

Supporting Information

Low Temperature Solution Processed Planar Heterojunction Perovskite Solar Cells with CdSe Nanocrystal as Electron Transport/Extraction Layer

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METHODS

CdSe QDs synthesis: CdSe nanocrystals were synthesized according to our previous reported procedure.¹³ In a typical synthetic process, CdO (76 mg), trioctylphosphine oxide (TOPO, 3.0 g) and oleic acid (OA, 3.0 ml) were added into the reactor and the mixture was heated to 285 °C under vigorous stirring in nitrogen atmosphere. Se (80 mg) was added into trioctylphosphine (TOP, 1.0 ml) and the mixture was sonicated until the solution became clear. The Se-TOP solution was then quickly injected into the reactor. 5 min later, the hot solution was quickly transferred into toluene (5 ml). The as-prepared CdSe QDs were washed with methanol and were centrifuged twice, then were dispersed in pyridine (15 ml) and stirred for 24 h. The resulting nanocrystals were flocculated by hexane and centrifuged.

Device fabrication: Prior to device fabrication, the ITO substrates were cleaned by sonication using detergent, deionized water, acetone, and isopropanol sequentially for every 15 min followed by 15 min ultraviolet ozone (UV-Ozone) treatment. Then a layer of CdSe nanocrystals with different thicknesses was spin-coated from solution (chlorobenzene/pyridine (9:1), 35 mg/ml) onto the cleaned ITO and baked in glove-box at

different temperatures for 10 min. For the perovskite layer, a 1:1 molar ratio of $\text{CH}_3\text{NH}_3\text{I}_3/\text{PbI}_2$ was mixed with concentration of 40 wt.%. The solution was spin-coated onto the CdSe layer at 2000 rpm and then annealed at 90°C for 30 min. After that, the spiro-OMeTAD-based hole-transport layer (80 mg spiro-OMeTAD, 28.5 μl 4-tert-butylpyridine and 17.5 μl lithium-bis(trifluoromethanesulfonyl)imide (Li-TFSI) solution (520 mg Li-TFSI in 1 ml acetonitrile) were dissolved in 1 ml chlorobenzene) was deposited by spin coating at 2500 rpm for 40 s. Subsequently, samples were loaded into a vacuum deposition chamber (background pressure $\approx 5 \times 10^{-4}$ Pa) to deposit a 100 nm thick Ag cathode with a shadow mask defining an active device area of 5.2 mm².

The electron mobilities of the CdSe and TiO₂ films were measured using the space-charge-limited current (SCLC) method. Electron-only devices were fabricated in a structure of : ITO/CdSe/poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN)/Al or FTO/TiO₂/PFN/Al. The device characteristics were extracted by modeling the dark current from 0 to 4V under forward bias using the SCLC expression

described by the Mott-Gurney law: $J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{L^3}$.

Device characterization: The J - V characteristics were measured with Keithley 2400 measurement source units with the devices maintained at room temperature in air. The photovoltaic response was measured under a calibrated solar simulator (Abet 300 W) at 100 mW cm⁻², and the light intensity was calibrated with a standard photovoltaic reference cell. The EQE spectrum was measured using a Stanford Research System Model SR830 Lock-in Amplifier unit coupled with a monochromator and a 500W xenon lamp, and a calibrated Si photodiode with known spectral response was used as a reference.

Material characterization: The UPS measurements were carried out in an integrated ultrahigh vacuum system equipped with multi-technique surface analysis system (Thermo

ESCALAB 250Xi) with the He (I) (21.2 eV) UV excitation source. A negative bias voltage of -10 V was applied to the samples in order to shift the spectra from the spectrometer threshold. The steady-state PL spectra were taken on a FluoroMax-4 HORIBA Jobin Yvon spectrofluorometer. The surface morphology of the CdSe nanocrystal film was measured by a Veeco Multimode atomic force microscopy (AFM). The morphologies of perovskite film and the cross-sectional image of the device configuration were recorded on the scanning electron microscopy (SEM, HITACHI S4800, 3 kV, 10 μ A) after being sputter-coated with Au. The morphological structures of the CdSe nanocrystal were investigated by the CM200 transmission electron microscope (TEM) at 160 KV.

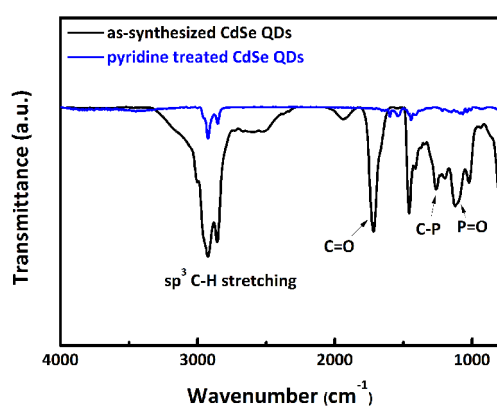


Figure S1. Fourier transform infrared spectroscopy (FTIR) spectra of the CdSe nanocrystals before and after ligand exchange with pyridine. The changes of ligands on the surface of CdSe QDs can be clearly characterized from the FTIR spectra. After ligand exchange with pyridine, the intensities of the peaks which can be attributed to C-H (at 2924, 2857 cm^{-1}), C=O (at 1718 cm^{-1}) and C-P (at 1260 cm^{-1}) stretching vibrations dramatically decreased, demonstrating the removal of surfactants of TOPO and oleic acid existed on the outer surface of the as-prepared QDs.

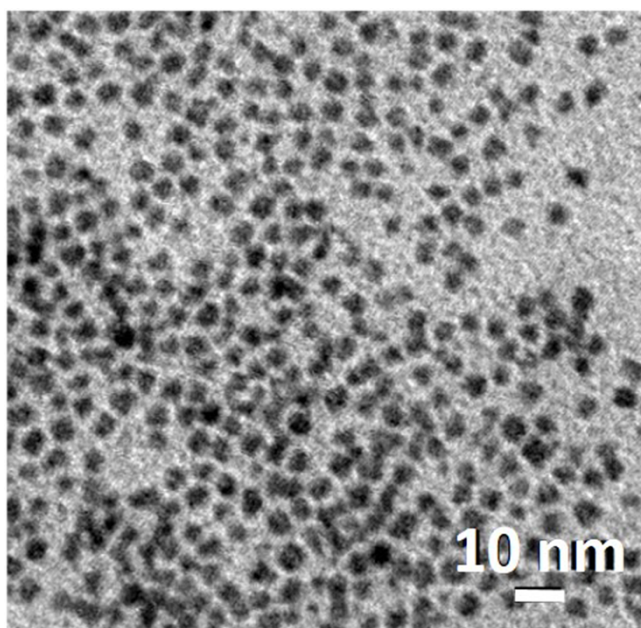


Figure S2. TEM images of the synthesized CdSe nanocrystals.

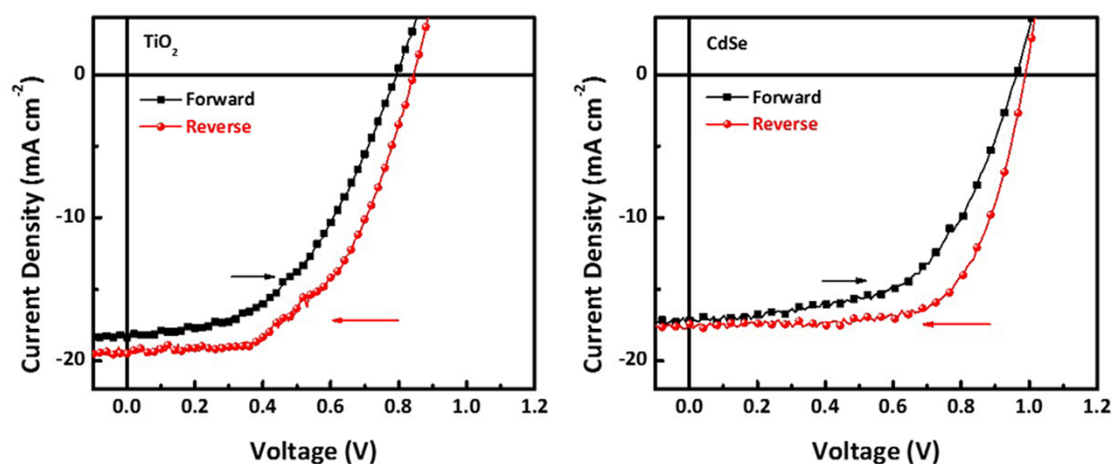


Figure S3. Influence of scanning direction on current-voltage characteristics of planar heterojunction perovskite solar cell. From forward bias to short-circuit (red) and from short-circuit to forward bias (black) current density-voltage curves are obtained under simulated AM 1.5 100 mW cm^{-2} sun light.

Figure S3 presents the J - V curves for a cell measured in reverse (from the open circuit voltage (V_{oc}) to the short circuit current (J_{sc})) and forward (i.e. from J_{sc} to V_{oc}) scan under standard air-mass 1.5 global (AM 1.5G) illumination.

To TiO₂ film based device: The J_{sc} , V_{oc} , and fill factor (FF) values obtained are 19.52 mA·cm⁻², 0.85 V, and 0.525, respectively, yielding a PCE of 8.66 % under standard AM 1.5 illumination conditions in the reverse scan. In contrast, the corresponding values from the J - V curve of the forward scan were 18.37 mA·cm⁻², 0.80 V, and 0.475, respectively, resulting in a 6.94 % efficiency.

To CdSe film based device: The J_{sc} , V_{oc} , and FF values are measured as 17.44 mA·cm⁻², 0.99 V, and 0.679, respectively, yielding a PCE of 11.68 % under standard AM 1.5 conditions in the reverse scan. In contrast, the corresponding values from the J - V curve of the forward scan are 17.19 mA·cm⁻², 0.97 V, and 0.566, respectively, and 9.40 % overall efficiency.

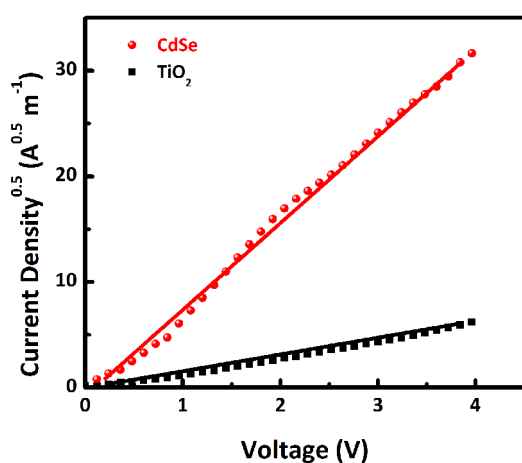


Figure S4. $J^{0.5}$ - V characteristics for SCLC fitting of electron-only devices using CdSe or TiO₂ film.