## **SOLAR CELLS**

# Conformal quantum dot-SnO<sub>2</sub> layers as electron transporters for efficient perovskite solar cells

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Improvements to perovskite solar cells (PSCs) have focused on increasing their power conversion efficiency (PCE) and operational stability and maintaining high performance upon scale-up to module sizes. We report that replacing the commonly used mesoporous—titanium dioxide electron transport layer (ETL) with a thin layer of polyacrylic acid—stabilized tin(IV) oxide quantum dots (paa-QD-SnO<sub>2</sub>) on the compact—titanium dioxide enhanced light capture and largely suppressed nonradiative recombination at the ETL—perovskite interface. The use of paa-QD-SnO<sub>2</sub> as electron-selective contact enabled PSCs (0.08 square centimeters) with a PCE of 25.7% (certified 25.4%) and high operational stability and facilitated the scale-up of the PSCs to larger areas. PCEs of 23.3, 21.7, and 20.6% were achieved for PSCs with active areas of 1, 20, and 64 square centimeters, respectively.

fforts to realize metal halide perovskite solar cells (PSCs) with power conversion efficiencies (PCEs) of >23% have focused on formamidinium-rich lead iodide (FAPbI<sub>3</sub>) formulations (1-7) because their narrower bandgap is closer to the Shocklev-Queisser optimum than for methylammoniumbased or mixed-halide perovskites (8). By fully using the broad absorption spectrum of FAPbI<sub>3</sub>, a certified PCE of 25.21% with a short-circuit current density  $(J_{sc})$  of >26 mA/cm<sup>2</sup> was obtained for the mesoporous-structure PSCs (7). However, the mesoporous-TiO<sub>2</sub> (m-TiO<sub>2</sub>) electron transport laver (ETL) may show unwanted photocatalytic effects under ultraviolet (UV) light illumination, and the low electron mobility of m-TiO2 limits the charge transport (9-11).

Among alternative metal oxide ETLs (10–17) for PSCs, SnO<sub>2</sub>-based PSCs could potentially be more efficient and stable given that SnO<sub>2</sub> is UV resistant and has a higher carrier mobility

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than TiO<sub>2</sub>, which facilitates electron extraction and transport (10-12). Several techniques, such as spin coating (11, 16), atomic layer deposition (1), and chemical bath deposition (CBD) (12, 17), have been used to deposit the SnO<sub>2</sub> ETLs. Spin-coated SnO<sub>2</sub> ETL from a SnO<sub>2</sub> colloidal quantum dot (QD-SnO<sub>2</sub>) solution onto the indium-doped tin oxide (ITO) substrate enabled a certified PCE of >23% for the corresponding planar-structure PSCs (2, 16). Recently, a thin SnO<sub>2</sub> ETL on fluorine-doped tin oxide (FTO) deposited with a well-controlled CBD method enabled PSCs with a certified PCE of 25.19%, because of the improved carrier properties of SnO<sub>2</sub> ETL (17). However, compared with the m-TiO<sub>2</sub>-based PSCs, the SnO<sub>2</sub>-based PSCs still suffered from a relatively low  $J_{sc}$  of <26 mA/cm<sup>2</sup>, which is attributed to the optical losses arising from reflection and destructive interference of the incident light waves at the interfaces.

One approach to reduce these optical losses is to use the textured surface of FTO as the front contact that scatters the incoming radiation, destroying the coherence of the incoming light and affording light trapping by increasing the optical path length (18). The enhanced light absorption by the perovskite benefits the photocurrent delivered by the photovoltaic (PV) cell. Similar strategies have been used for textured crystalline silicon-based PSCs (19). However, early efforts to deposit a thin, uniform, and high-quality SnO<sub>2</sub> ETL using a solution process were incompatible with the underlying textured FTO surface (1, 12, 20-22). causing optical losses. The highest reported  $J_{sc}$ of SnO<sub>2</sub>-based PSCs of  $\sim$ 25.2 mA/cm<sup>2</sup> (17, 20) still limits the overall PV performance.

Here we introduce an architecture for the ETL of PSCs that consists of a compact-TiO<sub>2</sub> (c-TiO<sub>2</sub>) blocking layer covered by a thin layer of polyacrylic acid (PAA)-stabilized QD-SnO<sub>2</sub> (paa-QD-SnO<sub>2</sub>) deposited in a contiguous and

conformal manner on the textured FTO. The uniform bilayer of paa-QD-SnO $_2$ @c-TiO $_2$  largely improved the perovskite's absorption of sunlight and formed an outstanding electron-selective contact with the perovskite film. The quantum size effect increased the bandgap of the QD-SnO $_2$  from 3.6 eV for bulk SnO $_2$  to ~4 eV (21, 23) and produced a corresponding upward shift of its conduction band edge energy. This shift aligned it well with the conduction band edge of the perovskite so that electron capture by the SnO $_2$ -based ETL proceeded with minimal energy losses (5, 11, 16, 21).

PAA, a polymer binder, was added to the SnO<sub>2</sub> QD solution to attach the colloidal QD-SnO<sub>2</sub> firmly to the c-TiO<sub>2</sub> surface, providing a contiguous, thin, and conformal SnO2 layer that fully covered the c-TiO2 layer underneath. The carboxyl groups of PAA undergo strong hydrogen and coordinative bonding with the metal oxide surface, facilitating the lamination process, especially for production on a large scale (24-26). By choosing FTO substrates with suitable diffuse transmittance and reflectance, the textured paa-QD-SnO<sub>2</sub>@c-TiO<sub>2</sub> bilayer enabled a PCE of 25.7% (certified 25.4%) with a  $J_{sc}$  of 26.4 mA/cm<sup>2</sup> and high stability for the corresponding PSCs. We further demonstrate that the paa-QD-SnO<sub>2</sub>@c-TiO<sub>2</sub> bilayer could be applied to realize large PSC modules with an active area up to 64 cm<sup>2</sup> while maintaining a PCE of >20%.

We investigated the microstructures of the spin-coated QD-SnO<sub>2</sub> layer on the c-TiO<sub>2</sub> using commercially available SnO2 colloidal QDs with and without PAA. Unless otherwise noted, the QD-SnO<sub>2</sub> solution was diluted by deionized water (1:20) in this study. Figure S1, A to C, shows the top-view scanning electron microscope (SEM) images of the c-TiO2, QD-SnO2@c-TiO<sub>2</sub>, and paa-QD-SnO<sub>2</sub>@c-TiO<sub>2</sub>, respectively. Because of the textured surface, the c-TiO<sub>2</sub> layer was not fully covered by the spin-coated QD-SnO<sub>2</sub> (fig. S1B). In contrast, a uniform, conformal paa-QD-SnO2 layer was formed (fig. S1C). Atomic force microscopy images (fig. S1, D to F) further confirmed the uniform morphology of the paa-QD-SnO<sub>2</sub>@c-TiO<sub>2</sub> (fig. S1F), which is different from that of the QD-SnO<sub>2</sub>@c-TiO2 (fig. S1E).

Figure 1, A and B, shows the cross-sectional transmission electron microscopy (TEM) images of the QD-SnO $_2$ @c-TiO $_2$  and paa-QD-SnO $_2$ @c-TiO $_2$  bilayers on FTO substrates, respectively. The QD-SnO $_2$ @c-TiO $_2$  bilayer presented an ununiform distribution over the FTO surface with a thickness that varied from ~30 (vertex region) to ~70 nm (valley region), while the paa-QD-SnO $_2$ @c-TiO $_2$  bilayer had a uniform and conformal distribution over the FTO surface with a uniform thickness of ~30 nm. The different distribution between QD-SnO $_2$  and paa-QD-SnO $_2$  layers can also be seen clearly from the cross-sectional SEM images (fig. S2, A and B),

suggesting that PAA played a key role in forming the uniform and contiguous layer of paa-QD-SnO<sub>2</sub> ETL, as shown in fig. S3.

Element mapping with energy-disperse x-ray spectroscopy of Ti (Fig. 1, C and D) and Sn (Fig. 1, E and F) revealed a coverage of TiO2 and SnO2 over the FTO surface for both QD-SnO2@c-TiO2 and paa-QD-SnO2@c-TiO2 bilayers. The selected-area electron diffraction generated by TEM for the paa-QD-SnO<sub>2</sub>@c-

TiO<sub>2</sub> bilayer (fig. S4) showed that both QD-SnO<sub>2</sub> and c-TiO<sub>2</sub> were polycrystalline. The paa-QD-SnO<sub>2</sub> had a particle size of ~4 nm (fig. S4C), which is also confirmed by the TEM images (fig. S5, A to C) and dynamic light scattering analysis (fig. S5, D and E).

The interactions between PAA and QD-SnO<sub>2</sub> were studied by the x-ray photoelectron spectroscopy (XPS) (fig. S6) and Fourier transform infrared spectroscopy (FTIR) measurements (fig. S7). It is clear from the XPS measurements that both QD-SnO2@c-TiO2 and paa-QD-SnO2@c-TiO2 bilayers showed characteristic peaks attributed to Sn (fig. S6A); however, the Sn 3d peaks of paa-QD-SnO2 shifted to high binding energy by ~0.2 eV compared with that of QD-SnO2, indicating that PAA was bonded to the QD-SnO2. No obvious difference was observed for the O 1s characteristic peaks (fig. S6, B to D). FTIR measurements showed

# Fig. 1. Microstructures of the ETLs.

(A and B) The cross-sectional TEM images of QD-SnO<sub>2</sub>@c-TiO<sub>2</sub> (A) and paa-QD-SnO<sub>2</sub>@ c-TiO<sub>2</sub> (B) over the FTO substrates. Scale bars, 0.1 µm. (C and D) EDS elemental analysis of Ti for both QD-SnO<sub>2</sub>@c-TiO<sub>2</sub> (C) and paa-QD-SnO<sub>2</sub>@c-TiO<sub>2</sub> (D) over the FTO surface. Scale bars, 100 nm. (E and F) EDS elemental analysis of Sn for both QD-SnO<sub>2</sub>@ c-TiO<sub>2</sub> (E) and paa-QD-SnO<sub>2</sub>@c-TiO<sub>2</sub> (F) over the FTO surface. Scale bars, 100 nm.

Current density mA/cm<sup>2</sup>)

 $(1/[s m^2 nm]) \times 10^{18}$ 

Photon flux

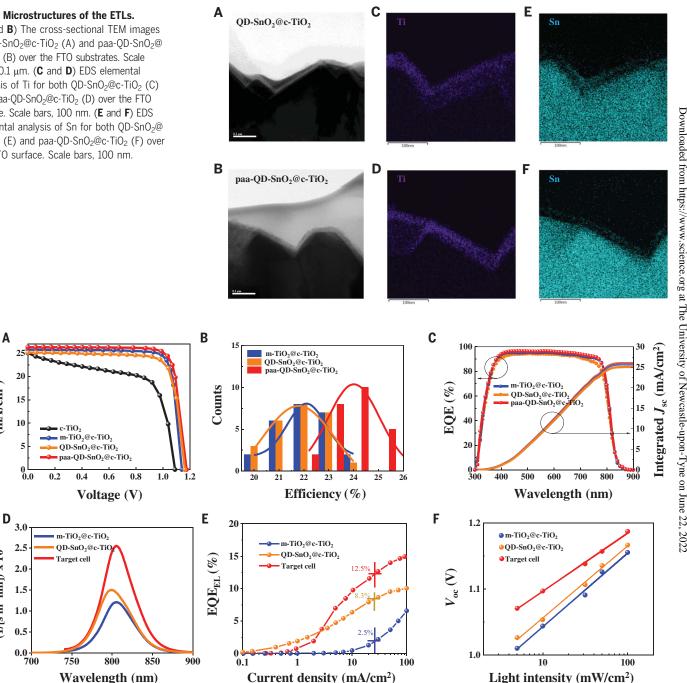


Fig. 2. Characterization of the PSCs. (A) The J-V curves of the PSCs with different ETLs measured under the QSS-IV method. (B) A statistical distribution of the PCE for PSCs with different ETLs. ( $\mathbf{C}$  to  $\mathbf{F}$ ) The EQE and integrated  $J_{\text{sc}}$  (C), steady-state PL spectral photon flux (D), EQE<sub>FL</sub> (E), and the light-dependent  $V_{\text{oc}}$  (F) for the PSCs with different ETLs.

peaks at ~2954 and ~1716 cm $^{-1}$  that arise from C–H and C=O stretching vibrations of PAA (fig. S7A) and a characteristic peak at ~574 cm $^{-1}$  of the Sn-O vibration (fig. S7B). The Sn-O peak shifted to ~594 cm $^{-1}$  for the paa-QD-SnO $_2$ , and the C–H and C=O stretching vibrations shifted to ~3012 and ~1628 cm $^{-1}$ , respectively (fig. S7C), demonstrating that PAA interacted with QD-SnO $_2$  (27).

We chose FAPbI<sub>3</sub> as the perovskite layer, and details of its fabrication can be found in the supplementary materials (SM) or a previous report (3). Top-view SEM images of the FAPbI<sub>3</sub> films spin-coated on different ETLs, including c-TiO2, m-TiO2@c-TiO2, QD-SnO2@c-TiO<sub>2</sub>, and paa-QD-SnO<sub>2</sub>@c-TiO<sub>2</sub>, are shown in fig. S8, A to D, respectively. Compact and dense surface morphologies were observed for all the perovskite films. Figure S9A showed identical x-ray diffraction (XRD) peak positions for all samples at 14.1° and 28.2°, which correspond to the (001) and (002) crystal planes of  $\alpha$ -FAPbI<sub>3</sub> (3–5). All the perovskite films had identical full width at half maximum for the main (001) peak (fig. S9B). We conclude that the morphology and crystallinity of the perovskite films are not affected substantially by the

The PSCs with an active area of 0.08 cm<sup>2</sup> were fabricated in a conventional n-i-p structure, FTO/ETL/perovskite/OAI/spiro-MeOTAD/Au, where OAI is octylammonium iodide and spiro-MeOTAD is 2,2',7,7'-tetrakis[*N*,*N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene. We performed the quasi-steady-state current-voltage (QSS-*IV*) measurement (Fig. 2A), which was used for the certification of PSCs by the National Renewable Energy Laboratory (NREL) and Newport Inc. Details of the QSS-*IV* measurements are given in the SM. All the PSCs were fully aged in the ambient condition for 100 hours before the measurements.

The c-TiO2-based cell had a low PCE of 17.27% under the QSS-IV measurement. For the m-TiO2@c-TiO2-based PSC, a PCE of 23.74% with a  $J_{\rm sc}$  of 25.74 mA/cm<sup>2</sup>, an opencircuit voltage ( $V_{oc}$ ) of 1.142 V, and a fill factor (FF) of 80.79% was obtained, which are consistent with the previous reports (3, 7). Compared with the mesoporous-structured devices, the QD-SnO<sub>2</sub>@c-TiO<sub>2</sub>-based cell had a higher  $V_{\rm oc}$  of 1.164 V but a lower  $J_{\rm sc}$  of 25.12 mA/cm<sup>2</sup>, resulting in a PCE of 23.29%. The  $J_{\rm sc}$  of the QD-SnO<sub>2</sub>@c-TiO<sub>2</sub>-based PSC is similar to the values reported for the SnO<sub>2</sub>-based cells in the literature (17, 20). With the paa-QD-SnO<sub>2</sub>@c-TiO<sub>2</sub> ETL, the PSC exhibited a high PCE of 25.18% with a considerably improved  $J_{\rm sc}$  of 26.28 mA/cm<sup>2</sup>,  $V_{\rm oc}$  of 1.177 V, and FF of 81.49%, matching the 25.39% efficiency certified by Newport Inc. (figs. S10 and S11).

The conventional *J-V* measurements under both forward and reverse scans were also performed (fig. S12). The detailed PV parameters are summarized in table S1. A substantially different PV value was obtained for the c-TiO<sub>2</sub>-based cell under QSS-IV (Fig. 2A) and conventional J-V measurements (fig. S12A), whereas the other cells showed similar PV results, indicating that the c-TiO<sub>2</sub>-based cell is unstable and that the single c-TiO2 layer is not a proper ETL for PSCs (28, 29). The contrasting feature of the c-TiO2-based cell compared with the other cells in Fig. 2A and fig. S12A is discussed in note 1 of the SM. Hereafter, the c-TiO<sub>2</sub>-based cells will not be discussed. A statistical distribution of the PCE of all the PSCs (Fig. 2B) shows that the paa-QD-SnO<sub>2</sub>@c-TiO2-based PSC had the highest averaged values. Details of the statistical PV parameters of all different ETL-based cells are shown in fig. S13. The paa-QD-SnO<sub>2</sub>@c-TiO<sub>2</sub>-based cell is the target of the discussions that follow.

The  $J_{\rm sc}$  of the PSCs measured under the solar simulator was verified with external quantum efficiency (EQE) measurements. The target cell had slightly higher EQE than the m-TiO2@c-TiO2-based PSC over the entire absorption spectrum (Fig. 2C), resulting in a higher integrated  $J_{\rm sc}$  of 26.01 mA/cm<sup>2</sup>; however, a relatively lower integrated  $J_{sc}$  of 25.06 mA/cm<sup>2</sup> was obtained for the QD-SnO<sub>2</sub>@c-TiO2-based device than for the m-TiO2@c- $TiO_2$ -based cell (25.69 mA/cm<sup>2</sup>). The high  $J_{sc}$ of the target cell was attributed to the desired light scattering that prolongs the optical length, enhancing the light absorption by the perovskite with the conformal structured paa-QD-SnO<sub>2</sub>@c-TiO<sub>2</sub> bilayer over the FTO substrate. This is confirmed with the highest diffuse transmittance (haze) of paa-QD-SnO2@c-TiO<sub>2</sub> when compared with the other ETLs shown in fig. S14A. The higher transmittance of paa-QD-SnO<sub>2</sub>@c-TiO<sub>2</sub> than the QD-SnO<sub>2</sub>@c-TiO<sub>2</sub> (fig. S14B) may be traced back to the thinner film thickness, as shown in the optical simulations (fig. S14, C and D), which could also contribute to the high  $J_{\mathrm{sc}}$ . We further compared the  $J_{sc}$  obtained for the paa-QD-SnO<sub>2</sub>@c-TiO<sub>2</sub>based PSCs using different substrates (fig. S15). The Asahi FTO glass with high diffuse transmittance was the most suitable substrate for achieving a high  $J_{sc}$ .

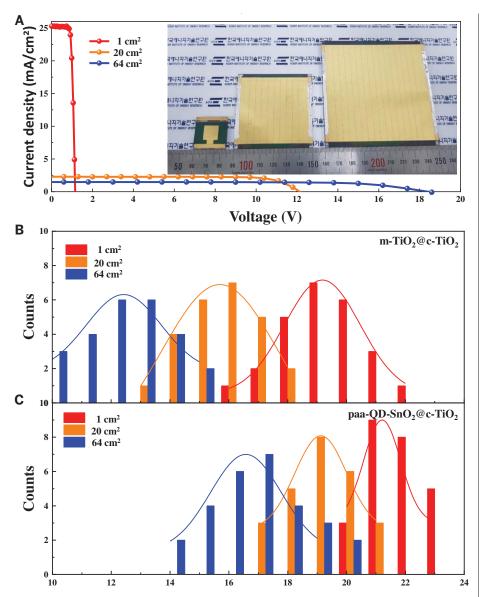
The effect of the ETL composition on the photon flux emitted by the PSCs measured in steady state at an excitation photon flux equivalent to 1 sun is shown in Fig. 2D. The investigated devices were complete solar cells without the Au back contact. Compared with the m-TiO<sub>2</sub>@c-TiO<sub>2</sub>- and QD-SnO<sub>2</sub>@c-TiO<sub>2</sub>-based devices, the target cell had much higher photoluminescence (PL) intensity, reaching a PL quantum yield (PLQY) of 7.5%. This indicates a reduced nonradiative recombination at the interface between perovskite and paa-QD-SnO<sub>2</sub> ETL. Details of the measurements and calculations of PLQY are shown in SM note 2. From the PLQY measurements, we derived

the quasi-Fermi level splitting ( $\Delta E_{\rm F}$ ) in the perovskite under 1 sun illumination (SM note 3) and compared the ( $\Delta E_{\rm F}$ ) with the  $V_{\rm oc}$  measured from the same device.  $\Delta E_{\rm F}$  and  $V_{\rm oc}$  showed the same trend, indicating that the  $V_{\rm oc}$  increase can be partly attributed to the reduced nonradiative recombination. The  $\Delta E_{\rm F}/q-V_{\rm oc}$  offset (where q is the elementary charge), however, is different. For the target cell, it is 10 mV lower than that of the m-TiO<sub>2</sub>@c-TiO<sub>2</sub>-based cells, indicating a better energetic alignment at the interfaces (30).

Ultraviolet photoelectron spectroscopy (UPS) measurements on the surface of different ETLs (fig. S16) showed that the conduction band of paa-QD-SnO<sub>2</sub> matched better with perovskite than the m-TiO<sub>2</sub>@c-TiO<sub>2</sub>, which could facilitate the charge transfer from perovskite to the ETL (fig. S17). Detailed analysis of the UPS data is shown in SM note 4. Figure S18, A and B, shows the time-resolved PL (TRPL) spectra of the perovskite films on different ETLs measured from both the perovskite and the glass sides. The perovskite film deposited on paa-QD-SnO<sub>2</sub>@c-TiO<sub>2</sub> had the fastest decay among all the samples. Because it has a low nonradiative recombination rate, the fast decay is dominated by the favored interfacial electron transfer. The electron mobility measurements (fig. S18C) revealed that the paa-QD-SnO<sub>2</sub>@c-TiO<sub>2</sub> layer had the highest carrier mobility. All these results indicate a superior charge extraction from perovskite to the paa-QD-SnO<sub>2</sub> ETL.

Regarding the reduced nonradiative recombination, we determined the EQE of electroluminescence (EQE<sub>EI</sub>) on representative PSC devices. Figure 2E shows an EQE<sub>EL</sub> of 12.5% for the target cell at an injection current density of 26 mA/cm<sup>2</sup> corresponding to the  $J_{\rm sc}$  under 1 sun illumination, whereas the m-TiO<sub>2</sub>@c-TiO<sub>2</sub>- and QD-SnO<sub>2</sub>@c-TiO<sub>2</sub>-based cells have an EQE<sub>EL</sub> of 2.5 and 8.3%, respectively, under the same conditions. Thus, the nonradiative recombination rate in the PSC was reduced by 80% simply by replacing the m-TiO<sub>2</sub> with a paa-QD-SnO<sub>2</sub> electron-selective contact layer. The highest obtained  $V_{\rm oc}$  of 1.22 V (fig. S19), which is near the  $V_{\rm oc}$  predicted from EQE<sub>EL</sub> according to the reciprocity theorem (31, 32), measured without the metal mask reached 98% of the radiative limit  $V_{\rm oc}$  (1.25 V) (2, 5). We also conducted transient photovoltage measurements for the PSCs (fig. S20A). The target cell showed a slower  $V_{\rm oc}$  decay than the reference cells, indicating a slower charge recombination rate. The dark J-V curves (fig. S20B) showed the lowest reverse saturation current for the target cell, pushing the onset of the dark current to the highest voltages, which also reflected the lowest interfacial nonradiative recombination.

Figure 2F shows the light intensity-dependent  $V_{\rm oc}$  measurements for the PSCs. For both the reference and target cells, the



**Fig. 3. Performance of the large-size PSCs. (A)** *J-V* curves of the large-size PSCs. (Inset) Photo of the large-size PSCs. (**B** and **C**) Statistical distributions of the PCEs for the m-TiO<sub>2</sub>@c-TiO<sub>2</sub>-based (B) and paa-QD-SnO<sub>2</sub>@c-TiO<sub>2</sub>-based (C) PSCs with pixel sizes of 1, 20, and 64 cm<sup>2</sup>.

**PCE** (%)

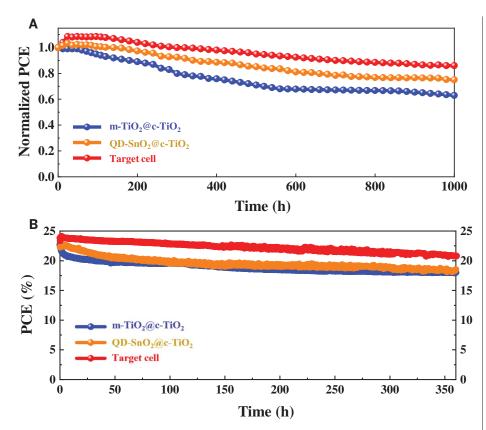
measured  $V_{\rm oc}$  was linearly dependent on the logarithm of the light intensity. The diode ideality factor  $n_{\rm id}$ , deduced from the slope described by  $n_{\rm id}k_{\rm B}T/q$ , where  $k_{\rm B}$  is the Boltzmann constant and T is temperature, was 1.83, 1.79, and 1.46 for the m-TiO<sub>2</sub>@c-TiO<sub>2</sub>– and QD-SnO<sub>2</sub>@c-TiO<sub>2</sub>–based cells and the target cell, respectively. The reduced  $n_{\rm id}$  contributed to the increased FF of the target cell, as the FF critically depends on the  $n_{\rm id}$  (33). The reduced  $n_{\rm id}$  is also consistent with the PLQY, TRPL, EQE<sub>EL</sub>, transient photovoltage decay, and dark J-V measurements, unambiguously supporting the conclusion of reduced nonradiative recombination of the target PSC using paa-QD-SnO<sub>2</sub>

ETL. The decreased nonradiative recombination manifests itself by much stronger photo-and electroluminescence (Fig. 2, C and D) as well as a lower ideality factor (Fig. 2E) enabling very high fill factor of 83.8% to be reached by our target device (table S2). Further strong support for our conclusion comes from the observation of a slower transient photovoltage decay (fig. S20A) and higher electron mobility (fig. S20B) as well as the dark J-V measurements of the paa-QD-SnO\_2@c-TiO\_based cell compared with the control devices. The substantial reduction of the trap-assisted nonradiative recombination is the main reason for the reduced  $V_{\rm oc}$  deficit of our target

cell of ~310 mV as compared with ~350 mV for the mesoporous-structure cell [bandgap of our perovskite film was calculated to be 1.53 eV (3)], which is one of the lowest values reported in the field of PSCs.

Scale-up of the PSCs to module size is another requirement for their commercial exploitation. We used paa-QD-SnO2@TiO2 ETL to fabricate perovskite solar mini-modules with active areas up to 64 cm<sup>2</sup>. Details of the fabrication process for the solar modules can be found in the SM and movie S1. Figure 3A shows the J-V curves and images of the perovskite mini-modules with different active areas. The highest PCEs achieved for the PSCs with active areas of 1, 20, and 64 cm<sup>2</sup> were 23.3, 21.7, and 20.6%, respectively. Movie S2 shows a typical measurement for the 64 cm<sup>2</sup> perovskite solar modules. Figure S21A illustrates a solar module with subcells connected in series with a magnified view of the contact connections, and a geometrical FF (GFF) was calculated to be 95.6% according to the SEM images (fig. S21B) of the interconnections. Details of the PV parameters are summarized in table S2. The decrease of the PCE with increased device size is mainly caused by a decreased FF. The  $V_{\rm oc}$  of the module (table S2) divided by the number of stripes is 18.5 V/16 = 1.156 V, which is equal to the  $V_{\rm oc}$  of the 1 cm<sup>2</sup> cell. Hence, there is no additional  $V_{\rm oc}$  loss in the module. Therefore, we attribute the FF decrease to the increased series resistance. including transport layer resistances, contact resistances, and interconnect resistance. We sent the PSC modules to an independent laboratory (OMA Company, Republic of Korea) for certification. PCEs of 21.66% (fig. S22) and 20.55% (fig. S23) were confirmed for the PSC mini-modules with active areas of 20 and 64 cm<sup>2</sup>, respectively, which agreed well with the measurements in our laboratory, and are compared with other reported values in fig. S24.

We further compared the statistical distribution of the PCEs for the mesoporous-based (Fig. 3B) and target (Fig. 3C) perovskite minimodules. For the perovskite modules with the same active area (1, 20, or 64 cm<sup>2</sup>), the target modules had higher averaged PCE and narrower PCE distributions than the mesoporousbased modules. The averaged PCE of the 64 cm<sup>2</sup> PSC module increased by ~30% by simply replacing the m-TiO<sub>2</sub> with paa-QD-SnO<sub>2</sub>, indicating that the paa-QD-SnO2 could be uniformly coated on the large-size substrates. The statistical distribution of the PV parameters (fig. S25) further revealed that the  $V_{\rm oc}$  and FF of the mesoporous-based modules decreased significantly more than that of the target PSC modules. The shunt resistance of our solar modules retained a typical value of >4000 ohms·cm<sup>2</sup> (table S3), indicating that losses from leakage currents across shunts



**Fig. 4. Stability of the PSCs with different ETLs.** The stability shown here represents the best stability results of our four tested samples. **(A)** Shelf life of the unencapsulated PSCs tested in ambient air at 25% RH and 25°C with different ETLs. **(B)** The operational stability test of the unencapsulated PSCs under MPP tracking conditions in a N<sub>2</sub> environment.

produced during scale-up are negligible. We attribute the small decrease of  $V_{\rm oc}$  and FF for the target PSC modules to the low contact resistance (fig. S26, A and B) because of the easier laser scribing as well as low series resistance and low interfacial defects of the paa-QD-SnO<sub>2</sub>@c-TiO<sub>2</sub> bilayer.

Figure 4A shows the 1000-hour shelf life tested with unsealed devices in ambient air at 25% relative humidity (RH) and 25°C. The target PSC retained 80% of the maximum PCE (25.7%) after 1000-hour storage, whereas the m-TiO<sub>2</sub>@c-TiO<sub>2</sub>- and QD-SnO<sub>2</sub>@c-TiO<sub>2</sub>based PSCs decreased to almost 30 and 40% of the initial efficiency, respectively, indicating that the target cell is more resistant to the moisture and oxygen than the widely used mesoporous structured PSCs. We also performed the operational stability test for the unsealed devices in a N2 environment under maximum power point (MPP) tracking conditions using a light-emitting diode lamp with a calibrated light intensity of 100 mW/cm<sup>2</sup>. More details about the MPP tests can be found in the SM and in previous reports (5, 7). Figure 4B shows that the target cell had higher PCE than the reference cell during the 350-hour MPP tracking test. From the detailed PV parameters during the MPP tracking measurements (fig. S27), it is clear that the higher performance of the target PSC is due to the higher and rather stable  $V_{\rm oc}$ , which decreased less compared with the reference cells. The main degradation of the target cell is the decline of FF (fig. S27), which is attributed to the de-doping of lithium from the hole-transport layer (HTL) (5, 34).

We further tested the sealed devices under ambient conditions. Figure S28 shows that 70.5% of the initial efficiency of the target cell was retained after 700-hour light-soaking test, whereas the efficiency of the m-TiO2@c-TiO<sub>2</sub>-based cell declined 45% over the same testing time. To assess the suitability of the cells for real applications, we performed an MPP stability test for the encapsulated target cell under ambient conditions. Figure S29 shows that 95% of the initial efficiency was retained for the sealed target cell after 100 hours MPP tracking and 2 hours dark recovery under ambient conditions. The substantial decline of FF is still the main reason for the performance loss. Future studies of additive-free HTLs will be conducted to enhance the stability of PSCs.

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# SUPPLEMENTARY MATERIALS

science.org/doi/10.1126/science.abh1885 Materials and Methods Supplementary Text Figs. S1 to S29 Tables S1 to S3 References (35–50) Movies S1 and S2

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# Conformal quantum dot-SnO layers as electron transporters for efficient perovskite solar cells

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## Tailoring tin oxide layers

Mesoporous titanium dioxide is commonly used as the electron transport layer in perovskite solar cells, but electron transport layers based on tin(IV) oxide quantum dots could be more efficient, with a better-aligned conduction band and a higher carrier mobility. Kim *et al.* show that such quantum dots could conformally coat a textured fluorine-doped tin oxide electrode when stabilized with polyacrylic acid. Improved light trapping and reduced nonradiative recombination resulted in a certified power conversion efficiency of 25.4% and high operational stability. In larger-area minimodules, active areas as high as 64 square centimeters maintained certified power conversion efficiencies of more than 20%. —PDS

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