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Supplementary information for

Enhanced efficiency and stability of perovskite solar cells by incorporating CdS and $Cd(SCN_2H_4)_2Cl_2$ into $CH_3NH_3PbI_3$ active layer

Liangxin Zhu,[a,b] Chong Chen,[a,b*] Fumin Li,[a,b] Zhitao Shen,[a,b] Yujuan Weng,[a,b] Qingsong Huang[c*], Mingtai Wang[d*]

[a]*Henan Key Laboratory of Photovoltaic Materials, Henan University, Kaifeng 475004, P.R.China,*

[b]*School of Physics and Electronics, Henan University, Kaifeng 475004, P.R.China and*

[c]*School of Chemical Engineering, Sichuan University, Chengdu 610065, P.R.China*

[d]*Institute of Applied Technology, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, 230031, PR China*

E-mail: chongchen@henu.edu.cn (C. Chen), qshuang@scu.edu.cn (Q. Huang), and mtwang@ipp.ac.cn (M. Wang).

1. First-principles calculations

Electronic structure calculations are performed with the density functional theory as implemented in the Vienna ab initio simulation package,[1,2] employing projected augmented wave potentials to describe the atomic core electrons and a plane wave basis set with a kinetic energy cutoff of 450 eV to expand the Kohn−Sham electronic states. For the exchange and correlation functional, the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) format was used.[3]

The bulk $CH_3NH_3PbI_3$ and $CdCl\{SC(NH_2)_2\}_2$ were optimized from experimental crystal structures.[4,5] In particular, a tetragonal cell ($a = b = 8.84$ Å and $c = 12.69$ Å) of $CH_3NH_3PbI_3$ and an orthorhombic cell ($a = 13.15$ Å, $b = 5.83$ Å and $c = 6.50$ Å) of $CdCl\{SC(NH_2)_2\}_2$ have been used. In the structural optimization, the k-point meshes to sample the Brillouin zone were 5 × 5 × 3 and 3 × 5 × 5 generated by Monkhorst–Pack scheme[6] for $CH_3NH_3PbI_3$ and $CdCl\{SC(NH_2)_2\}_2$, respectively. All atoms were allowed to relax until the atomic forces were smaller than 0.02 eV Å^{-1}, while the lattice constants were fixed to reduce computational cost. After structural optimization, the densities of states

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E-mail: chongchen@henu.edu.cn (C. Chen), qshuang@scu.edu.cn (Q. Huang).
(Dr. Chong Chen and Dr. Qingsong Huang)

were calculated using more dense k-point grids with 9 × 9 × 7 and 7 × 9 × 9 for $CH_3NH_3PbI_3$ and $CdCl\{SC(NH_2)_2\}_2$, respectively.

The $CH_3NH_3PbI_3$/CdS interface was described by 8 atomic layers $CH_3NH_3PbI_3$ (001) contacted with 16 layers CdS (001), and a vacuum thickness of 15 Å was added along the z direction. A 6 × 6 × 1 gamma centered k-point mesh was used to sample the Brillouin zone. The DFT-D3 method with Becke-Jonson damping was adopted to include van der Waals interactions.[7] During structural optimization, all the atoms and the lattice constants were fully relaxed until the atomic forces are smaller than 0.05 eV $Å^{-1}$.

The binding energy of the interface system was calculated to assess the structural stability. Here, the binding energy E_b per area is defined as

$$E_b = [E(\mathrm{CdS}) + E(\mathrm{CH_3NH_3PbI_3}) - E(\mathrm{CH_3NH_3PbI_3/CdS})]/A,$$

where E(CdS), $E(CH_3NH_3PbI_3)$ and $E(CH_3NH_3PbI_3/CdS)$ are the total energies of the CdS film, the $CH_3NH_3PbI_3$ surface and the combined systems, respectively. A is the surface area of the supercell.

References:

1. G. Kresse, J. Hafner, *Phys. Rev. B* 1993, **47**, R558
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3. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
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5. C. Marcos, J. M. Alía, V. Adovasio, M. Prieto, S. García-Granda, *Acta Cryst.*, 1998, **C54**, 1225.
6. H. J. Monkhorst, J. D. Pack, *Phys. Rev. B: Solid State*, 1976, **13**, 5188.
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2. Supplementary Figures

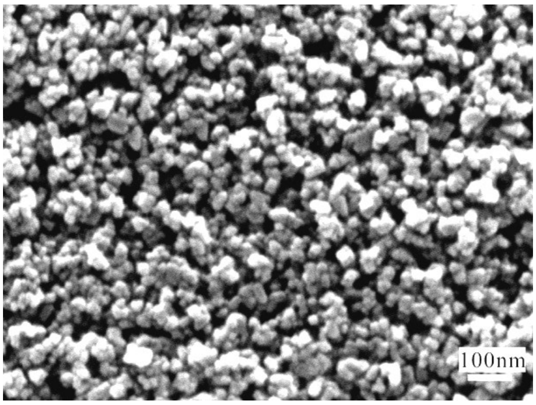

Figure S1

Fig. S1**.** Top-view SEM image of as-prepared FTO/cp-TiO_2/mp-TiO_2 film.

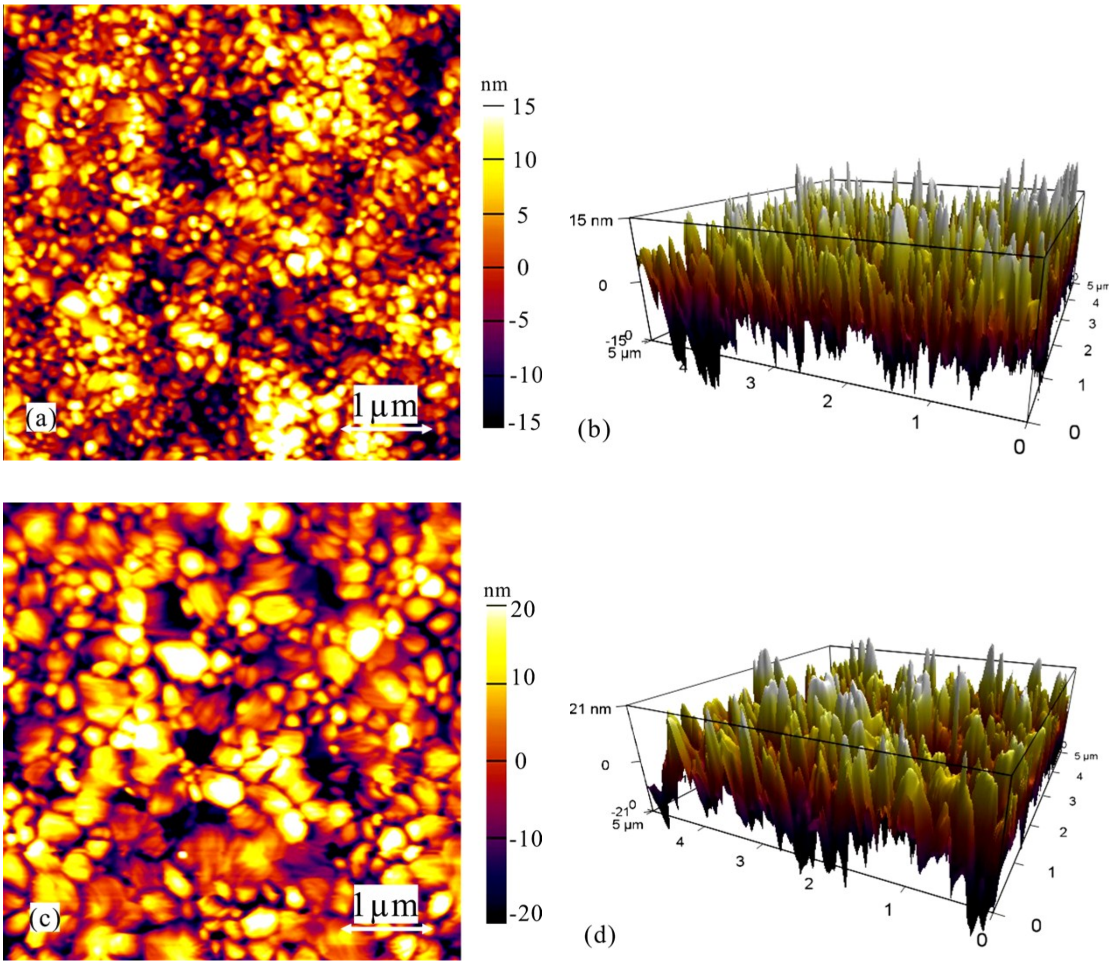

Figure S2

Fig. S2 SEM images of the capping layers on top of the (a) FTO/cp-TiO_2/mp-TiO_2/$CH_3NH_3PbI_3$ (a) and (b) FTO/cp-TiO_2/mp-TiO_2/C:C:$CH_3NH_3PbI_3$ films at 300, 000× magnification.

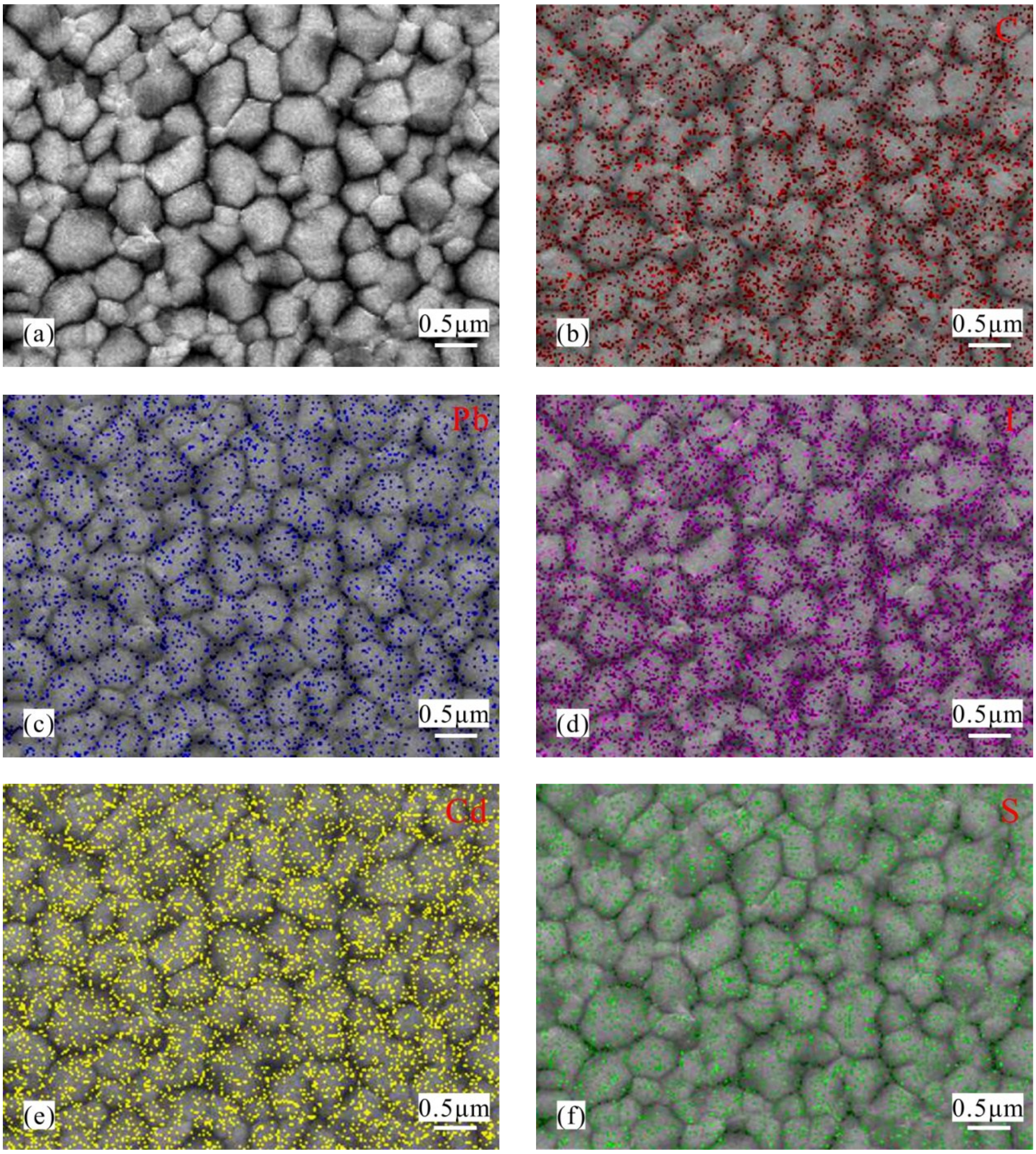

Figure S3

Fig. S3 Top-view (cross-sectional) SEM image and EDX spectrum of FTO/cp-TiO_2/mp-TiO_2/C:C:$CH_3NH_3PbI_3$ film (a), C element distribution (b), Pb element distribution (c), I element distribution (d), Cd element distribution (e), and S element distribution (f).

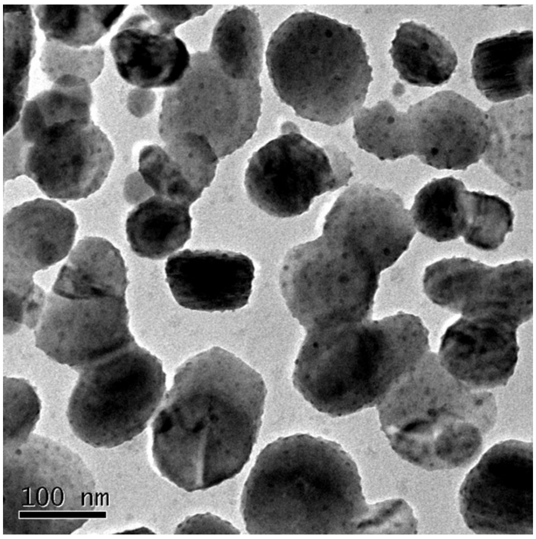

Figure S4

Fig. S4 (a) The low-magnification TEM image of C:C:$CH_3NH_3PbI_3$ nanoparticles after ultrasonic dispersion treatment. The small size CdS nanoparticles are clearly observed on the surface of large size $CH_3NH_3PbI_3$ crystals.

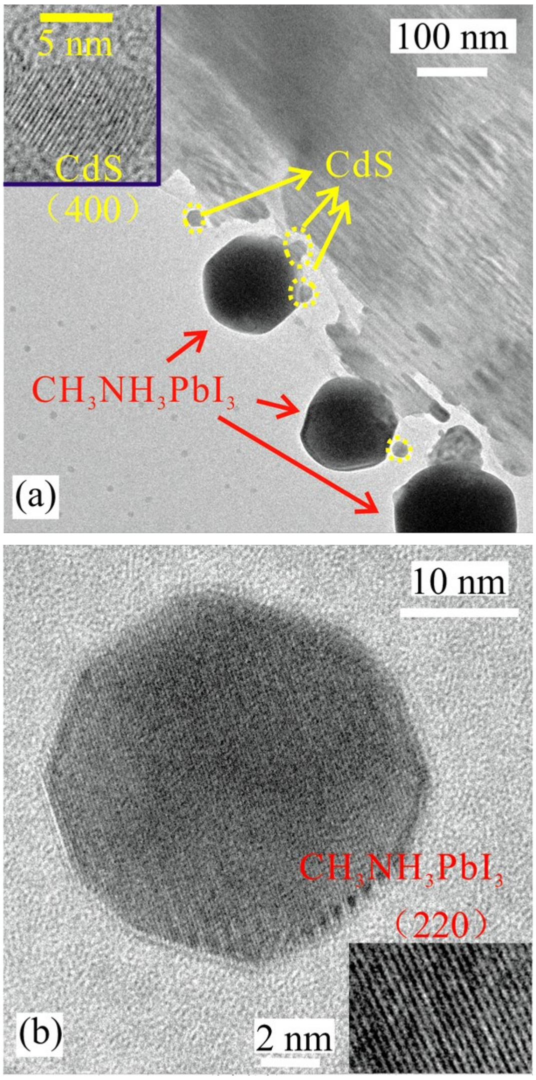

Figure S5

Fig. S5 (a) The TEM image of C:C:$CH_3NH_3PbI_3$ composite film and the inset is the HR-TEM image of one CdS nanoparticle. (b) The HR-TEM image of one single $CH_3NH_3PbI_3$ particle.

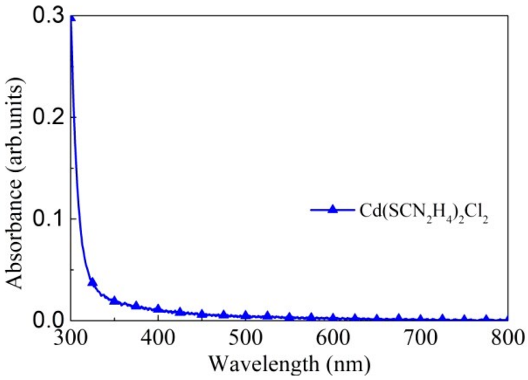

Figure S6 UV–vis absorption spectra of the $Cd(SCN_2H_4)_2Cl_2$ film.

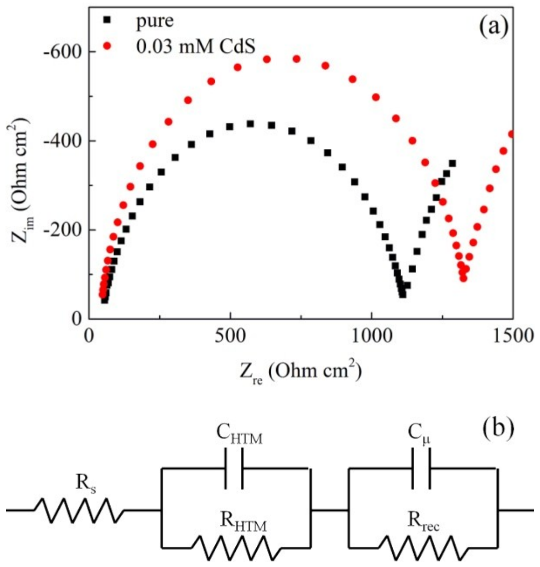

Fig. S7 Electrochemical impedance spectra (EIS) of the PSCs under illumination100 mW/cm^2.

Table S1 The fitting parameters for measured EIS results with different device.

Devices	**R_S(Ω cm^2)**	**R_{HTM}(mA cm^{-2})**	**R_{rec}(mA cm^{-2})**	**C_{HTM}(µF cm^{-2})**	**$C_µ$ (nF m^{-2})**
Solar cells with pure $CH_3NH_3PbI_3$	44.88	1202	1077	24.9	45.8
Solar cells with C:C:$CH_3NH_3PbI_3$	39.76	1345	1294	81.8	13.5