

Electronic Supplementary Information (ESI) for

Cadmium sulfide as efficient electron transport layer for inverted planar perovskite solar cells

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Experimental Section

Materials: Fluorine-doped tin oxide conducting glass (FTO) was obtained from Pilkington (14 Ω -square). Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$) and PbI_2 were obtained from TCI. Dimethyl sulfoxide (DMSO) and N, N-dimethylformide (DMF) were purchased from Sigma-Aldrich. PCBM (99.5%, Lumtec Co., Taiwan). All chemicals were used as received.

Preparation of the CdS colloid: The CdS was synthesized by a solvothermal method. In a typical synthesis, 5ml aqueous solution containing 0.5 g of NaOH was added to the mixture of 5 mL of linoleic acid and 15 mL of ethanol for about 30 min. Then 7 mL of aqueous solution containing 0.5 g of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, 8 mL of an aqueous solution containing an equal amount of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in mole ratio were added in order, and the mixture were transferred into a 50 mL Teflon vessel, which was treated under hydrothermal conditions for about 12 h at 180 °C. After the reaction, the autoclave was cooled to room-temperature naturally. The yellow precipitate at the bottom of the autoclave was collected, and washed with absolute

ethyl alcohol for several times. The obtained products were dispersed in toluene to form a well-distributed ink with concentration of $0.01 \text{ g}\cdot\text{mL}^{-1}$.

Solar cell fabrication: The FTO substrates were cleaned sequentially with detergent and acetone, isopropanol and ethanol under sonication for 30 min, and then the substrates were treated with plasma treatment for 5 min. Subsequently, Cu:NiO_x layer was formed by spin-coating onto the FTO and then annealing in ambient atmosphere for 45 min at $500 \text{ }^\circ\text{C}$. Detailed methods can be found in previous report.¹ The perovskite layer was deposited by simple one step spin-coating method in a nitrogen filled glove box. The precursor solution (461 mg of PbI_2 , 159 mg of $\text{CH}_3\text{NH}_3\text{I}$ and 78 mg of DMSO were dissolved in 600 mg of DMF) was spin-coated onto the $\text{Cu:NiO}_x/\text{FTO}$ at 4000 rpm for 20 sec and 0.1 mL of chlorobenzene was quickly dripped on the rotating substrate in 7 sec after 4000 rpm, followed by a thermal annealing at $100 \text{ }^\circ\text{C}$ for 5 min. The CdS layer was prepared by spin-coating a CdS dispersion at 3000, 4000, 5000 and 6000 rpm on $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Cu:NiO}_x/\text{FTO}$, respectively. The CdS films obtained from 3000 rpm, 4000 rpm, 5000 rpm and 6000 rpm were designated as CdS-3000, CdS-4000, CdS-5000, and CdS-6000, respectively. For comparison, a PSC device based on PCBM was prepared by spin-coating PCBM solution ($20 \text{ mg}\cdot\text{mL}^{-1}$ in chlorobenzene) at 1500 rpm for 30 s. Finally, Au counter electrode was deposited under vacuum through a shadow mask.

Characterizations: The CdS powder was measured with X-ray diffraction (XRD, $\text{Cu-K}\alpha$ radiation, SmartLab 3 kW, Rigaku, Japan). The morphologies and the thickness of CdS layers were observed using field-emission scanning electron microscopy (FESEM, Hitachi SU8010, Japan) and field emission transmission electron microscopy (FETEM) (Tecnai G2 F20). The

current density-voltage (J-V) curves were measured using a Keithley 2401 source-measure unit under $100 \text{ mW}\cdot\text{cm}^{-2}$ (AM 1.5 G) illumination provided by an Oriel Sol 3A solar simulator with pre sweep delay of 0.04 s, max reverse bias of -0.1 V , max forward bias of 2.0 V , dwell time of 30 ms in ambient environment. The light intensity was adjusted using a NREL-calibrated Si solar cell equipped with a KG-2 filter. IPCE curves were measured as a function of wavelength from 300 to 800 nm using the Newport Incident photo-to-electron conversion efficiency (IPCE) system (Newport, USA). The time-resolved photoluminescence (TRPL) spectrum measurement was acquired by using Zolix Omni Fluo-TRPL5 at 767 nm upon excitation at 507 nm. The photoluminescence (PL) measurement was acquired at room temperature using Thermo Scientific Lumina Fluorescence Spectrometer LF-1303003.

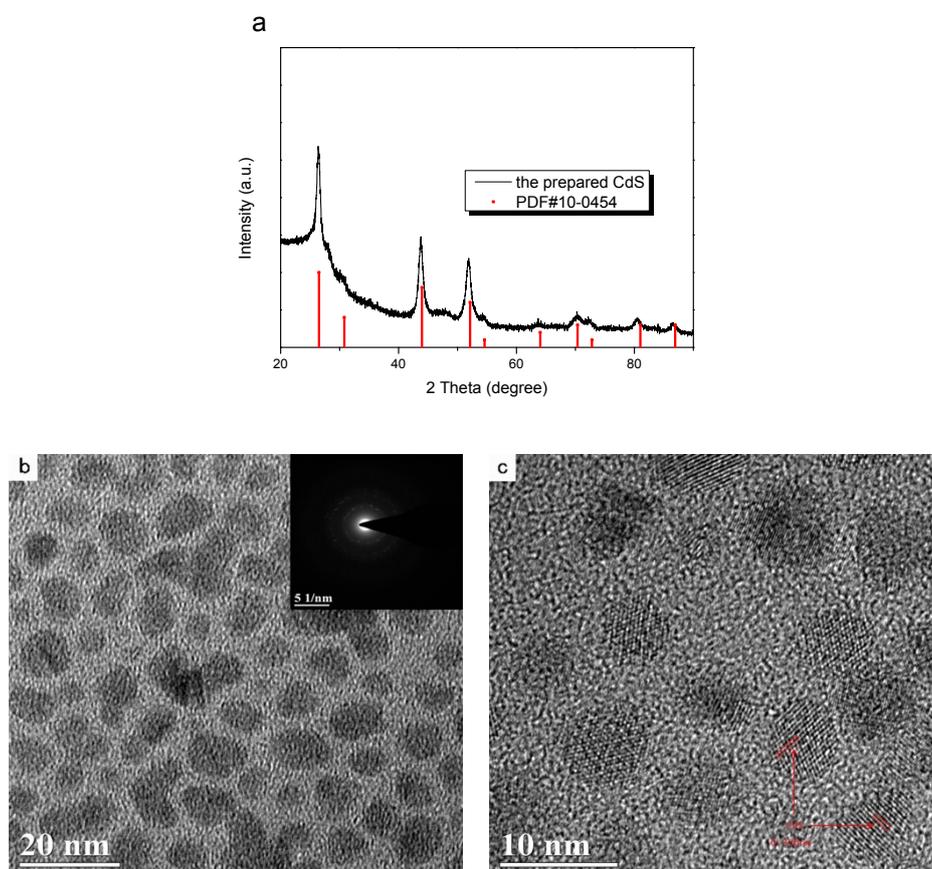


Fig. S1 (a) XRD of as-prepared CdS. (b) TEM and SAED images of as-prepared CdS. (c) High-resolution TEM image of as-prepared CdS.

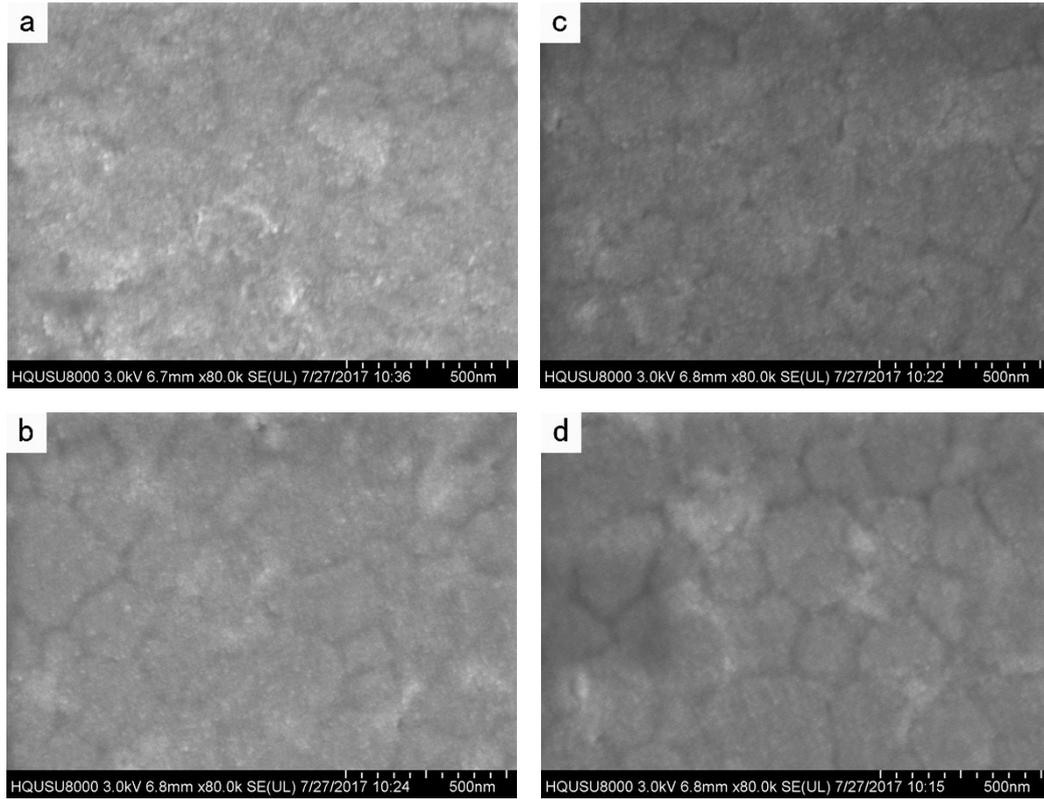


Fig. S2 Top view FESEM images of (a) CdS-3000, (b) CdS-4000, (c) CdS-5000, and (d) CdS-6000 layers on perovskite films.

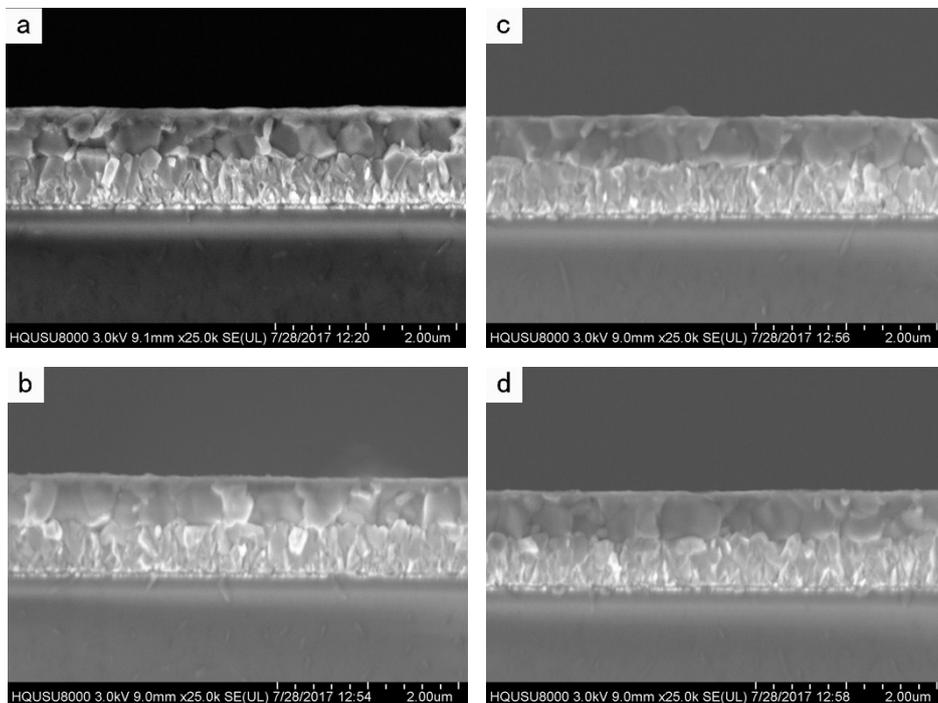


Fig. S3 Cross view FESEM images of (a) CdS-3000, (b) CdS-4000, (c) CdS-5000, and (d) CdS-6000 layers on perovskite films.

Table S1 TRPL parameters of perovskite films on different ETLs.

ETLs	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{ave} (ns)
CdS-3000	75.05	63.46	20.70	36.54	55.19
CdS-4000	64.88	51.88	21.02	48.12	43.77
CdS-5000	48.19	32.98	15.44	67.02	26.24
CdS-6000	61.87	45.09	15.26	54.91	36.28
PCBM	30.85	15.82	7.02	84.18	10.79

Table S2 Physical parameters of CdS and PCBM.^{2,3}

ETLs	CB(eV)	VB(eV)	$\mu(\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1})$
CdS ²	-3.8	-6.2	4.66
PCBM ³	-4.2	-6.2	4.6×10^{-3}

Reference

- 1 J. Jung, C. Chueh and A. Jen, *Adv. Mater.*, 2015, **27**, 7874-7880.
- 2 J. Liu, C. Gao, L. Luo, Q. Ye, X. He, L. Ouyang, X. Guo, D. Zhuang, C. Liao and J. Mei, *J. Mater. Chem. A*, 2015, **3**, 11750-11755.
- 3 Z. Bin, J. Li, L. Wang and L. Duan, *Energ Environ. Sci.*, 2016, **9**, 3424-3428.