Supporting Information:

Stabilizing n-type hetero-junction for NiO_x Based Inverted Planar Perovskite Solar Cells with Efficiency of 21.6%[†]

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Experiments

Materials: N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), chlorobenzene (CB), cesium iodide (CsI) were purchased from Sigma-Aldrich. Lead (II) iodide (PbI₂) and lead (II) bromide (PbBr₂) were purchased from TCI. Methylammonium bromide (MABr) and formamidinium iodide (FAI) were purchased from GreatCell Solar Ltd. $Cd_xZn_{1-x}Se_yS_{1-y}$ gradiently alloyed QDs were obtained from Mesolight Inc. BCP and C60 were obtained from Daeyeon Chemicals Co.,Ltd. All materials above were used as received.

Device fabrication. Inverted planar perovskite solar cells (PSCs) were fabricated with following configuration: ITO/NiO_x/perovskite/ETLs/BCP/Cu. ITO glass was cleaned by sequentially washing with detergent, deionized water, acetone, and isopropanol. The substrates were dried with N₂ and cleaned by UV ozone for 15 min. NiO_x HTLs were spin coated on the clean ITO substrates according to our previous reports. The CsFAMA mixed perovskite layers were fabricated according to our previously reported one-step antisolvent method. For perovskite passivation with QDs, QDs with different concentration (2-10 mg/ml) in octane were spin-coated on perovskites with 2000 rpm for 45 s and annealed at 110 °C for 10 min. The substrates were then transferred into high vacuum thermal evaporator where the C60 (23 nm), BCP (7 nm) and Cu (120 nm) were subsequently evaporated. The active area was defined with a shadow mask (15 mm²).

Device characterization. *J-V* measurements were carried out using a Keithley 2400 sourcemeter in ambient environment at ~23 °C and ~45% RH. The devices were measured both in reverse scan (1.2 V \rightarrow -0.2 V, step 0.01 V) and forward scan (-0.2

 $V \rightarrow 1.2$ V, step 0.01 V) with 10 ms delay time. Illumination was provided by an Oriel Sol3A solar simulator with AM1.5G spectrum and light intensity of 100 mW/cm², which was calibrated by a standard KG-5 Si diode. During I-V measurement, optical aperture mask (10 mm²) was used to verify the accurate the cell area. EOE measurements for devices were conducted with an Enli-Tech (Taiwan) EQE measurement system. Top-view morphology was analyzed by TESCAN MIRA3. A FEI Helios Nanolab 600i dual beam focus ion beam/field emission gun-scanning electron microscope (FIB/FEGSEM) was used to prepare cross-section for STEM imaging and analysis. FEI Talos transmission electron microscope (TEM) with Super-X EDX was employed to acquire the STEM-EDX data with STEM-HAADF (high-angle annular dark field) mode. Depth profiling data were obtained with ToF-SIMS 5 system from ION-TOF. The X-ray diffraction patterns were obtained using a BRUKER ECO D8 series. Absorption and transmission spectra were recorded by LAMBDA 950 UV/Vis spectrophotometer (PerkinElmer). Time resolved PL spectra were measured using a spectrofluorometer (FS5, Edinburgh instruments) and 405 nm pulsed laser was used as excitation source for the measurement. XPS measurements were performed on an ESCALAB 250Xi, Thermo Fisher (by using Al Ka x-ray source) under high vacuum (10⁻⁹ mbar). The XPS spectra were calibrated by the binding energy of C 1s. Mott-Schottky and density of states characteristics were analyzed with a Zahner IM6e electrochemical station (Zahner, Germany) in ambient environment of 25 °C and 38% RH. Contact angle measurements were performed with VCA Optima (AST Products, Inc.).

DFT calculation:

The surface defect formation energies were simulated by *ab initio* calculations with projector-augmented wave (PAW) method, which is implemented in *Vienna Ab-initio Simulation Package* (VASP 5.4.4).^{1, 2} PBEsol (PBE revised for solid) functional was used to describe the exchange-correlation, which gives accurate lattice constant comparing to experiments.³ The energy cutoff of plane waves was set as 550 eV. The interstitial I (i₁) and Pb (i_{Pb}) were the most possible defect as PbI₂ was excessive in the perovskite precursor solution. Therefore, only I₁ and I_{Pb} were considered in this work. Surface models were based on a 2×2 4-layer slab with bottom and top surfaces terminated with PbI. To simplify the simulation, CdS was used to imitate QDs used in the experiments. 2-layer of CdS was placed at the top surface of the perovskite slab. Two bottom layers of the perovskite slab were fixed and other two layers with defect and CdS layers were fully relaxed. Methyl ammonium (MA) ions were arranged as anti-parallel to neighboring MA ions, which was trying to reduce the huge dipole moment of slab with MA arrange in one direction.⁴



Fig. S1. Transmission electron microscopy (TEM) image of commercially obtained $Cd_xZn_{1-x}Se_yS_{1-y}$ gradiently alloyed quantum dots (QDs).



Fig. S2. Absorbance and emission of $Cd_xZn_{1-x}Se_yS_{1-y}$ QDs. The corresponding images of the QDs dispersed in octane with and without excitation (365 nm). Strong green emission of the QDs solution is observed after excitation.



Fig. S3. Scanning electron microscopy (SEM) topographic images of perovskite films and QDs coated perovskites.



Fig. S4. High resolution XPS spectra of Cd and Se core level peaks for the pure QDs and perovskite/QDs samples, respectively.



Fig. S5. Optimized structures of a perovskite unit cell with excess iodine (a) and lead (b) at the perovskite surface.



Fig. S6. TOF-SIMS profiles of the inverted planar perovskite solar cells with QDs passivation.



Fig. S7. I-V curves (reverse and forward scans) of the inverted planar PSCs without QDs passivation.



Fig. S8. Water contact angle measurements of the perovskite and QDs passivated perovskite films.



Fig. S9 Topographic AFM images of the perovskite/C60/Cu and perovskite/QDs/C60/Cu before and after aging.

References:

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