

# **Quantum-Dot-Induced Cesium-Rich Surface** Imparts Enhanced Stability to Formamidinium Lead Iodide Perovskite Solar Cells

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S Supporting Information

ABSTRACT: The stability of formamidinium lead iodide (FAPbI<sub>3</sub>) perovskites is generally improved by incorporating cesium (Cs) into the crystal structure. However, the effectiveness of this approach is limited by the intrinsically low solid-solubility of Cs in bulk FAPbI<sub>3</sub>. To circumvent this issue, we demonstrate a method that entails solution-deposition of high-Cs-content Cs<sub>1-x</sub>FA<sub>x</sub>PbI<sub>3</sub> alloy quantum dots (QDs) onto a bulk Cs-lean FAPbI<sub>3</sub>-based thin film. This results in a thin film with a Cs-rich QD surface layer, which stabilizes the thin film against the ambient environment. Stable, efficient perovskite solar cells based on these new thin-film structures are demonstrated.



ince the first report of perovskite solar cells (PSCs) in 2009,<sup>1</sup> the development of PSCs has been unprecedentedly rapid, with the certified record power conversion efficiency (PCE) of PSCs has now reached 24.2%.<sup>2</sup> While early studies focused on methylammonium lead iodide (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, or MAPbI<sub>3</sub>) perovskites,<sup>3</sup> the focus has gradually shifted in recent years toward perovskites based on formamidinium lead iodide (CH(NH<sub>2</sub>)<sub>2</sub>PbI<sub>3</sub>, or FAPbI<sub>3</sub>).<sup>4,5</sup> The promise of FAPbI<sub>3</sub> as light-absorber material is owing to its narrower band gap ( $\sim$ 1.47 eV) and higher thermal stability as compared to MAPbI<sub>3</sub>.<sup>6-9</sup> In fact, the state-of-the-art PSCs with the highest PCEs are generally based on FAPbI3 perovskite.<sup>10,11</sup> However, FAPbI3 tends to undergo polymorphic transformation from perovskite  $\alpha$ -phase to nonperovskite  $\delta$ -phase under ambient conditions, which poses a major hurdle in the path toward the realization of its full potential.<sup>12</sup> To overcome this issue, various strategies have been used for stabilizing FAPbI<sub>3</sub> perovskite thin films,<sup>13-15</sup> among which composition-engineering has been proven to be highly effective.<sup>15</sup> In particular, incorporating Cs into FAPbI<sub>3</sub> to form Cs<sub>1-x</sub>FA<sub>x</sub>PbI<sub>3</sub> alloy perovskites has been used widely to enhance the crystal structural stability of the films.<sup>16–18</sup> However, it has been shown that only a limited amount of Cs can be alloyed into the FAPbI<sub>3</sub> perovskite crystal lattice,

resulting in Cs-lean  $Cs_{1-x}FA_xPbI_3$  thin films (typically x > x0.85). Thus, simply increasing the added amount of Cs often results in uncontrolled phase segregation in Cs<sub>1-x</sub>FA<sub>x</sub>PbI<sub>3</sub> bulk thin films.<sup>11,16</sup> Furthermore, although their structural stability is improved compared with neat FAPbI3 perovskite, Cs-lean Cs<sub>1-x</sub>FA<sub>x</sub>PbI<sub>3</sub> perovskites can still be highly hygroscopic, because the high population of FA<sup>+</sup> surface terminations in such films favors facile interactions with ambient moisture.<sup>16,19</sup>

In this context, it has been demonstrated recently that perovskite quantum-dots (QDs) are capable of reaching compositions beyond those possible in bulk thin films, owing to their high surface energy and the existence of surfacepassivating ligands.<sup>20,21</sup> Thus, our approach is to exploit Csrich QDs and incorporate them into the surface layer of otherwise Cs-lean FAPbI3-based perovskite thin films to form a Cs-rich surface. Toward this goal, we have synthesized Cs<sub>1-r</sub>FA<sub>r</sub>PbI<sub>3</sub> alloy QDs across the entire composition range of x = 0-1, using a recently reported interparticle cation-exchange method.<sup>20</sup> The as-synthesized QDs are then readily solution-deposited on top of Cs-lean FAPbI<sub>3</sub> perovskite bulk

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thin films without the QDs losing their integrity. For proof-ofconcept demonstration,  $Cs_{0.57}FA_{0.43}PbI_3$  perovskite alloy QDs are used as a model system to achieve Cs-rich surfaces on FAbased thin films. This QD modification significantly reduces the film hygroscopicity, thereby imparting ambient stability. Moreover, the Cs-rich surface of the film in contact with the hole transport layer (HTL) in the PSC device favors more efficient hole extraction at that interface. PSCs with improved device stability and enhanced PCE up to 20.82% are demonstrated.

CsPbI<sub>3</sub> and FAPbI<sub>3</sub> perovskite QDs were synthesized and purified using modified methods that were previously reported (see details in the Supporting Information).<sup>22-25</sup> Figure 1a



Figure 1. (a) Absorption and (b) PL spectra of as-synthesized  $CsPbI_3$  and  $FAPbI_3$  QDs. Inset in panel a: photograph of the QDs sample solutions under UV-light illumination. TEM and HRTEM (insets) images of (c)  $CsPbI_3$  and (d)  $FAPbI_3$  QDs. Inset scale bars: 5 nm.

shows the ultraviolet-visible (UV-vis) absorption spectra of the as-synthesized CsPbI<sub>3</sub> and FAPbI<sub>3</sub> QDs. The corresponding photoluminescence (PL) peaks are centered at 685 nm (full-width at half-maximum, or FWHM, of 91.6 meV) and 785 nm (FWHM of 90.3 meV) for the CsPbI<sub>3</sub> and FAPbI<sub>3</sub> QDs, respectively (Figure 1b). Transmission electron microscopy (TEM) characterization shows that both CsPbI<sub>3</sub> and FAPbI<sub>3</sub> QDs possess a uniform cubic shape (Figure 1c,d). The average edge lengths of the CsPbI<sub>3</sub> and FAPbI<sub>3</sub> cubic QDs are  $11.5 \pm$ 2.0 and 10.6  $\pm$  1.6 nm, respectively. High-resolution TEM (HRTEM) images reveal the lattice fringes with *d*-spacings of 3.1 Å for CsPbI<sub>3</sub> QDs and 3.3 Å for FAPbI<sub>3</sub> QDs (insets in Figure  $1c_1d_1$ , which can be assigned to (002) planes of the cubic perovskite phase (space group:  $Pm\overline{3}m$ ). This perovskite phase has been further confirmed by powder X-ray diffraction (XRD) characterization, revealing lattice parameters of 6.21 and 6.34 Å for CsPbI<sub>3</sub> and FAPbI<sub>3</sub> QDs, respectively (Figure S1 and Table S1).

The as-synthesized CsPbI<sub>3</sub> and FAPbI<sub>3</sub> QD samples were then mixed in hexane to fabricate  $Cs_{1-x}FA_xPbI_3$  alloy perovskite QDs following an interparticle A-site cationexchange method (see details in the Supporting Information).<sup>20</sup> By controlling the feeding ratio between CsPbI<sub>3</sub> and FAPbI<sub>3</sub> QDs, a series of Cs<sub>1-x</sub>FA<sub>x</sub>PbI<sub>3</sub> alloy QDs with different A-site compositions (x = 0.22, 0.43, 0.63, and 0.82) were obtained (Figure S2 and Table S2). The entire alloy-formation process was closely monitored using spectroscopic and microscopy methods (Figure 2a-g). As shown in Figure 2b,c, the initial mixture exhibits two distinct PL peaks centered at 685 and 785 nm, which are attributed to individual CsPbI<sub>3</sub> and FAPbI<sub>3</sub> QDs, respectively (Figure 1b). During the reaction, the two PL peaks gradually move toward each other and eventually merge into a single peak centered at 735 nm (FWHM of 96.6 meV) after 96 h of mixing (Figure 2b,c). A similar spectral merging process is also observed in the convoluted absorption profile of the mixture solution (Figure 2a). These observations indicate the formation of homogeneous  $Cs_{1-x}FA_xPbI_3$  alloy QDs, which is in good agreement with the previous report.<sup>20</sup> TEM images of the intermediate (Figure 2e-g) and the final alloy QDs (Figure 2d) show a



Figure 2. (a) Absorption and (b) PL spectra evolution upon mixing of  $CsPbI_3$  and  $FAPbI_3$  perovskite QDs. Corresponding (c) 2D PL emission maps and (d-g) TEM images of the samples at different reaction times. Scale bars: 10 nm. (h) XRD patterns of the starting  $CsPbI_3$ ,  $FAPbI_3$  QDs, and the final  $Cs_{0.57}FA_{0.43}PbI_3$  QDs. Insets: schematic illustrations of the corresponding crystal structures. (i) Expanded XRD pattern of the area marked in panel h.

retained cubic particle shape with an average edge length of  $10.7 \pm 2.3$  nm in the latter. XRD confirms a cubic perovskite structure with a lattice parameter of 6.25 Å (Table S2), which is consistent with the (001) interplanar distance of 6.3 Å measured from the HRTEM images (Figure S3). Inductively coupled-plasma atomic-emission spectroscopy (ICP-AES) measurements have revealed an alloy composition of Cs<sub>0.57</sub>FA<sub>0.43</sub>PbI<sub>3</sub> (Table S3 and Figure 2h,i). Moreover, the energy dispersive spectroscopy (EDS) elemental mapping result shows homogeneous distributions of Cs, Pb, I, and N elements in the final alloy QDs (Figure S4). The optical characterization of other compositions (x = 0.22, 0.63, and0.82) was also performed (Figure S5), displaying similar spectral merging phenomena for the x = 0.43 case. All these results indicate a complete A-site cation-exchange reaction without any phase segregation. Furthermore, the Cs<sub>1-x</sub>FA<sub>x</sub>PbI<sub>3</sub> alloy QDs show good stability in ambient environment, as evinced by no change in their crystal phase and optical properties after at least 2 months of storage (Figure S6).

To demonstrate the advantage of applying the Cs<sub>1-x</sub>FA<sub>x</sub>PbI<sub>3</sub> alloy QDs in PSCs, the as-prepared Cs<sub>0.57</sub>FA<sub>0.43</sub>PbI<sub>3</sub> alloy perovskite QDs were used as a model system and spin-coated onto a Cs-lean FAPbI<sub>3</sub> (Cs<sub>0.02</sub>FA<sub>0.98</sub>PbI<sub>3</sub>) perovskite thin film. The film was then annealed at 150 °C for 1 min, resulting in the formation of a Cs-rich perovskite surface (see details in the Supporting Information, Figure S7). XRD and scanning electron microscopy (SEM) results show that the bulk Cslean FAPbI<sub>3</sub>-based thin film exhibits no significant changes after the deposition of the Cs<sub>0.57</sub>FA<sub>0.43</sub>PbI<sub>3</sub> QDs onto its surface (Figures S8 and S9). Figure 3a shows steady-state PL spectra of the FAPbI<sub>3</sub> films with and without QD modification. While only a single PL peak (centered at 804 nm) from the QDs-free Cs-lean FAPbI3 thin film is observed, an additional PL peak at 785 nm emerges after QD modification, which can be assigned to the emission of Cs<sub>0.57</sub>FA<sub>0.43</sub>PbI<sub>3</sub> QDs. The slight redshift (~10 nm) can be attributed to photon reabsorption



Figure 3. (a) Steady-state PL spectra, (b) time-resolved PL spectra, and (c) UPS spectra of Cs-lean FAPbI<sub>3</sub>-based perovskite film with and without  $Cs_{0.57}FA_{0.43}PbI_3$  QDs. (d) Schematic illustration of the film surface VBM shift after  $Cs_{0.57}FA_{0.43}PbI_3$  QD modification. HOMO level of Spiro-OMeTAD HTL is also shown.

and re-emission processes in the dense film.<sup>26</sup> In addition, thermal annealing of the as-synthesized thin film (80  $^{\circ}$ C, 12 h) did not significantly change the PL features (Figure S10). These observations confirm the existence of a new Cs-rich surface of the perovskite thin film with enhanced structural stability. The preservation of QD integrity after the solution deposition is attributed to the negligible solubility of the Cs<sub>0.57</sub>FA<sub>0.43</sub>PbI<sub>3</sub> QDs into Cs-lean FAPbI<sub>3</sub> bulk perovskite thin film. Note that this situation is different from the case of "fusing" of CsPbX<sub>3</sub> QDs into the surfaces of bulk MAPbI<sub>3</sub> perovskite thin film reported earlier.<sup>27-29</sup> Time-resolved PL spectra of the FAPbI3-based thin films with and without QD modification exhibit a biexponential decay characteristic (Figure 3b). The fitted average PL lifetimes  $(\tau_{avg})$  are 36.9 and 28.4 ns for the films with and without QDs, respectively (Table S4). This prolonged exciton recombination dynamic suggests reduced nonradiative recombination in the film after QD modification. This could be due to the QD-passivation effect for the surface traps of the Cs-lean FAPbI<sub>3</sub> bulk perovskite thin film, as evinced by no obvious changes in the microstructure and grain-boundary density of the film (Figures S9). The thin-film trap densities were evaluated based on dark current-voltage (I-V) measurements of single-carrier planar devices, where trap-filled voltages  $(V_{\text{TFL}})$  were determined. The results shown in Figure S11 confirm significantly reduced trap density of  $1.75 \times 10^{15}$  cm<sup>-3</sup> for the QD-modified film as compared to  $2.21 \times 10^{15} \text{cm}^{-3}$  for the QD-free film. Furthermore, ultraviolet photoelectron spectroscopy (UPS) measurements indicate that the QD modification induces an upshift of the valence band maximum (VBM) of the Cs-lean  $FAPbI_3$  perovskite thin film (Figure 3c). The VBMs for the film with and without QDs were determined to be -5.32 and -5.48 eV, respectively (Figure S12). As seen in Figure 3d, the final VBM level (-5.32 eV) of the film after QD modification (Cs-rich surface) is located between that of the Cs-lean FAPbI<sub>3</sub> film (-5.48 eV) and the highest occupied molecular orbital (HOMO) level of the commonly used HTL material Spiro-OMeTAD (-5.22 eV), forming a cascade hole-extraction heterostructure, which is similar to that reported in the literature.<sup>30-32</sup> This new perovskite-HTL interface demonstrates a more efficient PL-quenching effect compared to the conventional FAPbI<sub>3</sub>-HTL interface (Figure S13), and it is expected to reduce voltage loss in the PSCs.

To evaluate the device performance using the QD-modified thin film, PSCs were fabricated in the planar heterojunction device structure, where the perovskite thin film is sandwiched between an FTO/SnO2 anode and a Spiro-OMeTAD/Au cathode (Figure 4a). The current density-voltage (I-V)curves (both forward and reverse scans) of the best-performing PSCs with and without QD modification are shown in Figure 4b, and the corresponding photovoltaic (PV) parameters are summarized in Table S5. With QD modification, the device shows a PCE (reverse scan) of 20.82% with a short-circuit current density  $(J_{SC})$  of 24.44 mA·cm<sup>-2</sup>, an open-circuit voltage  $(V_{OC})$  of 1.121 V, and a fill factor (FF) of 0.760. All these parameters are superior to those extracted from the J-Vcurves of the QD-free device. In addition, the QD-modified device shows significantly reduced hysteresis compared with its QD-free counterpart (Figure 4b). These improvements can be attributed not only to the reduced trap densities on the perovskite surfaces but also to the formation of the new cascade-structure perovskite-HTL interface (Figure 3d). The steady-state power output of the best-performing devices with



Figure 4. (a) Schematic illustration of the PSC device structure (left) and cross-sectional SEM image of the actual device (right) with the different layers indicated by false-coloring. (b) J-V curves of the PSCs with and without  $Cs_{0.57}FA_{0.43}PbI_3$  QD modification (both reverse and forward scans). (c) Stabilized photocurrent and PCE output at the maximum power point (V = 0.88 V). Key PV parameter statistics: (d)  $V_{OC}$  and (e) PCE of Cs-lean FAPbI<sub>3</sub>-based PSCs with and without  $Cs_{0.57}FA_{0.43}PbI_3$  QD modification.

QDs was measured at the maximum power point, which stabilized at  $\sim 19.6\%$  (Figure 4c), close to the PCEs determined using J-V curves. The statistics of the key parameters (V<sub>OC</sub> and PCE) are presented in Figures 4d and 4e, respectively, and in Table S6, which attest to the reproducible enhancement of the device performance through QD modification. Here, it should be mentioned that recently Zheng et al.<sup>29</sup> have suggested that the surface ligands of QDs may also contribute to the passivation effect in the thin films, which may enhance device performance. In this study, we purified the QDs thoroughly to minimize the amount of the remaining organic ligands (see Supporting Information). Therefore, we believe that the Cs-rich surface of the thin film is mainly responsible for the device performance improvement in this study. Nevertheless, we recognize that a tailored ligand incorporation may further optimize the device performance, which is an interesting topic for future research.

Ambient stability is one of the most critical issues in FAPbI<sub>3</sub>based PSCs. Here, the introduction of a Cs-rich perovskite QD on the surface of Cs-lean FAPbI<sub>3</sub> bulk perovskite thin film may suppress the degradation of the perovskite phase under ambient conditions. To investigate device stability improvement, UV–vis spectra of the Cs-lean FAPbI<sub>3</sub> thin films with and without QD modification were recorded as a function of storage time under ambient conditions (90% relative humidity, or RH; 30 °C). After 96 h, the absorption of the Cs-lean FAPbI<sub>3</sub> perovskite thin film without QD modification decreased significantly while that of the QD-modified thin film remained nearly unchanged (Figure 5a). The absorbance



Figure 5. Spectral evolution of Cs-lean FAPbI<sub>3</sub> perovskite thin films with and without Cs<sub>0.57</sub>FA<sub>0.43</sub>PbI<sub>3</sub> QD modification upon storage under ambient conditions (90% RH, 30 °C): (a) UV-vis spectra and (b) absorbance variation at 650 nm as a function of storage time. (c) PCE evolution of PSCs with and without QD modification after storage under ambient conditions (20% RH for the initial 3 days, and 90% RH for the rest of the time; 30 °C). Inset: photographs of corresponding devices after storage for 24 h.

variations at 685 nm as a function of the storage time under the same ambient conditions were also monitored for both cases. For the QD-modified thin film, 83.4% of its initial absorbance is retained after 300 h, as compared to only 8.6% for that of the QD-free one (Figure 5b). The associated XRD data and photographs of the thin films confirm that the Cs<sub>0.57</sub>FA<sub>0.43</sub>PbI<sub>3</sub> QD modification imparts the improved stability and integrity to the resulting FAPbI<sub>3</sub>-based perovskite thin film (Figure S14). To further evaluate the stability of final device performance, the PCE was monitored for 4 days (Figure 5c). The PCEs of both devices (with and without QD modification) are found to be stable for the initial 3 days under relatively mild storage conditions (20% RH; 30 °C). Device degradation processes were significantly accelerated by increasing the RH to 90%. Consequently, the stability difference between the two types of devices became more evident (Figure 5c). Within only 24 h, the PCE of QD-free device decreased by ~90% of its initial value, while only a  $\sim$ 20% decrease was observed for the QD-modified device. These results unambiguously prove the stability enhancement effects, for both thin films and associated PSCs, of enriching the surface layer of FAPbI<sub>3</sub>-based bulk thin films with Cs using the QD modification approach.

In summary, we have demonstrated the fabrication of FAPbI<sub>3</sub>-based bulk perovskite thin films with a Cs-rich surface using solution-deposition of  $Cs_{1-x}FA_xPbI_3$  alloy perovskite QDs. The QD-modified film structure not only improves the charge dynamics in the devices but also significantly enhances the ambient stability of the FAPbI<sub>3</sub>-based thin films and the associated PSCs. The film modification approach described here, where the incorporation of specifically designed QDs passivates the thin-film surfaces, can extend the existing composition-engineering methods used in perovskite thin films, leading to highly efficient PSCs with enhanced stability.

Finally, we envision that our study will pave the way for harnessing the interplay between nanoscale QDs and bulkscale thin films for future PSCs and other optoelectronic devices.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergy-lett.9b01262.

Experimental methods, including synthesis of perovskite QDs and fabrication of perovskite films and the corresponding devices; XRD patterns; additional PL spectra; SEM/TEM images; dark current–voltage curve measurements; and UPS calculations (PDF)

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# Author Contributions

M. Que and Z. Dai contributed equally to this work. M. Que, Y. Zhou, and O. Chen conceived and designed the experiments. M. Que conducted QD syntheses and optical characterization. Z. Dai and Y. Zong fabricated the thin films and the perovskite solar cells, and they performed the measurements. H. Yang and H. Zhu carried out the TEM and ICP-AES measurements. W. Que, N. P. Padture, Y. Zhou, and O. Chen supervised the entire project. M. Que, Z. Dai, N. P. Padture, Y. Zhou, and O. Chen cowrote the manuscript. All authors discussed the results and commented on the manuscript.

#### Notes

The authors declare no competing financial interest.

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