Electronic Supplementary Information (ESI)

High Photocurrent from PbSe Nanocrystals based Solar Cell with Thin Active Layer

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1. Specific Temperature and Times for Individual Particle Sizes

Table S1. Growth temperature and growth time for achieving the desired PbSe NC sizes.

NC diameter (nm)	Growth time (s)	Growth temperature (°C)
1.74	320	62.5
2.34	465	72.9
2.63	180	73.6
2.88	210	73.6
3.26	370	73.6
3.69	150	113.4

2. Layer-by-layer PbSe NC Film Deposition

All process occurred in a nitrogen-filled glovebox. PbSe NCs dispersed in octane with a concentration of 10~12 mg/ml (OD=8) was used for the device fabrication. The layer-by-layer deposition technique was carried on a spincoater according to the following recipe:

1) Spin-cast the PbSe NC solution at 1000 rpm for 40 seconds.
2) Soak the deposited PbSe NC film with 0.1 M EDT solution in anhydrous anetonitrile for 1 minute and then spin.
3) Wash the EDT treated PbSe NC film with pure anetonitrile and then spin.
4) Wash the film with octane and then spin.
5) Repeat steps 1-4 until desired thickness is reached.
6) Finish the PbSe NC layer fabrication by annealing the film at 90°C for 30 minutes.

3. High-resolution TEM Micrographs of PbSe NCs

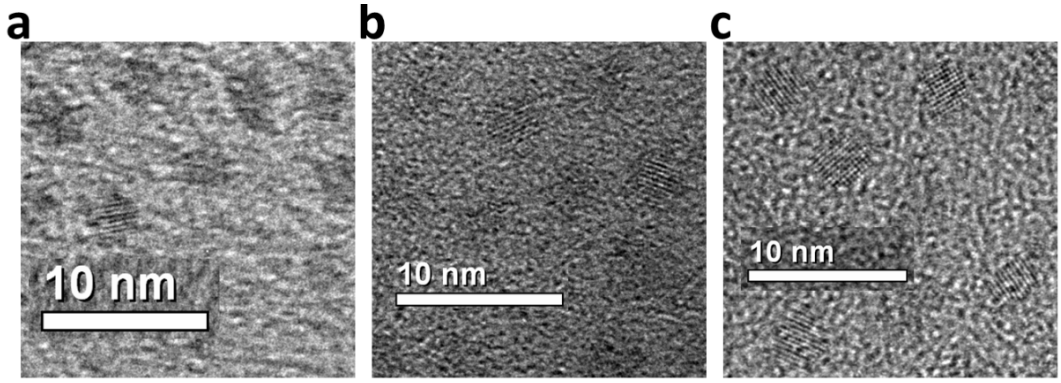


Figure S1. High-resolution TEM micrographs of PbSe NCs. (a), (b) and (c) are images of QD sizes of 2.9 nm, 3.3 nm and 3.7 nm, respectively.

4. TEM Micrographs of ZnO NCs

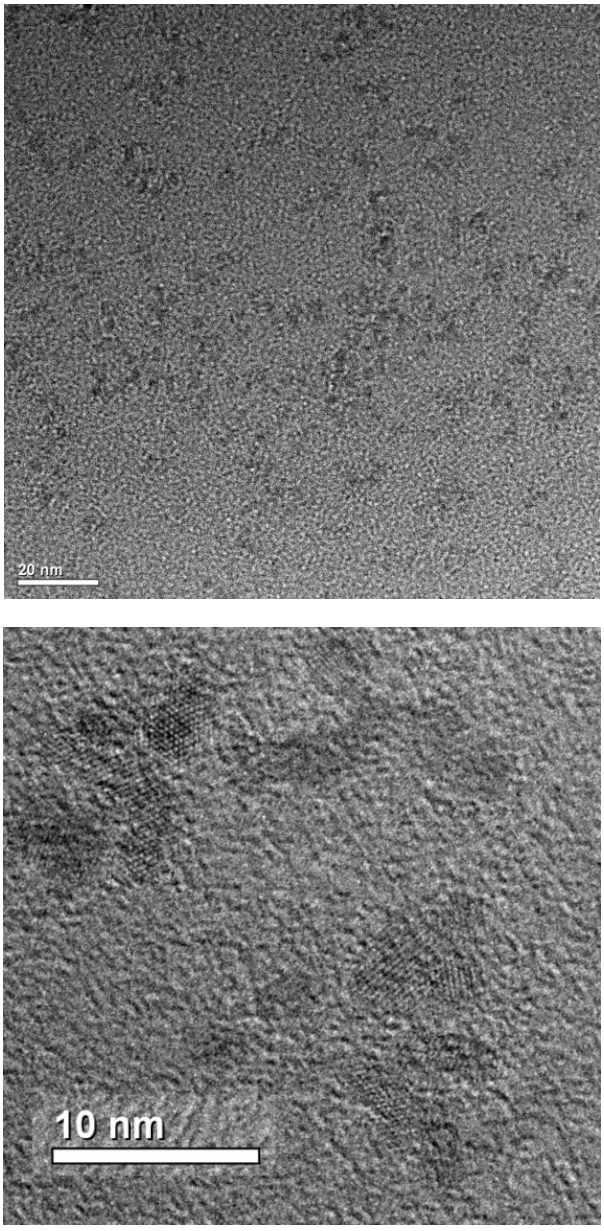


Figure S2. TEM images of ZnO NCs.

5. Comparison of PbSe NC Films with 50 and 100 nm Thicknesses

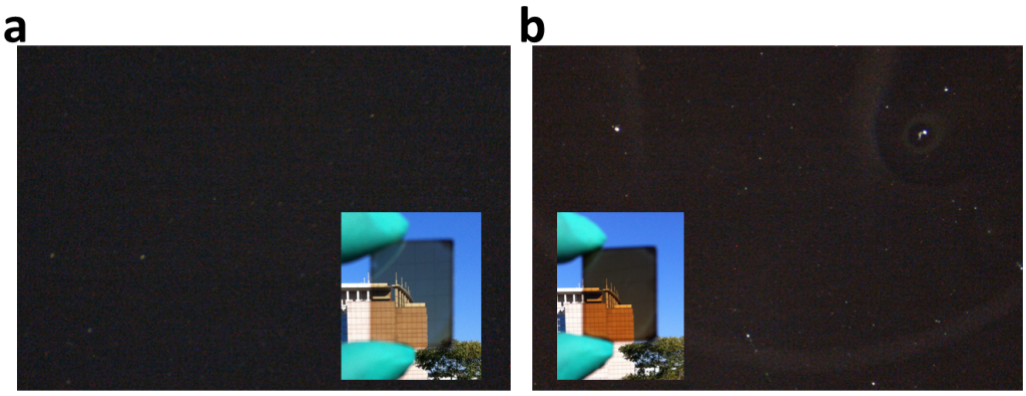


Figure S3. Electron microscope images of PbSe NC films with different thicknesses. The left (a) represents a 50 nm thickness film, while the right (b) represents a 100 nm thickness film. When the PbSe film thickness increases, accumulation of defects in each spin-coating step or aggregation of the NCs may happen, and each of them will destroy the smooth surface of the NC films. As shown in the electron microscope image, the 50 nm NC film was smooth, while for the 100 nm one, a few defect points were found. Insets show outdoor photos of the semi-transparent films for each thickness.

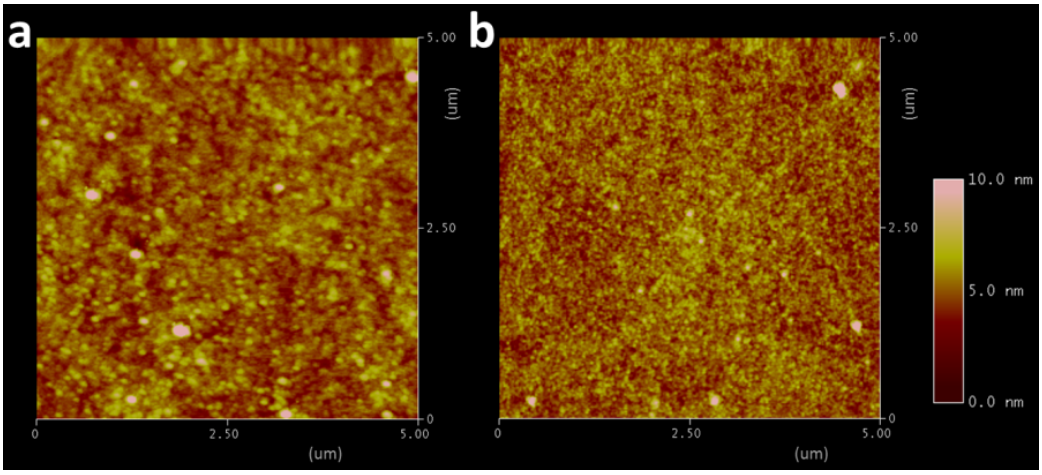


Figure S4. (a) Atomic force microscopy (AFM) image of 50 nm PbSe NC film. (b) AFM image of 100 nm PbSe film. The surface root-mean-square (RMS) roughness of the 50 nm PbSe layer was ~0.88 nm, and the thicker one was ~0.87 nm. Although similar RMS roughness was obtained from these two different films, the thinner one

showed larger aggregations, which might produce better contact with ZnO layer, and induced better charge-carrier separation.

6. Optical Constants

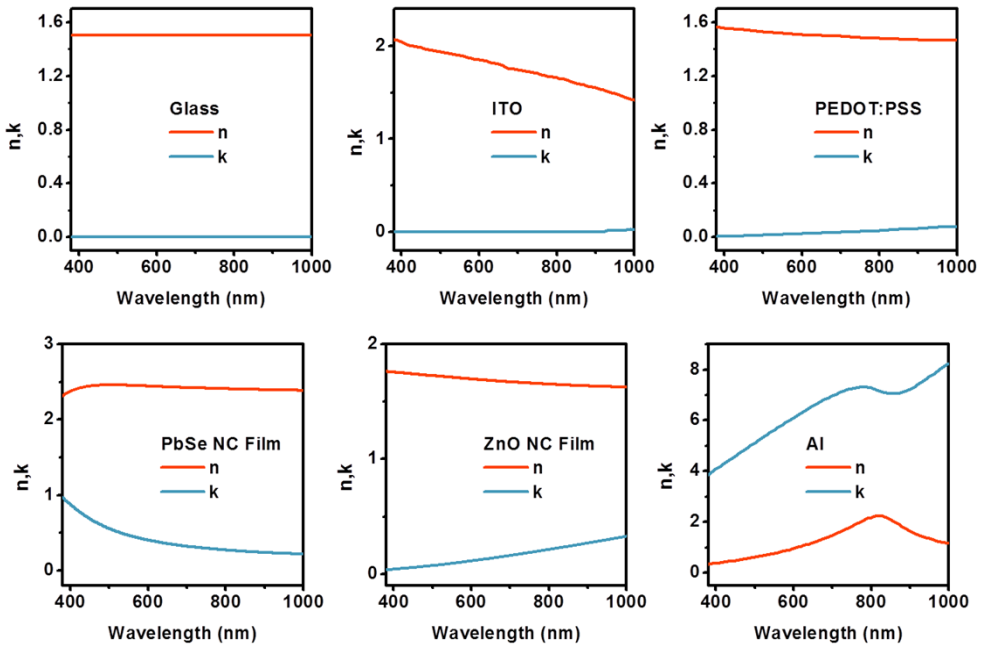


Figure S5. Optical constants used for each material in the optical admittance analysis.

7. Calculated Absorption Results of The Optical Admittance Analysis

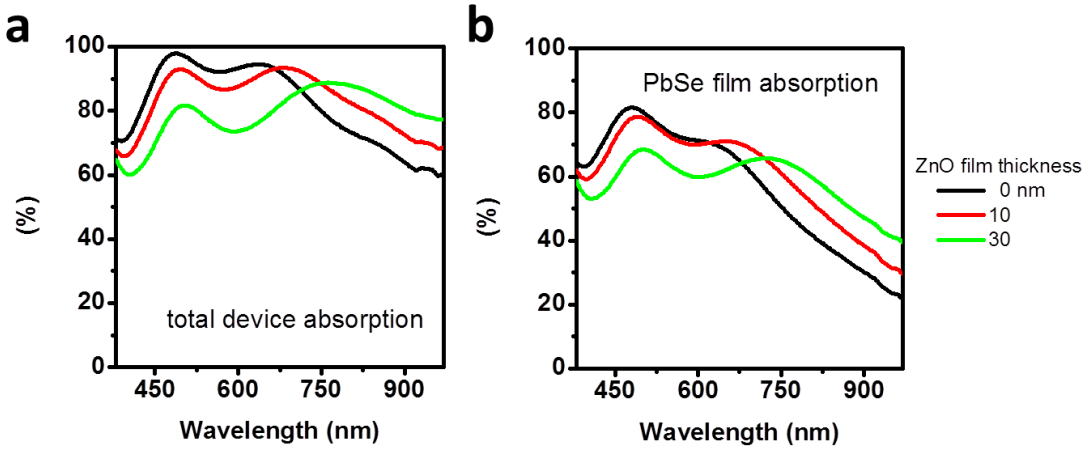


Figure S6. (a) Absorption of the fabricated solar cells with a PbSe layer of 60 nm with different ZnO film thickness. (b) PbSe layer absorption inside the fabricated devices with ZnO layer thickness adjustment.

8. Calculated Optical Electric Field for Light of Different Wavelengths

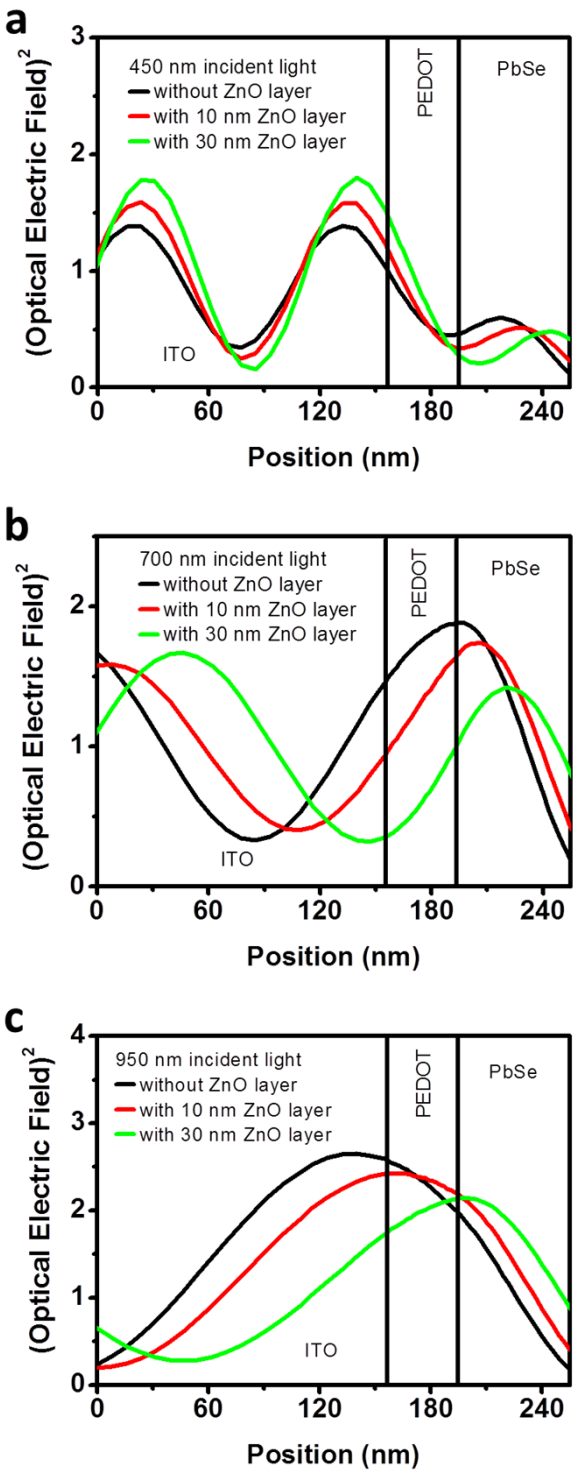


Figure S7. The spatial distribution of the square of the optical electric field for devices prepared with ZnO optical spacer of 0 to 30 nm.

9. J-V Curves of Devices with Variable PbSe Film Thickness

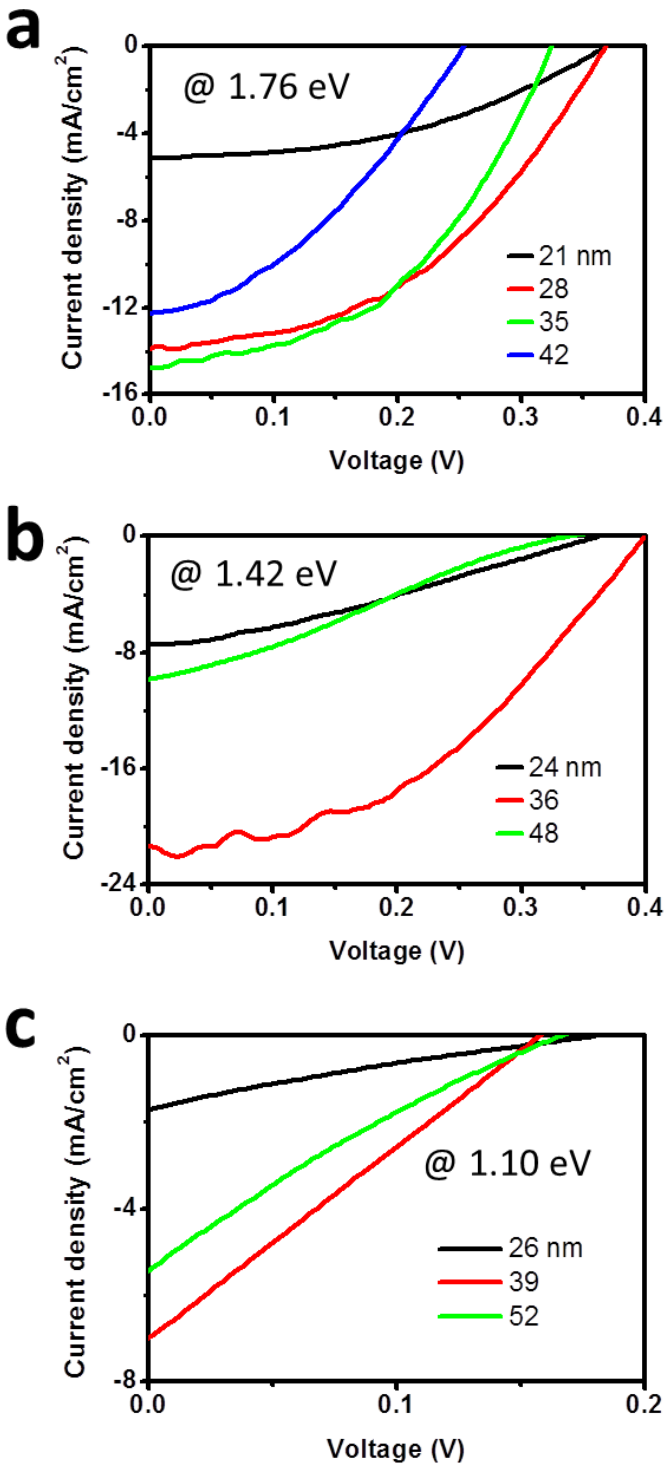


Figure S8. J-V curves of devices with different PbSe layer thicknesses of different NC sizes.

10. Device Performance Improved from Air Exposure

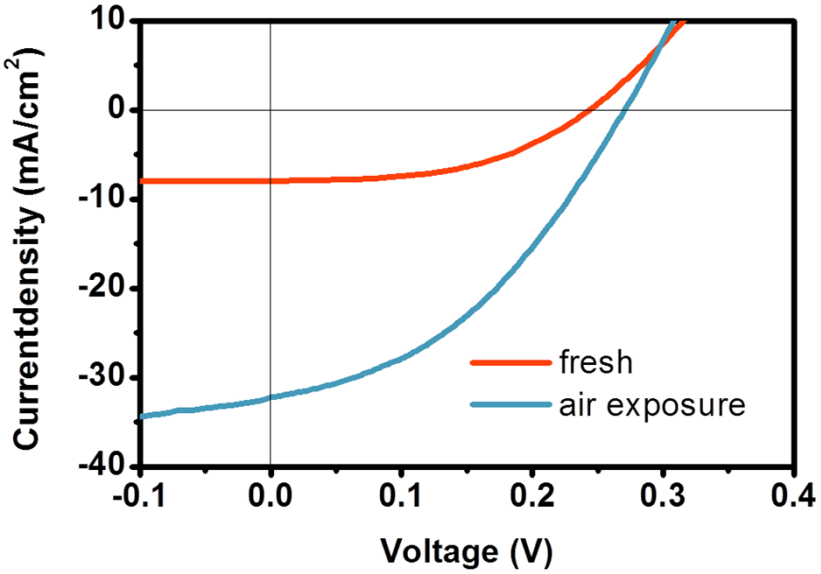


Figure S9. Solar cell performance characterizes in nitrogen and air. The device employed NCs of band gap of 1.35 eV.

11. Effect of Absence of PEDOT:PSS layer on Device Performance

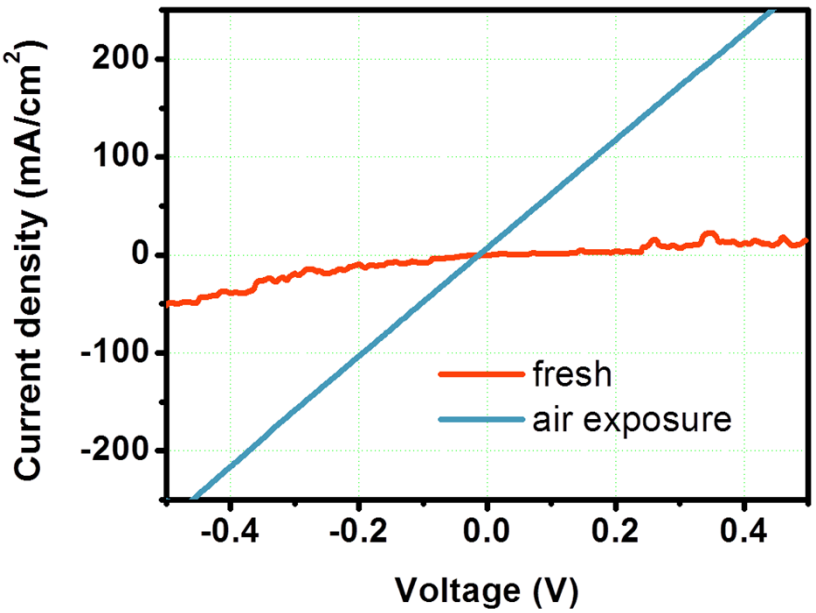


Figure S10. Curves tested in dark of a device without the PEDOT:PSS layer. The PbSe NC film becomes more conductive in less than 5 min air exposure. NCs of band gap of 1.35 eV were employed.

12. Dead Zone and Exciton Diffusion Region Changes from Air Exposure

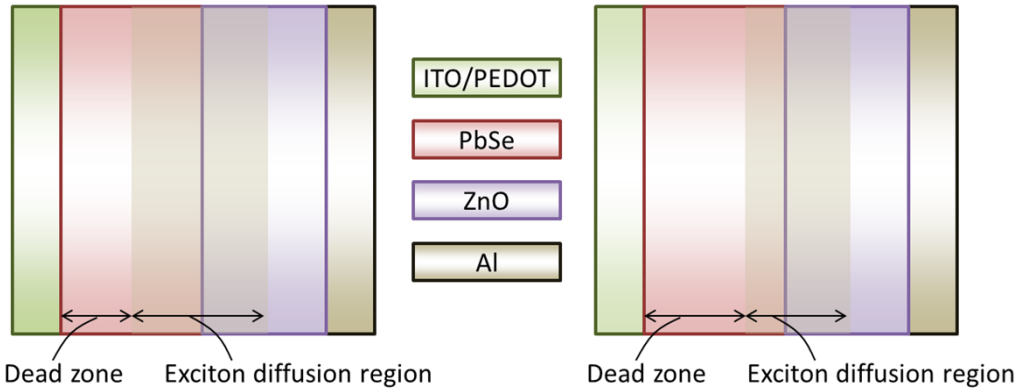
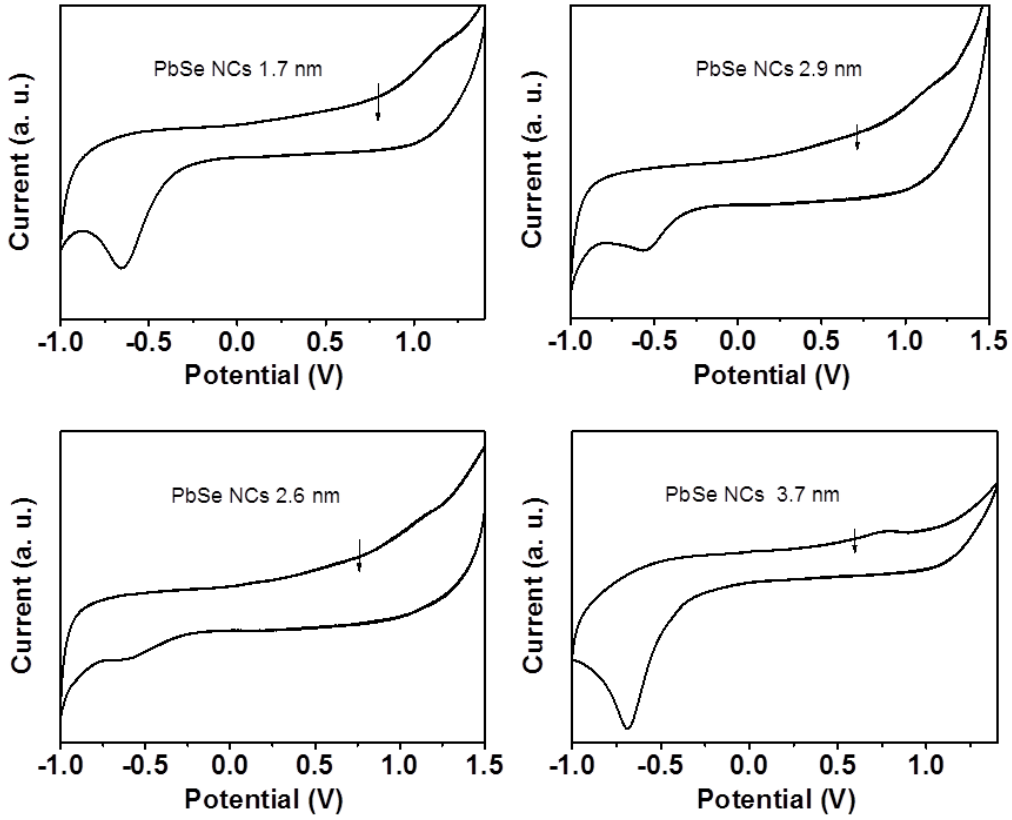


Figure S11. Schematic diagram of the dead zone and exciton diffusion region changes from air exposure. The right one shows the increase of the dead zone and decrease of the exciton diffusion region after the air exposure.

13. PbSe NCs Energy Levels Determined by Cyclic Voltammetry Method



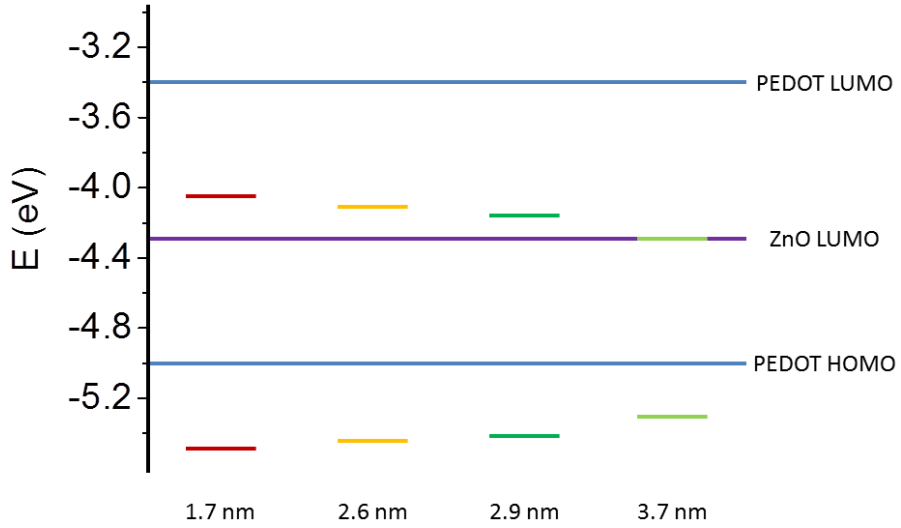


Figure S12. Cyclic voltammograms of PbSe NCs with average diameters of 1.7, 2.6, 2.9, and 3.7 nm. The energy levels of PbSe NCs with different average diameters.

The highest occupied molecular orbital (HOMO) of PbSe NC was calculated from the onset oxidation potential (E^{OX}), according to the following equation:[1]

$$E_{HOMO} = - I_p = - (E^{OX} + 4.71)\ eV$$

The lowest unoccupied molecular orbital (LUMO) was determined by plus optically measured energy gap and the HOMO value.

In the cyclic voltammetry, glassy carbon discs were employed as the working electrode, a Pt wire as the counter-electrode, and Ag/Ag^+ (Ag wires with 0.01M $AgNO_3$ in acetonitrile) as the reference electrode. 0.1 M tetrabutylammoniumhexafluorophosphate dissolved in acetonitrile was employed as the supporting electrolyte. A NC film was formed by depositing NC solution onto the surface of the working electrode. Before depositing the NC solution, the working electrodes were polished, cleaned, and dried. The electrolyte solutions were thoroughly deoxygenated by bubbling high purity nitrogen, a nitrogen atmosphere was maintained over the solution. Cyclic voltammograms were recorded on a CorrTest CV electrochemical workstation. The scan rate was 50 mV/s.

14. Histogram Distribution Diagram of Battery Efficiency

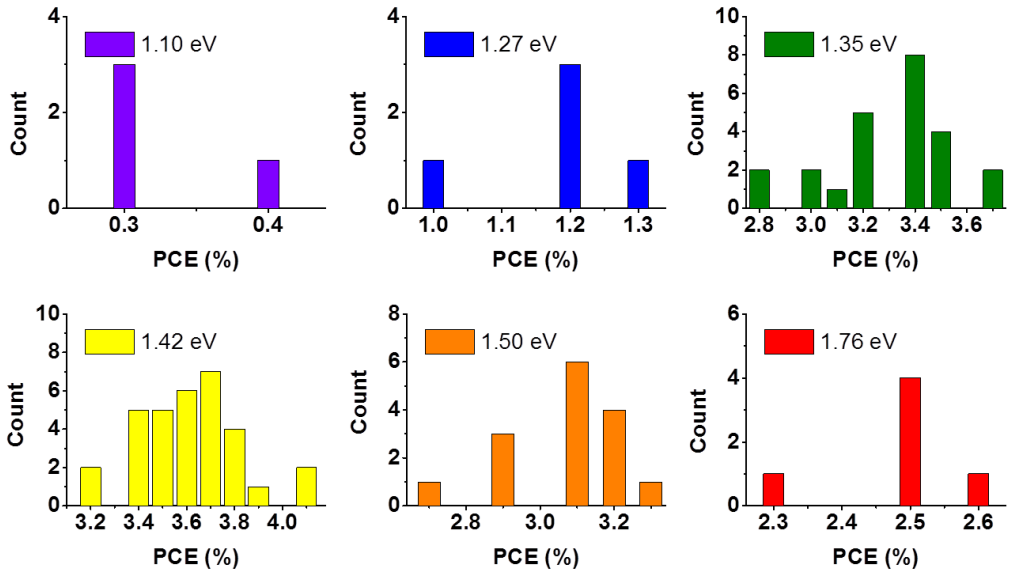


Figure S13. The histogram distribution diagrams of solar cell power conversion efficiencies (PCEs) about different-sized PbSe NCs. Take NCs of 1.42 eV as an example: 32 devices were fabricated, with 2 devices shows the highest PCE of 4.1%, and an average efficiency of 3.62%; about 80% of these devices gave efficiency values over 3.5%.

15. Schematic of the Device Structure Used in Reflection Geometry Measurement

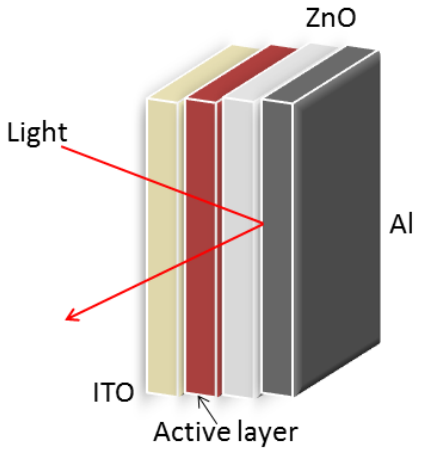


Figure S14. A schematic illustration of the device structure used for absorption measurements.

16. Equation of the Particle Size and First Absorption Peak Position

The relationship between particle size and the first absorption peak position is given as follows:[2]

$$D = (\lambda - 143.75)/281.25$$

Where D (nm) is the average particle diameter of the PbSe NC sample, and λ (nm) is the first absorption peak position of the corresponding sample.

References

1 H. Zhong, S. S. Lo, T. Mirkovic, Y. Li, Y. Ding, Y. Li and G. D. Scholes, *ACS Nano*, 2010, **4**, 5253-5262.

2 Q. Dai, Y. Wang, X. Li, Y. Zhang, D. J. Pellegrino, M. Zhao, B. Zou, J. Seo, Y. Wang and W. W. Yu, *ACS Nano*, 2009, **3**, 1518-1524.