

Electronic Supplementary Information

Improving Carrier Extraction in a PbSe Quantum Dot Solar Cell by Introducing a Solution-processed Antimony-doped SnO₂ Buffer Layer

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Experimental Details

Preparation of TiO₂ layer

The TiO₂ electron transport layer (ETL) was prepared the same as we reported before.¹ 10ml ethanol, 0.35ml deionized water and 6 drops of hydrochloric acid were mixed in a 50ml flask. Then 0.75ml titanium ethoxide was slowly added to the above solution while under vigorous stirring. After that, the stirring was maintained and the solution was placed under nitrogen for 24h. FTO-8Ω (Dyso glass substrates) were cleaned by ultrasonic for 15mins in detergent, acetone, isopropyl alcohol (IPA), deionized water respectively, then an ultraviolet and ozone (UVO) pretreatment for 15min followed. The sol-gel was spin-coated on the pre-cleaned FTO glass substrates with the rate of 1500rpm for 30s. Finally, the film was annealed at 450°C in the muffle furnace for 30min in air.

Preparation of SnO₂ and Sb: SnO₂ layer

The SnO₂ thin film was fabricated referring to Anaraki's work.² 0.5mmol (0.175g) SnCl₄·5H₂O (Sigma) was placed in 10ml IPA under stirring at room temperature for 3h to form a stable sol-gel solution. Then the sol-gel was spin-coated on the UVO pre-treated TiO₂ thin film at 3000rpm for 30s. Then the film was annealed at 120°C for 10min and 200°C for 1h in air. As for Sb: SnO₂, 20mmol (4.568g) SbCl₃ (Sigma) was dissolved in 40ml hydrochloric acid (HCl) followed by ultrasonication for 10min to make the Sb precursor solution. For 0.5mol%, 1mol% and 1.5mol% doping levels, 5.1 μL, 10.2 μL, 15.3 μL of Sb precursor solution was added into 10ml SnO₂ sol-gel respectively. The Sb: SnO₂ thin film was deposited on the TiO₂ layer and annealed in the

same way as the SnO₂. The TiO₂ films with buffer layers were then placed vertically in SnCl₄ aqueous solution (0.7g SnCl₄·5H₂O in 100ml deionized water) at 70°C for 10min to treat the surface and dried in nitrogen flow.

Synthesis of PbSe QDs

The cation exchange method^{1, 3} with some modification was used in this work. To synthesize PbSe QDs with a first exciton peak at 860nm, CdSe QDs were synthesized first. 0.315g Se powder was dispersed in 10ml octadecene (ODE, Sigma-Aldrich, 90%) by sonication as the Se precursor for further use. Meanwhile, 0.512g CdO (Sigma), 3.14g oleic acid (OA), and 25g ODE were mixed together in a 100ml 3-neck bottom flask and degassed at 80°C for 30min. The temperature was then increased to 260°C under nitrogen and maintained that way until the solution became transparent. Then the temperature was decreased to 240°C for hot injection. 5ml Se precursor solution was swiftly injected into the Cd solution and cooled down to room temperature naturally. The production was purified by centrifugation for three times by using hexane, chloroform, and ethanol. Then the wet pellets on the centrifuge tube wall were dispersed in 5ml ODE as a starter solution for cation exchange. For PbSe synthesis, 1.251g PbCl₂ (Alfa Aesar) and 15ml oleyamine (OLA) were added into a 3-neck round bottom flask and degassed at 80°C for 30min, then heated up to 140°C under nitrogen and maintained at that temperature for 10min. The temperature was then reduced to 80°C for hot injection. The CdSe QDs were then quickly injected into the solution for cation exchange and the temperature was maintained for 12min before water bath cooling. 20ml hexane and 16ml OA were injected into the solution at 75°C and 40°C respectively during the cooling process. The solution was kept under stirring at 40°C for another 15min then cooled down to room temperature. For

purification, hexane and ethanol were applied and finally the QDs were dispersed in hexane with a concentration of $15\text{mg}\cdot\text{mL}^{-1}$.

Synthesis of CsPbBr₃ perovskite QDs

CsPbBr₃ QDs with a first exciton peak at 485nm were synthesized following the work of Protesescu et al.⁴ The hot injection temperature was 175°C and the reaction was kept for 5s before quenched in an ice bath. The QDs were washed by 1:1/v:v IPA and centrifuged at 8000rpm for 4min. The wet pellets were finally dispersed in hexane with a concentration about 5mg mL^{-1} .

Device fabrication

The PbSe QDs were deposited by a hand-dip coating method. Substrates with TiO₂ or SnO₂/TiO₂ were first dipped into the PbSe QDs hexane solution and then removed slowly. After the film dried naturally, it was then dipped into a PbI₂ ligand solution (10×10^{-3} M in N, N-dimethylformamide, DMF) for 30s for ligand exchange, then rinsed several times by acetonitrile and dried in a nitrogen flow. Eighteen PbI₂ treated PbSe QD layers were deposited, followed by another two layers treated with MPA (10% volume in methanol) and rinsed with methanol before soaking into CsPbBr₃ QD solution for 30s to passivate the surface.¹ For a complete device, 100nm of gold was deposited by thermal evaporation at a pressure of 2×10^{-6} mbar.

Characterization

The absorption spectra of the solution-based samples were measured by a Perkin Elmer Lambda1050 UV–vis–NIR spectrophotometer in ambient conditions.

The steady-state PL spectra of PbSe QDs hexane solution were measured by QuantaMaster 500 (Horiba) with an excitation at 600 nm (generated by xenon arc lamp) and detected by a thermoelectronically cooled InGaAs TE detector.

The J–V measurements were performed using an IV5 solar cell I–V testing system from PV measurements, Inc. A Keithley 2400 source meter measured the I-V response of the cells under an illumination power of 100 mW cm^{-2} provided by an AM1.5G solar simulator (Oriel model 94023A). The cell area was 0.071 cm^2 . The EQE of the devices was measured by using a PV Measurement QXE7 Spectral Response system with monochromatic light, generated from a xenon arc lamp. The system was calibrated by a silicon diode.

XPS measurements were performed on a Thermo Scientific ESCALAB250Xi, with a monochromatic Al X-ray source. The power was 150 W and spot size was $500 \mu\text{m}$. A flood gun was used to remove charge build up on the samples during the measurement.

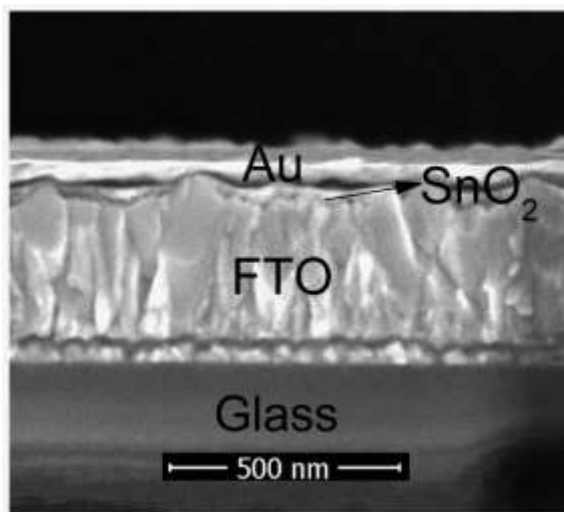


Figure S1. Cross-sectional scanning electron microscopy (SEM) image of Sb: SnO₂ single layer deposited on pre-cleaned FTO.

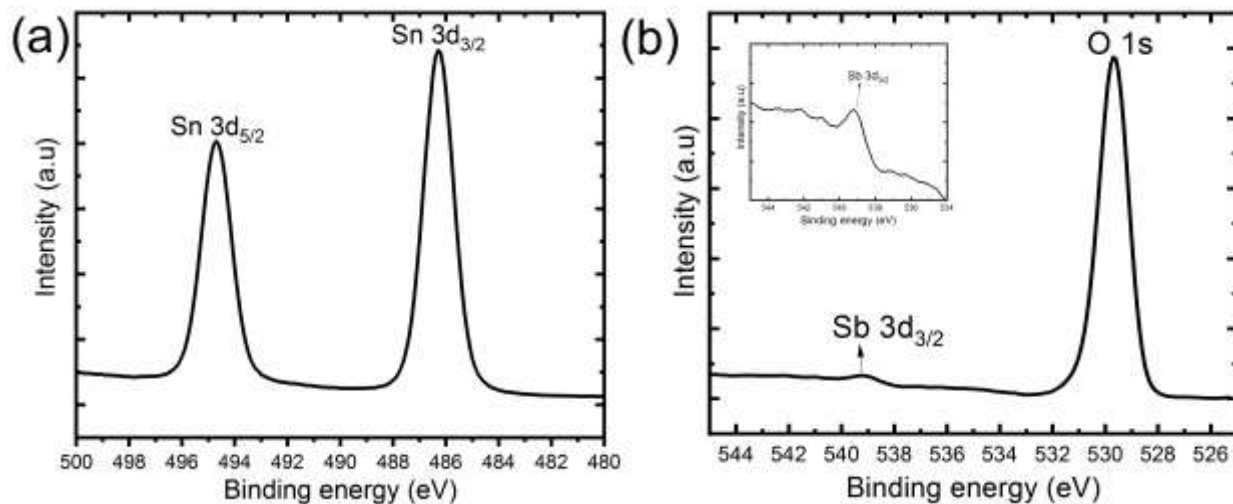


Figure S2. X-ray photoelectron spectroscopy (XPS) spectra of the Sb: SnO₂ layer. (a) The Sn3d_{3/2} and Sn3d_{5/2} peaks located at binding energies of 486.3 eV and 494.7 eV can be observed from the XPS spectra. (b) The characteristic peak of Sb 3d_{5/2} overlaps with O1s at 529.7 eV, however the Sb 3d_{3/2} peak at 539.2 eV can be observed.⁵⁻⁷ Magnified of peak Sb 3d_{3/2} is shown in insert of Figure S2b. The relatively low peak intensity is due to the low doping concentration of 1%.

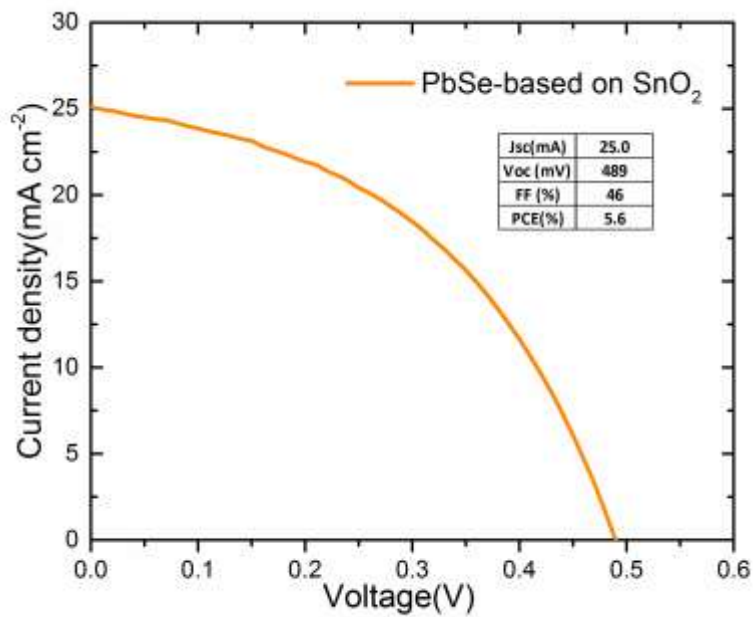


Figure S3. J-V curve of the PbSe QDSC based on SnO₂ alone (without TiO₂).

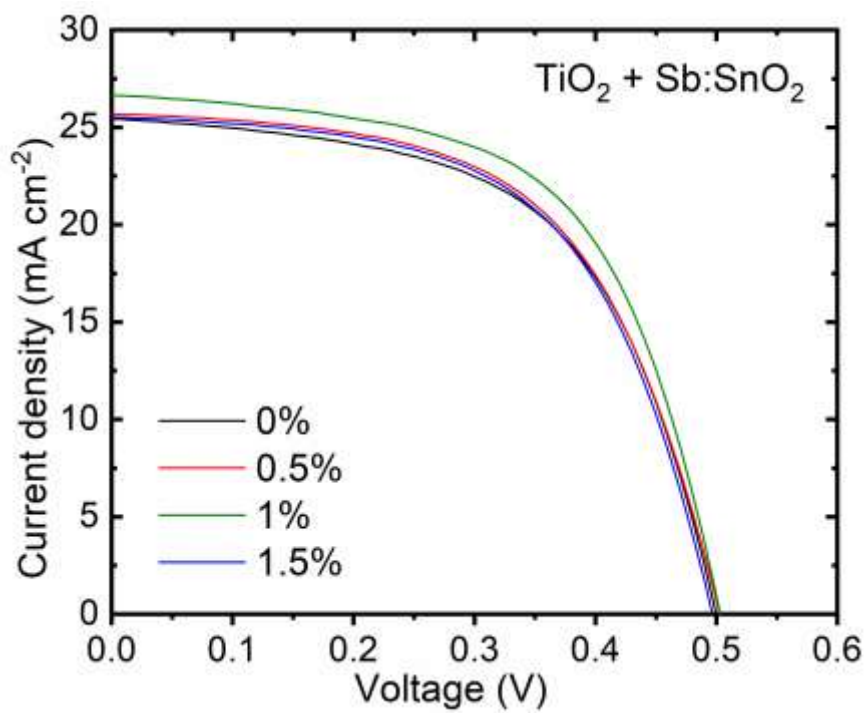


Figure S4. J-V curve of the PbSe QDSCs with SnO₂ buffer layers with different Sb³⁺ doping levels.

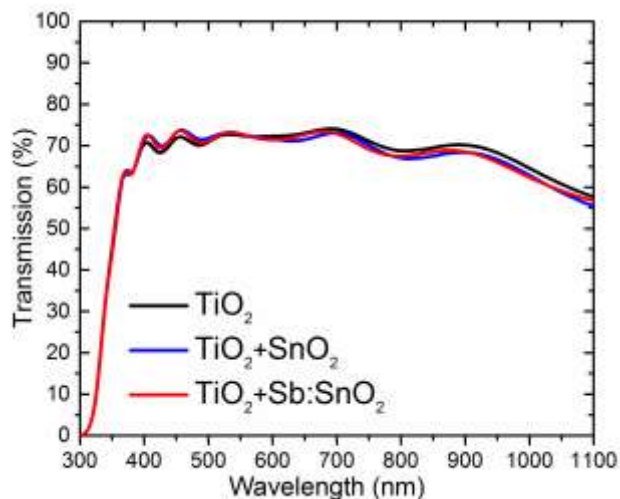


Figure S5. Transmission of TiO_2 , $\text{TiO}_2+\text{SnO}_2$ and $\text{TiO}_2+\text{Sb}:\text{SnO}_2$ (1%) deposited on pre-cleaned FTO.

Finite-Difference Time-Domain (FDTD) Simulation

The optical properties of PbSe QDSC are analyzed using a commercial finite-difference time-domain (FDTD) software package (Lumerical).⁸ A multilayer plane structure is employed in the simulation, as illustrated in Figure 3b. The thicknesses of the FTO, TiO_2 , PbSe, and gold are 800 nm, 100 nm, 300 nm and 100 nm, respectively. Since the glass on the front side is too thick (~2mm) to be included in the FDTD simulation, a semi-infinite thickness of this layer is used into which a plane wave excitation (light) is injected. The influence of the reflection occurring on the front glass/air interface is ignored. The frequency-dependent real and imaginary parts of the dielectric function of the different layers are referred from literature (glass substrate, FTO, TiO_2 , $\text{Sb}:\text{SnO}_2$ and gold)⁸⁻¹² and obtained from ellipsometry measurement (PbSe QD layer, Figure S6).

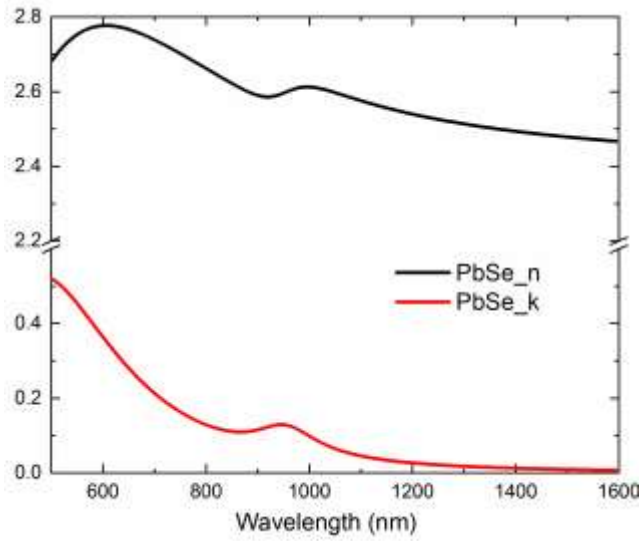


Figure S6. Optical properties of the PbSe QD absorber layer obtained by ellipsometry measurements.

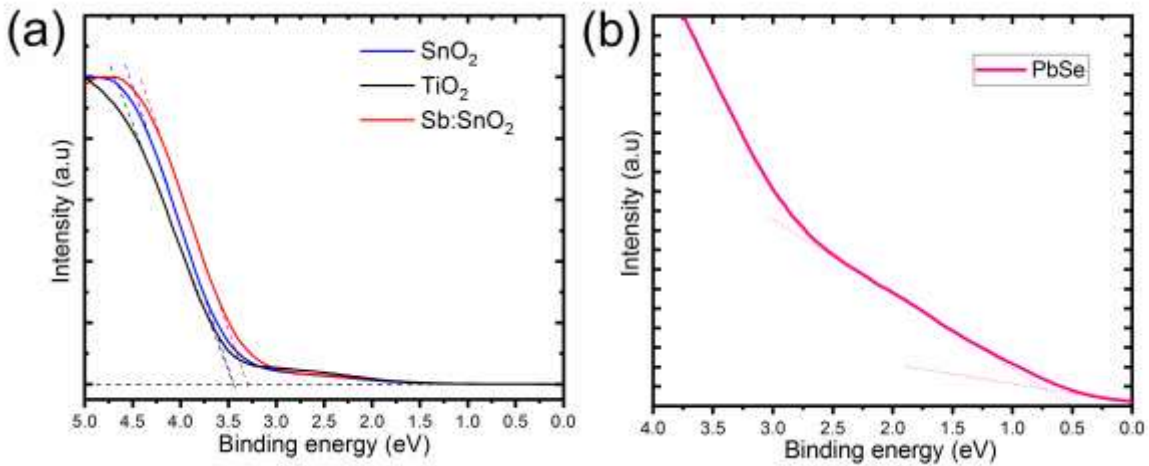


Figure S7. Ultraviolet photoelectron spectroscopy (UPS) showing the onset energy (E_{onset}) for (a) TiO_2 , SnO_2 and Sb:SnO_2 (b) PbSe layer. The samples are prepared by depositing the thin films on performed on pre-cleaned ITO.

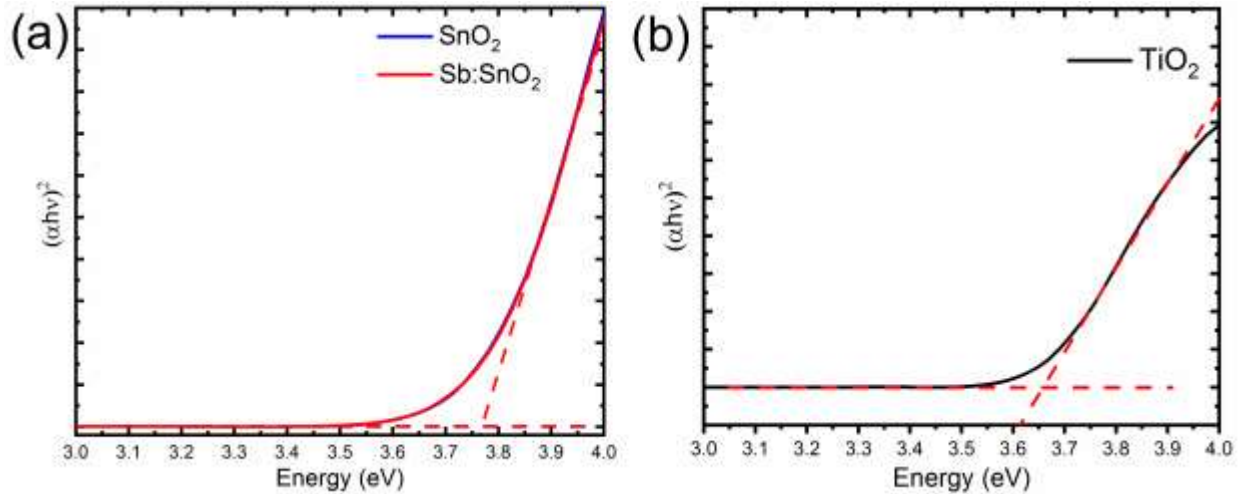


Figure S8. Tauc plot calculated from absorbance curves for (a) SnO₂ and 1% Sb:SnO₂ layer respectively. (b) Tauc plot for TiO₂.

The difference between valence band maximum (VBM) and Fermi level (E_f), which is $-E_{onset}$, can be calculated by fitting the linear part of the curve extrapolating the line to the baseline (Figure S7). The calculated values are 3.45eV, 3.45eV, 3.30eV and 0.75eV for TiO₂, SnO₂, 1% Sb:SnO₂ and PbSe, respectively. In order to determine the band alignment, E_g for TiO₂, SnO₂ and 1% Sb:SnO₂ are estimated using Tauc Plot as shown in Figure S8. The bandgap of each material can be determined by linear extrapolation of the absorption edge to the baseline, indicating the E_g for TiO₂ and SnO₂ are 3.65 eV and 3.78 eV, respectively, consistent with those reported elsewhere.¹³ For PbSe QDs the E_g is directly obtained from its absorption spectra (Figure 1a). We did not see obvious change in the E_g of the 1% Sb:SnO₂ compared to that of SnO₂. The difference between CBM and E_f for each material was estimated to be 0.20eV for TiO₂, 0.33eV for SnO₂, 0.48eV for 1%Sb:SnO₂ and 0.65eV for PbSe by using following equation.^{13, 14}

$$|E_f - E_{CBM}| = E_g + E_{onset}$$

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