Electronic Supplementary Information

Low-temperature, solution processed metal sulfide as electron transport layer for efficient planar perovskite solar cells

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Experimental section

CH_3NH_3I Synthesis

The material CH_3NH_3I was synthesized based on the literature.[1] In short, to prepare CH_3NH_3I, hydroiodic acid (10 mL, 57 wt % in water, Sigma-Aldrich) and methylamine (24 mL, 33 wt% in absolute ethanol, Sigma-Aldrich) were reacted in a round bottomed flask in ice-cold water with stirring for 60 min. Raw CH_3NH_3I was obtained by removing the solvent at 50 °C on a rotary evaporator. The material was then washed in diethyl ether and filtered several times. The precipitate was then dried in vacuum oven overnight at 50 °C and then kept in nitrogen-filled glove box.

Fabrication of CdS films

CdS films were deposited on either ITO or glass substrates by Chemical Bath Deposition (CBD). The reaction solution was prepared by adding 5 ml of 3 M ammonium chloride (NH_4Cl, Sinopharm Chemical) aqueous solution, 5 ml of 0.2 M cadmium chloride ($CdCl_2$, Sinopharm Chemical) aqueous solution and 5 ml of 1 M thiourea (NH_2CSNH_2, Sinopharm Chemical) aqueous solution to 185 ml deionized water. Ammonium hydroxide (NH_4OH, 28-30%, Sinopharm Chemical) was added to adjust the PH to 9. The substrates were vertically placed in the alkaline aqueous solutions. Then the solution was placed in 65 ^{o}C water bath. After the deposition, the substrates were removed, rinsed with deionized water, dried in an argon flow and heated on hot plate at 100 ^{o}C for 10 minutes. To make 50 nm thickness CdS film, the deposition time was 30 min. To make 100 nm thickness CdS film, the same process was repeated twice.

Fabrication of ZnS films

Chemical Bath Deposition was adopted to fabricate ZnS thin films on ITO-coated glasses. $Zn(CH_3COO)_2$ (0.1 M, 50 ml aqueous solution), $CS(NH_2)_2$ (0.12 M, 50 ml aqueous solution), $Na_2C_4H_4O_6.2H_2O$ (0.072 M, 50 ml aqueous solution) and $Na_3C_6H_5O_7$ (0.08 M, 50 ml aqueous solution) were reacted together in a beaker. Aqua ammonia was added to adjust the PH to 10. The beaker with samples vertically placed in the solution was placed in water bath at 80 ^oC. The samples were taken out from the reaction solution after bathing for 90 minutes. The samples were then washed by deionized water, dried in an argon flow and heated on hot plate at 100 ^oC for 10 minutes. The thickness of the prepared ZnS films is approximately 30 nm.

Solar cell fabrication

Solar cells with ITO/CdS (or ZnS)/perovskite/spiro-OMeTAD/Au planar device structure were prepared. Before deposition of other films, the ITO-coated glass substrates (1.5 cm × 1.5 cm) were ultrasonically cleaned with detergent, deionized water, acetone and ethanol sequentially, and then were blow-dried in nitrogen. After that, CdS (or ZnS) films were deposited by Chemical Bath Deposition. The preparation procedure of perovskite absorbers is based from a previously reported process.[2] The perovskite precursor solution was prepared by mixing 1.2 mmol PbI_2 (99.99%, Alfa Aesar) and 1.2 mmol CH_3NH_3I in a mixture of 700 μl γ-butyrolactone (GBL, Sigma-Aldrich) and 300 μl dimethylsulfoxide (DMSO, Sigma-Aldrich). 60 μL of perovskite precursor solutions were spin coated onto the substrates at 3000 rpm for 45 s. During the spin-coating, 50 μL of toluene were dropped in the center of the substrates at 20 s. A detailed time-rotation profile for the spin-coating is represented in Figure S1. The spin-coated films were then dried on a hot plate at 100 ^oC for 10 min. A hole-transport material (HTM) solution was spin-coated on the perovskite layer at 4000 rpm for 45 s. The HTM solution was prepared by dissolving 72.3 mg (2,29,7,79-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene) (spiro-MeOTAD, 99.5%, Lumtec), 28.8 μl 4-tert-butylpyridine (TBP, 96%, Aldrich) and 17.5 μl of a stock solution of 520 mg/ml lithium bis(trifluoromethane)sulfonimide (LiTFSI, 99.95%, Aldrich) in acetonitrile in 1 ml chlorobenzene. Finally, a 100 nm thick Au layer was deposited by evaporation through an aperture mask under a base pressure of 7×10^{-6} Torr. The active device area is about 0.12 cm^2.

Measurement and characterization

The work function of the films was measured by ultraviolet photoelectron spectroscopy (UPS), which was performed with a VG ESCA Lab system equipped with an ultrahigh vacuum system and a He discharge lamp. The UPS spectra were recorded using an unfiltered He I (21.22 eV) excitation source, and the samples were biased at -5.0 V to observe the low-energy secondary cutoff. SEM images were obtained using Hitachi S5200. Film absorbance spectra were measured by Shanghai UV-VIS SP-752 spectrometer. Hall effect measurement were performed on an

HL5500PC Hall system using a Van der Pauw four-point configuration at room temperature. The compositions of the films were tested by X-ray fluorescence (LAB CENTER XRF-1800). Current-voltage measurements were carried out using Keithley 2400 at room temperature under AM 1.5G illuminations (1000 W/m^2) from a solar simulator which was calibrated using a standard silicon solar cell device. The JV curves were obtained in the air through reverse with the step size of 5 mV. For the measurement of hysteresis, the JV curves were obtained in the air through reverse (1.2 V → -0.2 V) or forward scan (-0.2 V → 1.2 V) with the same step size. Impedance spectra (IS) were measured using an electrochemical workstation (Zahner, Zennium) with a 20 mV rms amplitude over the frequency range of 1 Hz to 1 MHz under low light intensity (0.1 sun).

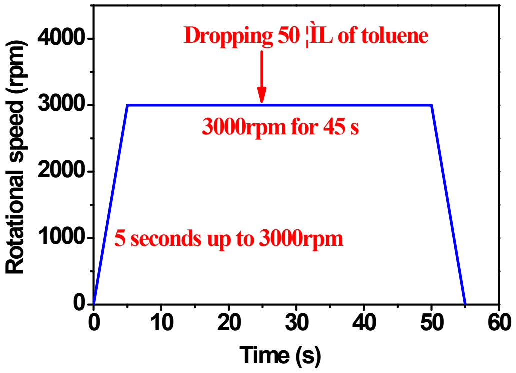

Figure S1. Time-rotation profile for the spin-coating of perovskite layers.

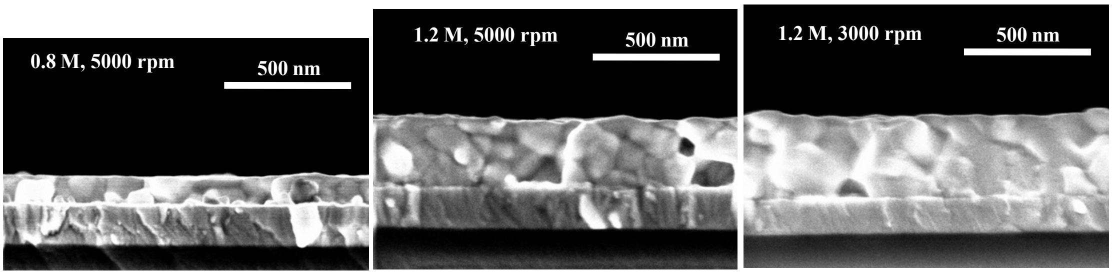

Figure S2. Thickness dependence of perovskite films on the deposition condition.

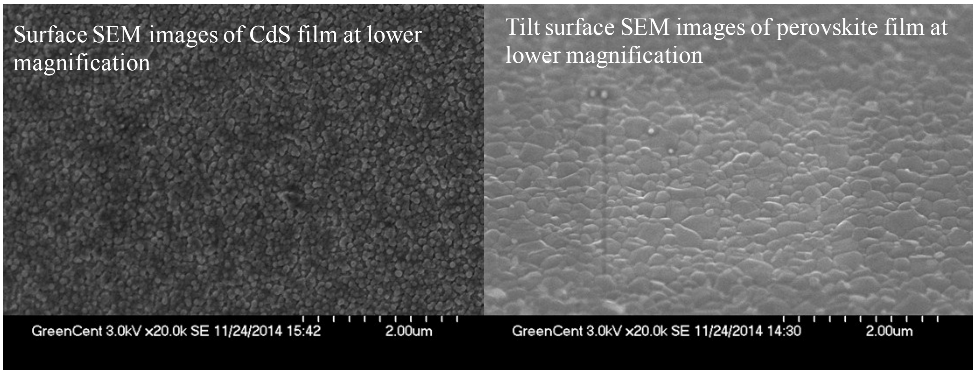

Figure S3. Surface SEM images of CdS (left) and perovskite (right) films.

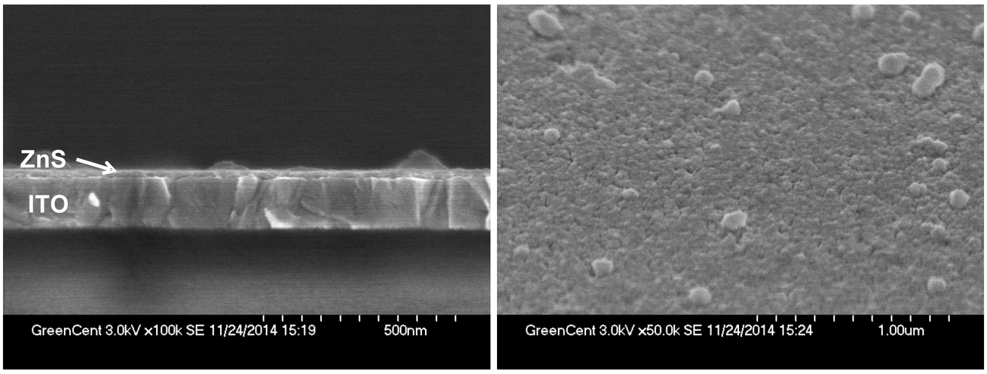

Figure S4. Crosss-section (left) and tilt surface (right) SEM images of ITO/ZnS sample

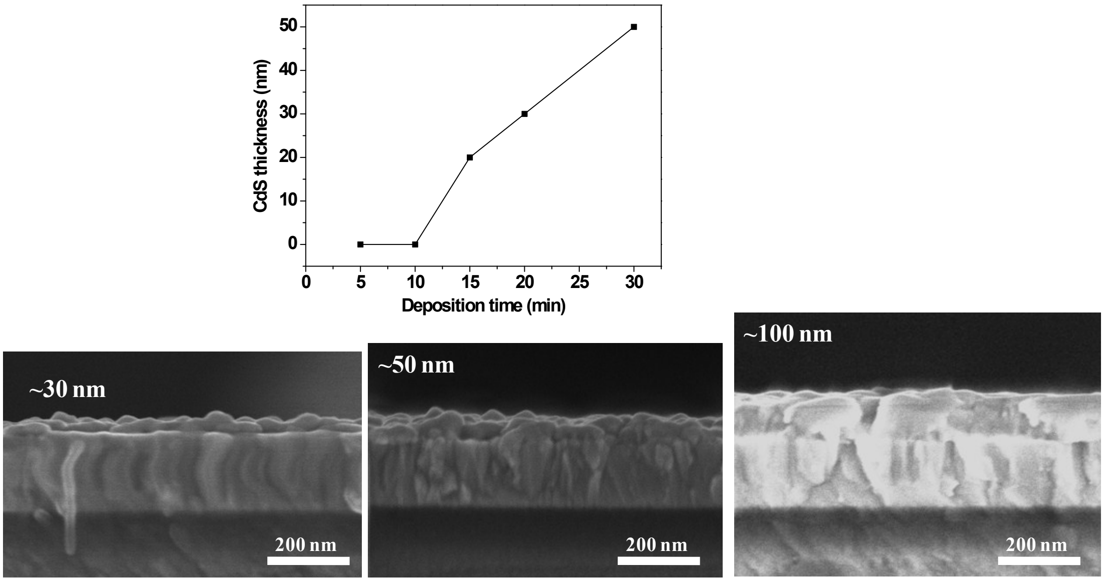

Figure S5. Thickness dependence of CdS films on the deposition condition.

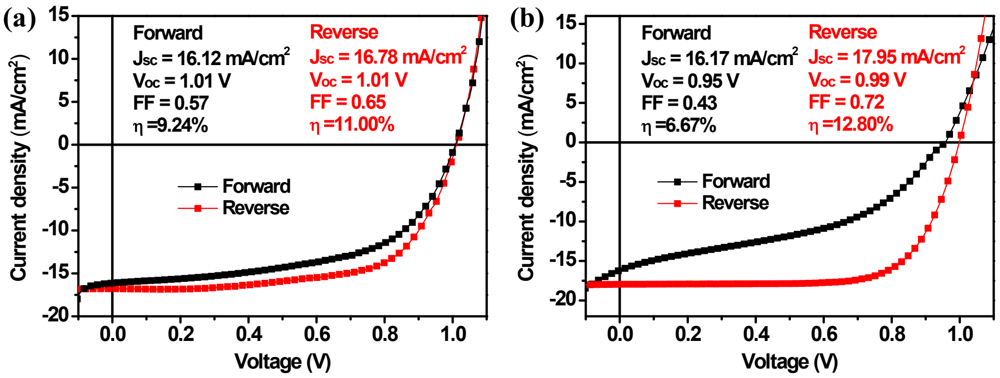

Figure S6. Typical J-V curves measured under forward and reverse scan directions for the planar perovskite solar cells using CdS and TiO_2 as electron transport layers.

1. M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, **338**, 643-647.
2. N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ry and S. I. Seok, *Nature materials*, 2014, **13**, 897-903.