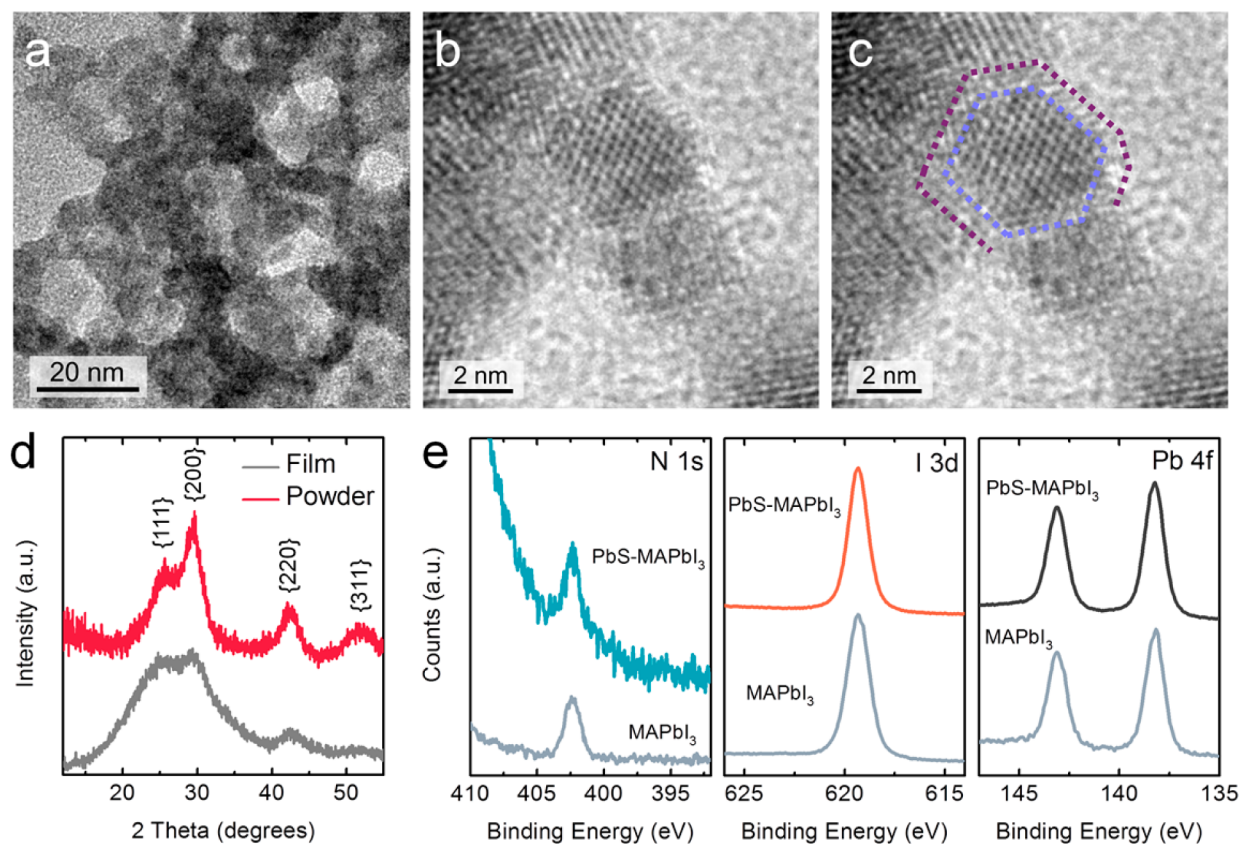
We therefore turned to TEM to investigate whether a thin perovskite shell/matrix was being formed. As seen in Figure 2a, a continuous solid matrix connects together the PbS quantum dots. Careful analysis with high resolution imaging (Figure 2b–c) indicates that the resultant lattice is coherent with that of nearby quantum dots. Scanning tunneling electron microscope (STEM) imaging provided additional information regarding the presence of perovskite (Figure S2): the majority of CQDs examined showed lattice fringes spaced by 3.4 Å, and this

corresponds to the {111} plane spacing for cubic PbS.<sup>38</sup> STEM also revealed another set of lattice fringes with *d*-spacing of 3.7 Å, consistent with the {022} plane spacing for MAPbI<sub>3</sub> crystals.<sup>39</sup>

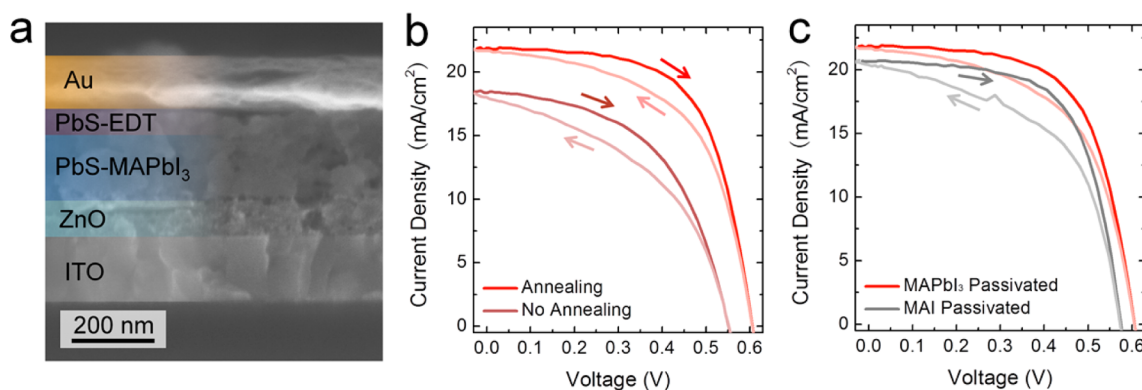
XPS of the annealed MAPbI<sub>3</sub>-CQD mixed materials showed appreciable nitrogen 1s (~402 eV), iodine 3d (~619 eV), and lead 4f (142.5 and 137.5 eV for 4f<sub>5/2</sub> and 4f<sub>7/2</sub>, respectively), and the oxidation state of the N and I are closely aligned with those of pure MAPbI<sub>3</sub> perovskite crystals (Figures 2e).

CQD solar cells have recently been shown that leverage a stable n-type CQD solid combined with a p-type top layer.<sup>22</sup> We projected that the MAPbI<sub>3</sub> CQD layers would exhibit similar band positions to TBAI-passivated layers, and we therefore constructed devices following a similar architecture (Figure 3). Indium-doped tin oxide (ITO) coated glass was used as substrate, on top of which a layer of solution-processable ZnO nanoparticles was deposited by spin-casting. The concentrated butylamine solution of exchanged MAPbI<sub>3</sub>-passivated CQD was directly spin-cast and formed a uniform mirror-like dark-brown film. This was further annealed at 70 °C under inert atmosphere for 10 min to allow formation of perovskite in the manner documented in Figure 2. A layer consisting of oleic-acid-capped CQDs (original absorption peak at 870 nm) was then deposited on top of the MAPbI<sub>3</sub>-PbS main absorber and solid-state ligand-exchanged using EDT to form a p-type top layer.<sup>13,14</sup> The optimized thickness of MAPbI<sub>3</sub>-PbS and EDT-PbS layers were 200 and 50 nm, respectively (Figure 3a).

We observed that annealing, with the goal of transforming the perovskite precursors into a thin crystalline matrix, was required to achieve the best device performance levels reported



**Figure 2.** Characterization of perovskite-capped CQD films. (a) TEM images of MAPbI<sub>3</sub>-capped CQD solid. (b) High-resolution TEM image showing the core–shell structure. (c) TEM image (same as in b, but with dotted lines to guide the eye to evidence of a thin perovskite shell). (d) XRD patterns of MAPbI<sub>3</sub>-capped CQD solid indicating the presence of PbS CQDs. (e) XPS results of nitrogen 1s, iodine 3d, and lead 4f regions of MAPbI<sub>3</sub>-capped CQD film indicate the incorporation of MAPbI<sub>3</sub>.

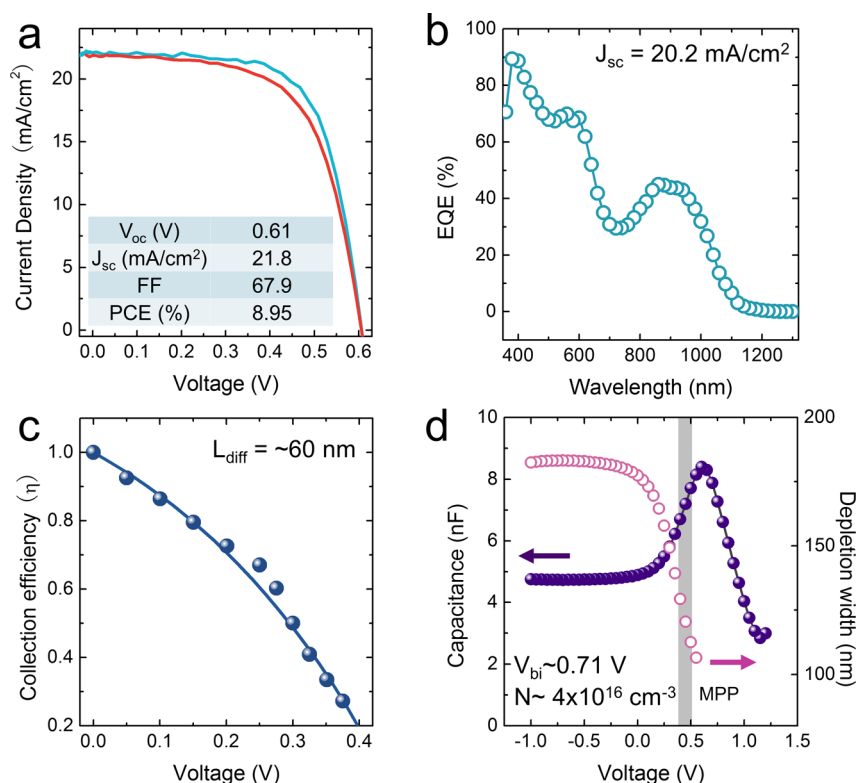


**Figure 3.** Photovoltaic device architecture and performance. (a) Cross-sectional SEM image with labels to indicate each component. (b) Current–voltage ( $J$ – $V$ ) characteristics under simulated AM 1.5 illumination for MAPbI<sub>3</sub>-passivated devices with and without annealing. Lighter curves showing the  $J$ – $V$  properties under reverse scanning indicate the reduction of hysteresis following annealing. (c) Comparison of  $J$ – $V$  characteristics under simulated AM 1.5 illumination between MAPbI<sub>3</sub>- and MAI-passivated devices.

herein. Annealed and nonannealed performance under AM 1.5 solar illumination are reported in Figure 3b and Table S1. The  $J_{sc}$  and  $V_{oc}$  of annealed devices are  $\sim 21.9$  mA/cm<sup>2</sup> and 0.61 V, over 10% and 22% higher than the parameters of the nonannealed sample, respectively. The improvement is also reflected in higher fill factor (FF) and reduced hysteresis, yielding a power conversion efficiency (PCE) of 8.5%. All device parameters are significantly higher than those from the best device treated using the previously published MAI ligand exchange (Figure 3c).<sup>35</sup> We conclude that the inclusion of the

coherently lattice-matching passivating thin layer of MAPbI<sub>3</sub> perovskite limits CQD aggregation and thus achieves a better balance of  $V_{oc}$  and  $J_{sc}$ , yielding improved device performance.

Considering the band misalignment between MAPbI<sub>3</sub>- and EDT-capped PbS layers, we further optimized the device by using an EDT treated layer incorporating slightly larger dots (absorption peak of purified OA-capped dots at 896 nm). The optimization led to an increase in FF to  $\sim 68\%$  and the resultant PCE of 8.95%. This is 1.45 $\times$  higher than the previous record of a CQD solar cell based on a directly deposited solution-



**Figure 4.** Performance of perovskite-shelled CQD photovoltaic devices. (a)  $J$ - $V$  characteristics under simulated AM 1.5 illumination for MAPbI<sub>3</sub>-shelled dot devices that employ smaller dots (blue) and larger dots (red) in the realization of the top EDT-solid-state-treated CQD layer. (b) EQE spectrum of a champion graded MAPbI<sub>3</sub>-passivated device. (c) A diffusion length ( $L_{diff}$ ) of 60 nm is obtained by fitting the collection efficiency with the aid of an analytical model (see methods). (d) Depletion width ( $W_D$ ) as calculated from capacitance–voltage spectroscopy measurements. Devices remain fully depleted at short-circuit conditions. At maximum power point conditions (MPP), a  $W_D$  of 120 nm is obtained, consistent with the importance of drift in achieving efficient charge collection in these films. The perovskite shelling leads to more depleted films ( $4 \times 10^{16} \text{ cm}^{-3}$ ) compared to previously reported passivation strategies.

processed principal active layer. We found that the materials do change gradually under time, especially in the presence of light exposure (Figure S3),<sup>40</sup> leading to a decrease in  $J_{sc}$  over the course of characterization, a fact that accounts for the slightly lower overall external quantum efficiency than in TBAI-passivated devices (Figure 4b).<sup>13,14</sup>

We sought to elucidate the origins of improved performance relative to prior direct-deposit reports. We characterized the diffusion length ( $L_{diff}$ ) and depletion width ( $W_D$ ) in our solar cells for comparison to controls.  $L_{diff}$  was obtained by measuring the bias-dependent collection efficiency (see Methods) and fitting to a previously reported analytical model.<sup>41</sup> We found  $L_{diff}$  to be of order 60 nm (Figure 4c). Given the thickness of the active layer in our devices ( $\sim 200 \text{ nm}$ ) and the high fill-factor attained (68%), this suggests that drift is playing a significant role in charge collection. Indeed, capacitance–voltage spectroscopy (Figure 4d) reveals that perovskite-passivated dot films remain fully depleted at short-circuit conditions, with a depletion width of 120 nm at maximum power point conditions. The obtained carrier density of  $4 \times 10^{16} \text{ cm}^{-3}$  suggests that the perovskite matrix passivation results in a more fully depleted CQD solid compared to prior passivation schemes such as those based on TBAI.<sup>14</sup> This is consistent with the highly intrinsic nature of perovskite active layers observed in perovskite photovoltaic studies.

In conclusion, the present study demonstrates the fabrication of perovskite-passivated CQD solids. Solution ligand exchange using perovskite precursors, followed by annealing to promote

matrix crystallization, led to the formation of perovskite thin shells onto CQD surfaces. The addition of a larger-bandgap perovskite matrix created a more intrinsic CQD film exhibiting a deeper depletion region of 120 nm at working conditions, notably thicker than in prior solid-state-exchanged reports. Optimization of the device and its processing led to a PCE of 8.95%, a major advance over prior directly deposited CQD devices. Since excellent surface passivation for improved open-circuit voltage is the most quantitatively significant opportunity for improved CQD solar cell performance, we believe that further effort is warranted in epitaxial matrix incorporation in CQD photovoltaic solids.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b03271.

Experimental details of PbS CQD synthesis, perovskite ligand exchange, device fabrication and characterization, as well as TEM images of OA- and MAI-capped PbS CQDs. The material also includes STEM images of perovskite-capped CQDs, time-dependent short circuit current measurements of MAPbI<sub>3</sub>-shelled devices, and a table that shows performance parameters of CQD devices with different surface ligands and preparation processes (PDF)

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## Author Contributions

Z.Y. and A.J. contributed equally.

## Notes

The authors declare no competing financial interest.

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