Supplementary Information (ESI) for

Size-controlled CdSe quantum dots to boost light harvesting and stability in perovskite photovoltaic cells

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■ Detail for experimental details

Quantum dot sizes

The expected size of quantum dots (QDs) have been determined using the following equation of

$$D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + 41.57$$

where D (nm) is the expected size of quantum dots and λ (nm) is the wavelength of the first excitonic absorption peak of quantum dots. By utilizing the absorption peak information of CdSe quantum dots, we determined the expected size of QDs. To calculate the optical bandgap of a semiconductor material, we have used Tauc plot equation of

$$(h\upsilon\, F(R))^{\frac{1}{n}} = A(h\upsilon - E_g)$$

where $h\upsilon$ (eV) is the energy of incoming light upon a material, $F(R)$ is the absorption coefficient, n is the power factor for the transition mode, which reflect the nature of a material. The possible values of 1/2, 3/2, 2, and 3 correspond to the values for direct allowed, direct forbidden, indirect allowed, and indirect forbidden transition modes, respectively. A is the constant and E_g is the band gap energy. We have summarized all the information regarding optical properties of CdSe quantum dots in regard to the size as mentioned at **Table S1**. The TCSPC measurements were also conducted to determine the PL decay behaviors for designated samples, which was calculated using the tri-exponential function of

$$f(t) = \sum_i A_i\, exp(-t/\tau_i) + B$$

where A_i is the decay amplitude, τ_i is the decay lifetime, B is the constant and i is the exponential constant value used for decay fitting where we used 3 in the tri-exponential fitting. Also, the average lifetime was obtained using the following equation of

$$\langle\tau\rangle = \frac{f_1\tau_1^2 + f_2\tau_2^2 + f_3\tau_3^2}{f_1\tau_1 + f_2\tau_2 + f_3\tau_3}$$

where $\langle\tau\rangle$ is the average life time, f is the relative amplitude and τ is the decay life time. The average lifetime were measured according to the specific PL peak observation. The perovskite has the PL peak location at 770 nm. The PL peak for CdSe QDs in 2nm size is observed at 525 nm and that for CdSe QDs in 4nm size is determined at 610 nm.

■ Synthesis and characterization details

Synthesis of QDs

All the experiments were carefully conducted under the fume hood to avoid any leakage of gas and liquid due to the toxicity. Three-neck flasks were prepared accordingly with the reflux instrument and the Schlenk line system was used to manage the inert atmosphere inside the reaction vessel. Initially selenium solution was prepared using a three-neck flask under inert atmosphere. 0.756 gram of Selenium powders was measured and dissolved into 6.25 ml of TOP reagent inside a three-neck flask. Reflux instrument, thermocouple, and rubber septa were placed appropriately on each neck not to hinder the syringe injection as well as the withdrawal process. Argon inert atmosphere was also introduced into the system through the Schlenk line prior to the annealing treatment of selenium solution. The flask was heated up using the heating mantle to 250°C while being stirred by the flea stir bar. The solution was maintained at 250˚C for around 90 minutes and then cooled down to let the solution achieved the stable condition as selenium precursor stock solution at room temperature. In addition, Cadmium acetate dehydrate, Trioctylphosphine oxide (TOPO) and Hexadecylamine (HDA) powder were weighed for 0.0534 g, 4 g, and 2 g, respectively, inside a three-neck flask. Reflux instrument, thermocouple and rubber septa were set down in such a way that anhydrous process was employed. The chemical was degassed under the vacuum condition for about 30 minutes and filled with argon. The vessel was heated up to 300˚C and kept at a given temperature for 30 minutes until solution became clear transparent. Subsequently, 5ml of selenium precursor was injected abruptly at once into the vessel through the rubber neck to assure the growth of CdSe QDs. The color change was observed during this period and the results showed the QDs ranging from the small size (yellow color) into the bigger size (red color). Aliquots were then taken after 2 and 20 minutes of the growing time into 10 ml vial with methanol to stop the growth reaction. The solutions were kept for several hours and precipitated by centrifugation with the 10.000 rpms for 15 minutes, which was on a size-selective precipitation method. Finally, the samples were re-dispersed into toluene solvent on the concentration of 19.2 mg/ml.

Fabrication of PSCs with QDs

Unless being stated otherwise, all the processes for deposition were conducted inside the Ar filled glovebox with the moisture level of 10-15 ppm. FTO-etched glasses were cleaned sequentially with DI water, ethanol and acetone for about 15 minutes in the ultrasonic bath.

Substrates were treated with UV-ozone plasma during 20 minutes. The TiO_2 blocking layer was deposited using the spin-coating instrument at a velocity of 2000 rpms for 60 seconds using 0.15 M titanium diisopropoxide bis(acetylacetonate) in 1-butanol solution that was heated afterward at 125°C for 5 minutes. These steps were repeated twice and followed up by another deposition using a higher concentration of the same solution, 0.3 M, with the same deposition scheme and baked at 500°C for 90 minutes. Next, the TiO_2 paste in ethanol (2:7 weight ratio) solution was spin-coated onto the substrate at 2000 rpms for 60 seconds and annealed at 125°C for 5 minutes. Subsequently, the substrates were annealed at 500°C for 90 minutes and then followed by treatment in 40 mM $TiCl_4$ aqueous solution at 70°C for 6 minutes. Finally, the substrates were washed right after with DI water, ethanol and blow-dried with argon and annealed at 500°C for 90 minutes. A two-step method for the sequential deposition was used for deposition of the perovskite layer. PbI_2 (DMSO) solution was deposited on the top of the cell by spin-coating at 6500 rpms for 90 seconds and the substrates were annealed at 70°C for 10 minutes. MAI solution was spin-coated on the top of PbI_2 film at the speed of 2000 rpms for 60 seconds and then foregoing by the wetting process for 60 seconds. The films were annealed at 100°C for 15 minutes reaching a brown-like color. The solution to prepare CdSe QDs was drop-wise deposited upon the perovskite film and spin-coated at 6500 rpms for 90 seconds. The wetting time of 5-10 seconds was necessary to ensure a decent number of QDs on the perovskite film. Meanwhile, it is notable that the amount of QDs could depend on the dropping amount and concentration of solution. The substrate was annealed at 70°C for 1 minute. The Spiro-MeOTAD solution to fabricate a hole-transport material was deposited by spin-coating at 4000 rpms for 30 seconds. Then, the solution was prepared by dissolving 72.3 mg of Spiro-MeOTAD powders into a mixed solution of 28.8 μl 4-tert-butyl pyridine, 17.7 μl of stock solution of 52 mg of Li-TFSI in 100 μl acetonitrile, and 1 ml of chlorobenzene solvent. Finally, the 60 nm thick gold layer was deposited using the thermal evaporator for the back electrode of cell with the deposition rate of 1-1.5 Å/s.

Characterization

Photoluminescen (PL) and Absorption spectra: PL spectra have been obtained using the fluorometer spectroscopy (QM-400, HORIBA) with the 405 nm laser diode excitation source. UV-Vis absorption spectroscopy measurements were carried out using JASCO spectrometer, model V-570, for both QD solutions and perovskite or perovskite/QDs thin films.

Scanning electron microscopy (SEM): In the SEM (JEOL, JSM-7600F) measurement, we used a mild electron beam, 0.5 KeV acceleration voltages in the gentle beam mode to avoid structural damage. We observed the morphology of the photocatalysts.

Transmission electron microscopy (TEM): The TEM images were collected by JEOL (JEM-ARM200F) Cs-corrected scanning transmission electron microscopy.

Photovoltaic characterization: Current density-voltage (J-V) were measured under simulated AM 1.5G illumination (100 mW cm^{-2}) with a scan rate of 0.02 mV/s at both reverse and forward scans. The aperture mask (0.105 cm^2) was applied on the top of the cells during the measurments. The quantum efficiency (QE) spectra were recorded using a spectrum measurement system (PEC-S2026, Bunkoukeiki Co. Ltd.), composed of a Xenon lamp light source (150 W), a monochromator (600-grooves mm^{-1} grating, 0.1 mm slit, with ± 2 nm or less wavelength accuracy).

Electrochemical impedance spectroscopy (EIS): All the measurements were performed under the open circuit condition and the 100 mW/cm^2 illumination in the frequency range of 1-10^6 Hz with the Ivium Compactstat potentiostat and the modulated voltage of 10 mV.

X-ray photoelectron spectroscopy (XPS): XPS spectra were obtained using a K-alpha spectrometer from Thermo VG Scientific, which is equipped with a 350 W Al anode X-ray source along with a multi-anode, a pulse counting, and a hemispherical analyzer. All the spectra were calibrated reffering to the C 1s peak (C-C bond) at 285.0 eV. The valence band maximum positions were estimated by extrapolation of the leading edge for valence band spectra.

Time-correlated single photon counting (TCSPC) spectrometer: The time-correlated florescence decay spectra at the emission peak of a 520 nm laser were collected by the Edinburgh EPLED.
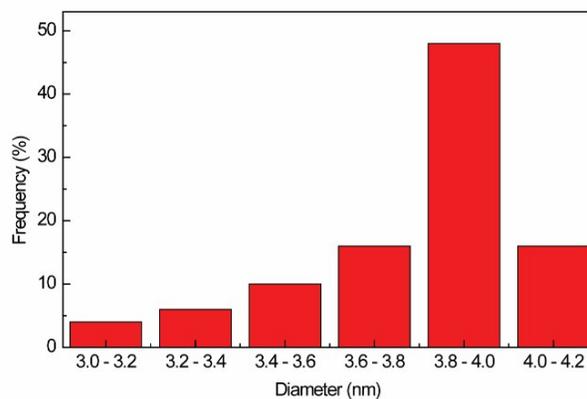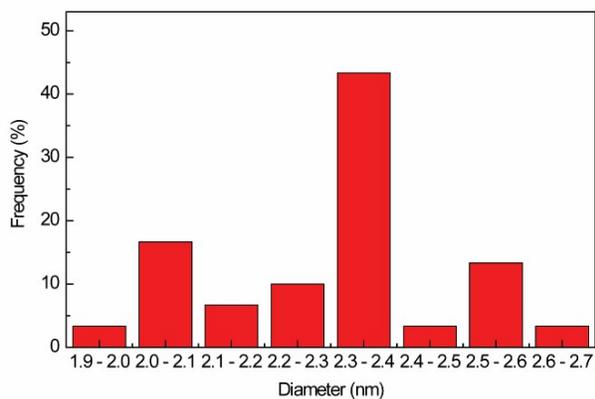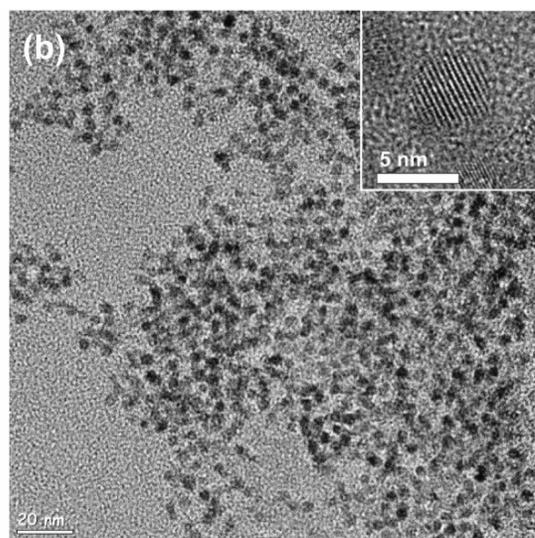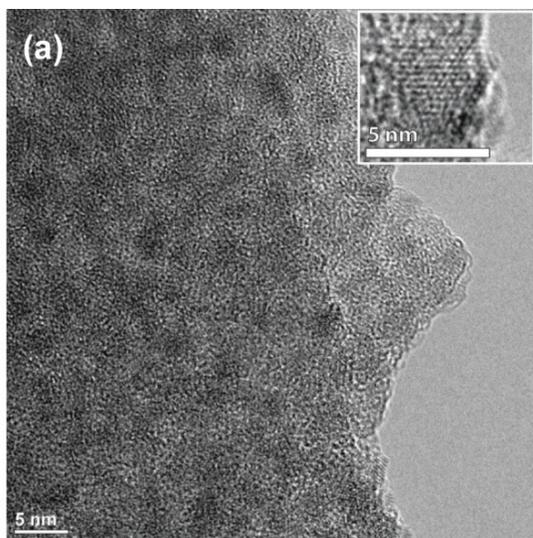
Figure S1. TEM and HRTEM (inset) images of CdSe quantum dots (QDs) on the different growth times of (a) 2 min, (b) 20 min. The histogram for size distribution of corresponding QDs was determined using the direct observation of monodisperse QDs by the TEM analysis.
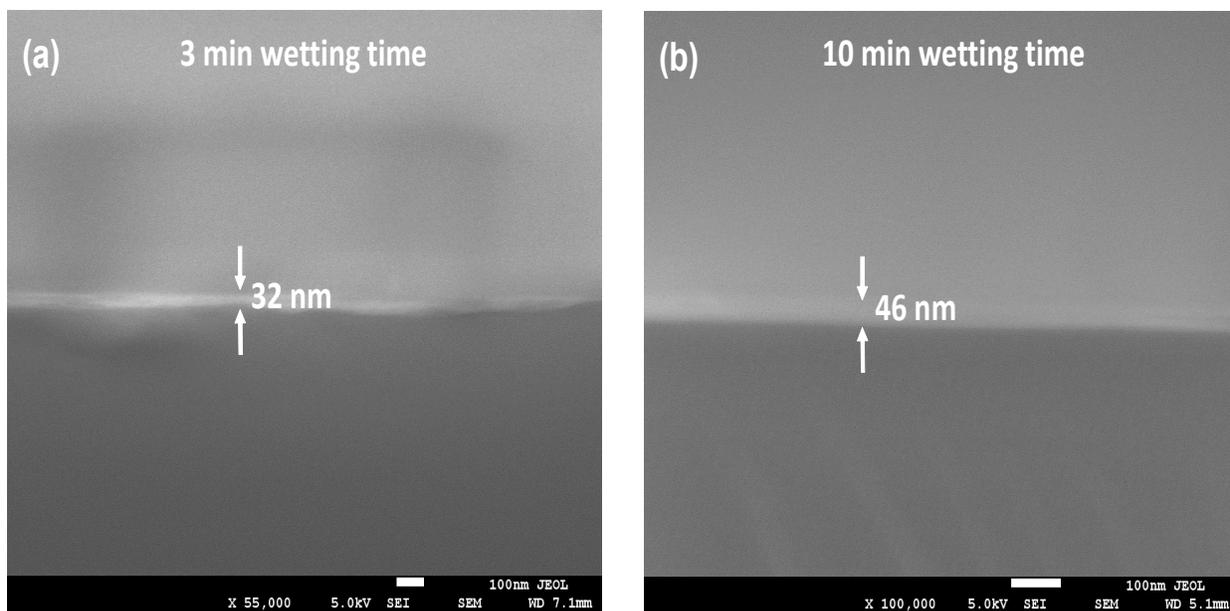
Figure S2. SEM images of CdSe QD layers, where the films with (a) 32 nm and (b) 46 nm thicknesses have been prepared and the scale bar is on the 100 nm size.
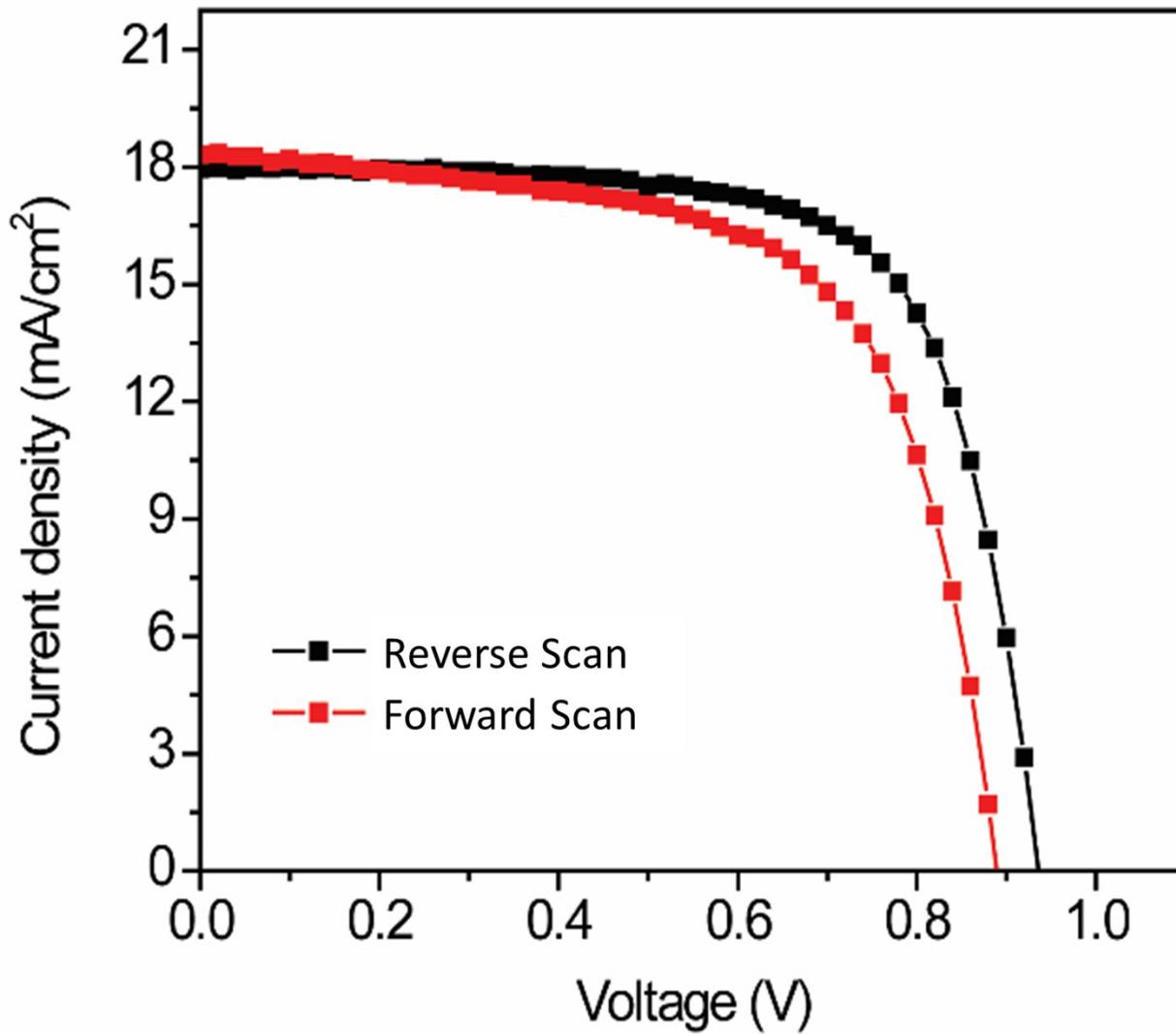
Figure S3. Hysteresis behaviors of PSCs with QDs, where the IV curves were obtained as the function of reverse and forward scan directions.
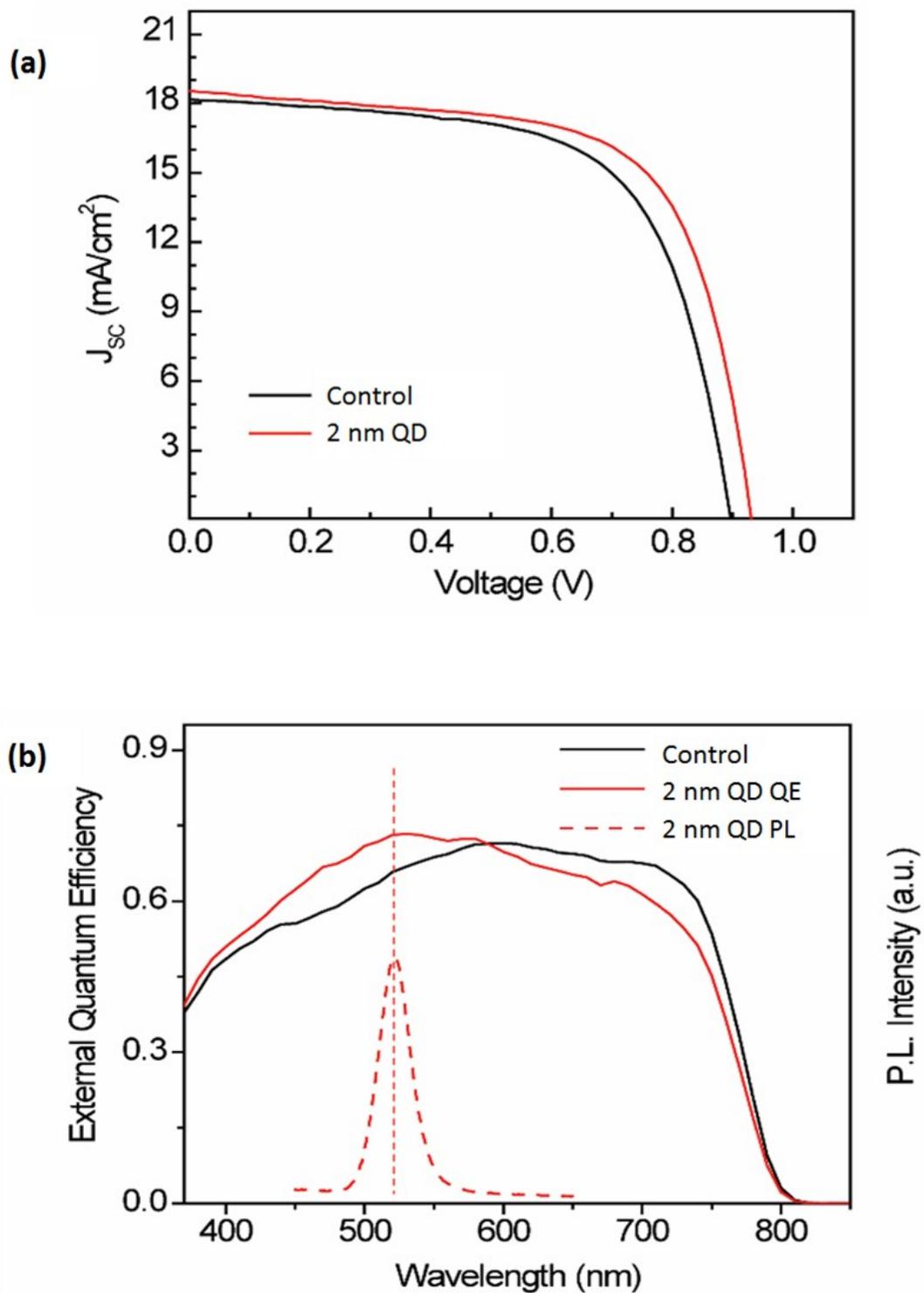
Figure S4. Performance of PSCs with small QDs fabricated in the ambient atmosphere. (a) IV curves of PSC with QDs or the control PSC without QDs, denoted in red and black lines, respectively. (b) Incident photon-to-current efficiency (IPCE) for the control PSC and the PSC with small QDs along with their PL peak.
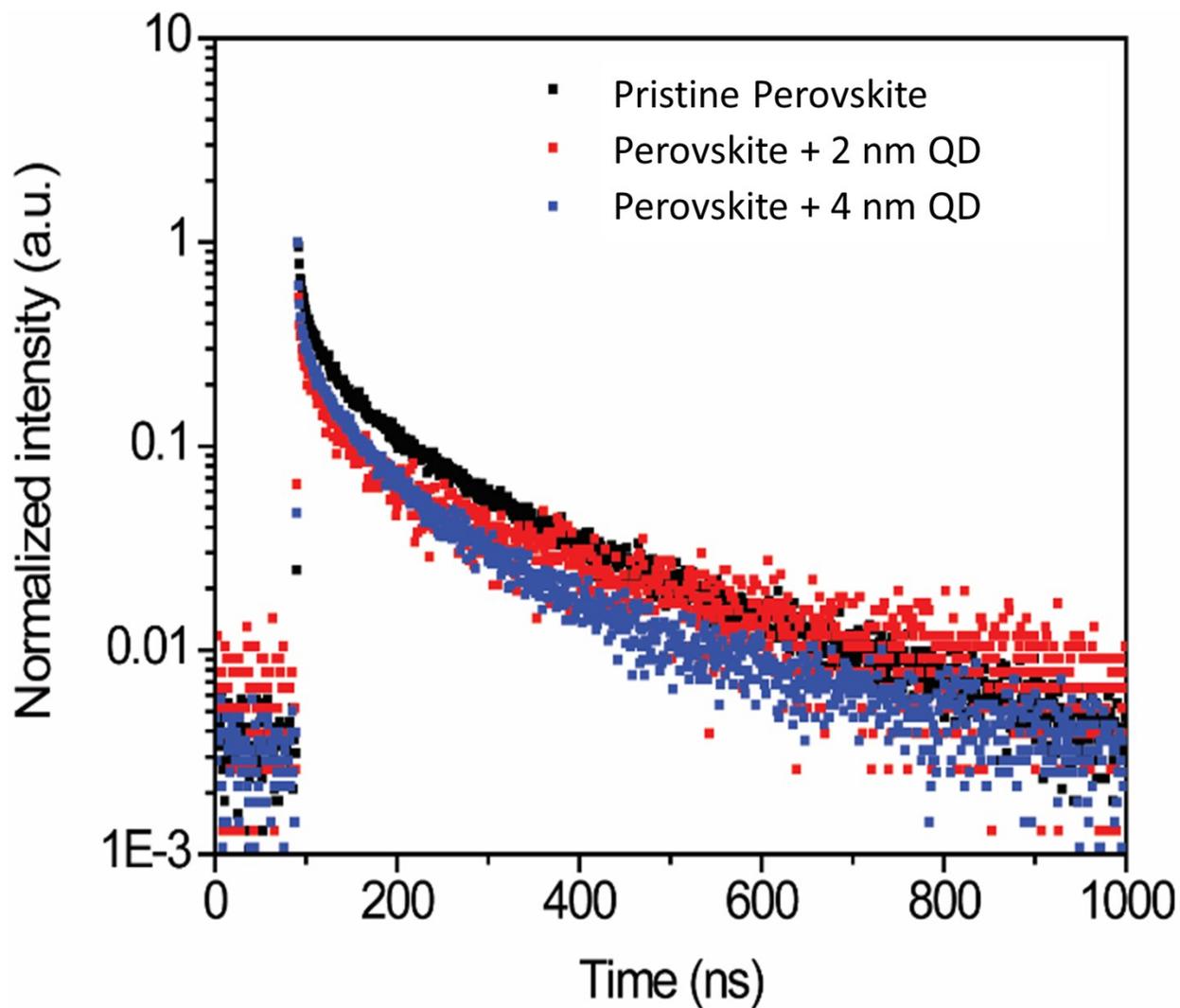
Figure S5. Measurement of the decay for the PL peak for the perovskite at 770 nm, where the black square depicts the perovskite without QDs as "Pristine perovskite", the red-square shows the perovskite with QDs in 2 nm as "Perovskite + 2nm QD", and the blue square represents the perovskite with QDs in 4 nm as "Perovskite + 4nm QD".
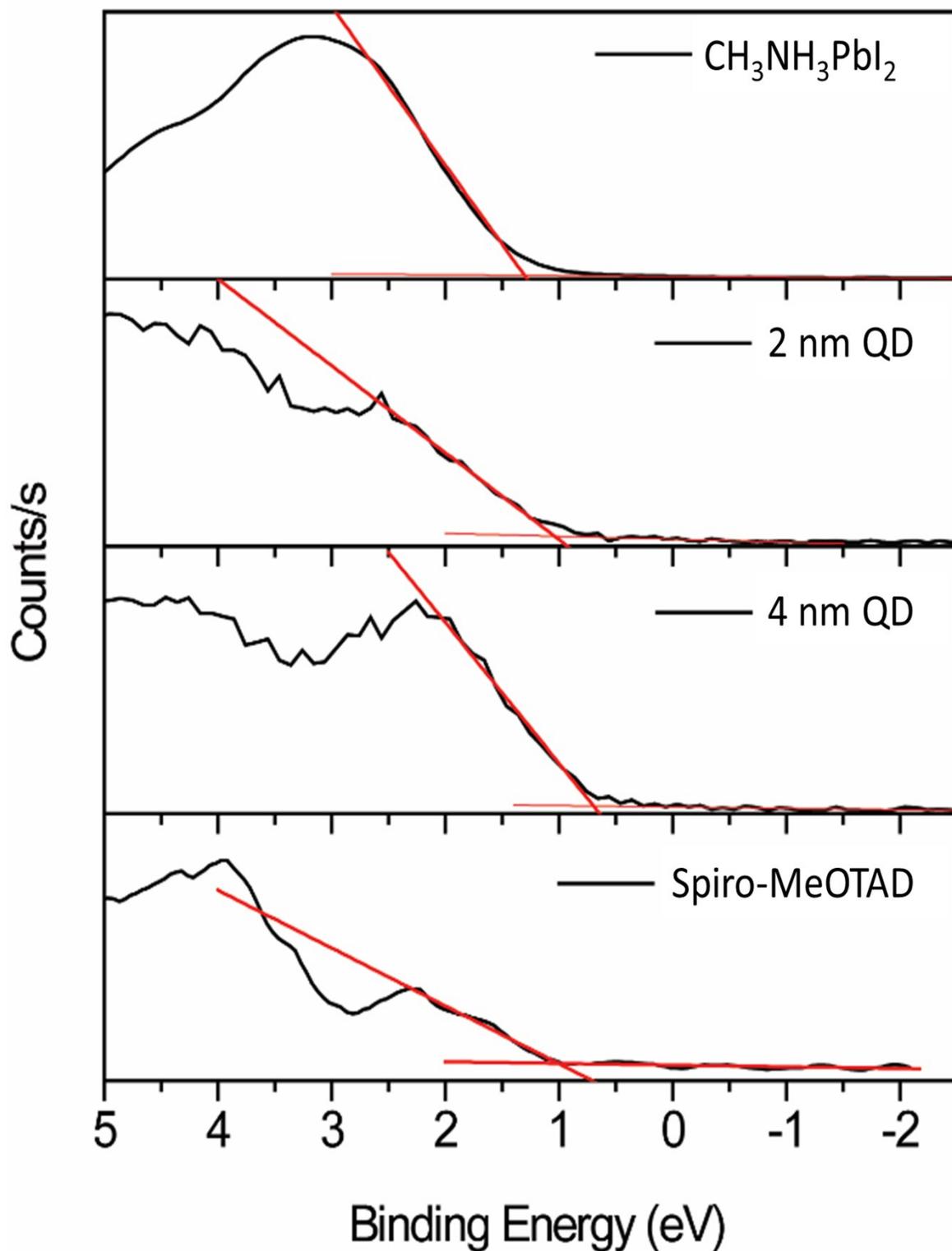
Figure S6. XPS spectra for the valence band of each QD and Spiro-MeOTAD in the PSC with QDs, where the measured valence edge is determined relative to the Fermi energy and the calibration of XPS spectra was made with respect to the C 1s emission peak at 285.0 eV.
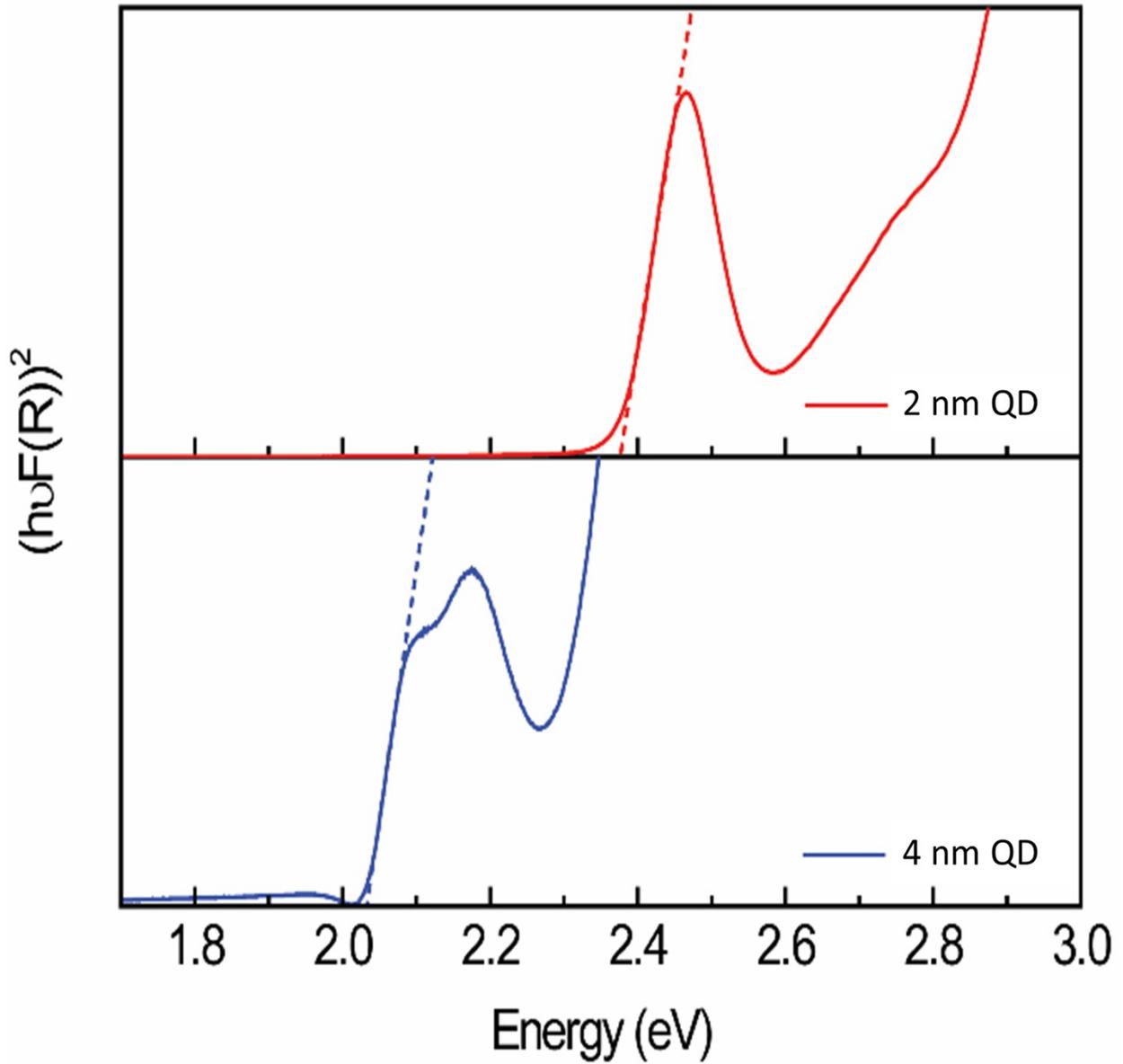
Figure S7. Tauc plots to determine the band gap of CdSe QDs grown during different times. The growth times of 2 min and 20 min are determined to result in formation of QDs in 2 nm (red line) and 4 nm (blue line), respectively.

Table S1. Calculated sizes and the band gaps of CdSe QDs determined through the optical spectroscopy analysis.

Growth Time (min)	Absorption Peak (nm)	Emission Peak (nm)	Expected Size (nm)	Band gap (eV)
2	502	515	2.4	2.38
20	571	610	3.6	2.04

Table S2. Photovoltaic characteristics of the best performing perovskite cells fabricated under the controlled atmosphere.

Device	V_{OC}(V)	J_{SC} (mA/cm^2)	FF	PCE (%)
Control	0.99	18.6	0.59	10.9
Perovskite/ QD (2 nm)	1.01	19.8	0.60	12.0
Perovskite/ QD (4 nm)	1.01	19.1	0.61	11.7
Perovskite/ QD (Hybrid)	1.03	20.1	0.60	12.5