Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Support Information

3-Dimentional ZnO/CdS Nanocomposite with High Mobility as Efficient Electron Transport Layer for Inverted Polymer Solar Cells

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Author contributions. Haiyan Fu and Yilin Wang contributed equally to this work.

Experimental Section

Cadmium nitrate [$Cd(NO_3)_2 \cdot 4H_2O$], hexamethylenetetramine [$(CH_2)_6N_4$), HMT] thiourea (CH_4N_2S), poly(3-hexylthiophene) (P3HT, Mw = 60 000 ~ 75 000, Rieke Metals Inc.), thieno[3,4-b]-thiophene/benzodi-thiophene (PTB7, 1-Materials), (6,6)-phenyl-C61 butyric acid methyl ester ($PC_{61}BM$ 99.5%; Nano-C), triphenylphosphine(>99.0%; Aladdin), [6,6]-phenyl C71-butyric acid methyl ester ($PC_{71}BM$, 99%, Nano-C) and diethyl azodicarboxylate (>97.0%, Aladdin) were used as received. All chemicals were analytical grade and commercially available, and were used without further treatment.

Synthesis of CdS nanocrystals

The different CdS nanocrystals were prepared by hydrothermal synthesis according to the previous report[1]. In a typical procedure, 1 mmol $Cd(NO_3)_2 \cdot 4H_2O$, 1 mmol HMT and 3 mmol thiourea were added into a given amount of super-pure water, respectively. The resulting mixture was transferred into a Teflon-lined stainless-autoclave (100 mL capacity), which was then sealed and maintained at 200 °C for 12 h. After the mixture was cooled to room temperature, the final product was collected and washed with super-pure water and ethanol several times, then dried under vacuum, and kept for further characterization.

Preparation of ZnO/CdS electron transport layer

ZnO was synthesized according to the Hegger’ s report[2]. The detail procedure was as follows. The ZnO precursor was prepared by dissolving zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, Aldrich, 99.9%, 1 g) and ethanolamine ($NH_3CH_2CH_2OH$, Aldrich, 99.5%, 0.28 g) in 2-methoxyethanol ($CH_3OCH_2CH_2OH$, Aldrich, 99.8%, 10 mL) with vigorous stirring for 12 h by a hydrolysis reaction in air. Then, the precursor was coated onto an ITO substrate and annealed in air for 1 h at 150 ^{o}C to obtain ZnO nanaoparticles. The different CdS nanocrystals, including flower-like CdS, branched CdS and small spherical CdS were dispersed in ethanol, which were then respectively spin-coated on the ZnO layer to obtain ZnO/F-CdS, ZnO/B-CdS ZnO/S-CdS hybrid ETLs. Then the hybrid ZnO/CdS layers were annealed at 100 ^{o}C for removing the solvent and keeping better contact with ZnO layer.

Fabrication of inverted polymer solar cells

The ITO-coated glass substrates (35 Ω cm^{-2}) were cleaned with alcohol, detergent, deionized water and isopropyl alcohol and dried by nitrogen flow followed by plasma treatment for 15 minutes. All the electron transport layers were grown in situ on the ITO-coated glass substrates. The blended solution of P3HT:$PC_{61}BM$ (1:1w/w, 1,2-dichlorobenzene, 60 ^{o}C) or PTB7:$PC_{71}BM$ (1:1.5 w/w, chlorobenzene/1,8-

diiodooctane (97:3 v/v), 70 ^{o}C) was stirred in a glovebox overnight, which was spin coated on the top of the cathode buffer layer as an active layer. Finally, anode buffer layer MoO_3 (7 nm) and anode Ag (90 nm) were deposited on the top of the active layer by thermal vaporation under a high vacuum (<10^{-7} Torr). Current density-voltage (*J-V*) characteristics were tested using a Keithley 2400 Source Meter in the dark and under simulated AM 1.5 G (100 mW cm^{-2}) irradiation (Abet Solar Simulator Sun2000). Incident photon-to-current efficiency (IPCE) was measured under monochromatic illumination (Oriel Cornerstone 260 1/4m monochromator equipped with Oriel 70613NS QTH lamp), while the calibration of the incident light was performed with a monocrystalline silicon diode. The active area is 0.06 cm^2 of single chip, all values represent averages from twelve devices on a single chip.

Characterizations

Ultraviolet-visible (UV-vis) absorption spectra were obtained by a PerkinElmer Lambda 750 spectrophotometer. A Hitachi F-7000 spectro luorophotometer was applied for the measurement of photoluminescence (PL). The Philips X'Pert Pro MPD with Cu Kα radiation (λ = 1.54056 Å) was applied to gather the X-ray diffraction (XRD) data. The morphology analysis was studied by atomic force microscopy (AFM, Digital Instrument Nanoscope 31), transmission electron microscopy (TEM; JEOL JEM-2100F) and scanning electron microscopy (SEM, FEI Quanta 200F). Ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) measurements were carried out by AXIS-ULTRA DLD spectrometer (Kratos Analytical Ltd.) using He(I) (21.2 eV) as the monochromatic light source. The current-voltage (*J-V*) characteristics of the devices under illumination were tested via a Keithley 2400 Source Meter. The light intensity of the simu-lated AM 1.5G illumination (Abet Solar Simulator Sun2000) was 100 mW/cm^2. The incident photon-to-current efficiency (IPCE) was measured by using of an Oriel Corner-stone 260 1/4 m monochromator equipped with an Oriel 70613NS QTH lamp, and the incident light was calibrated with a monocrystalline Si solar cell.

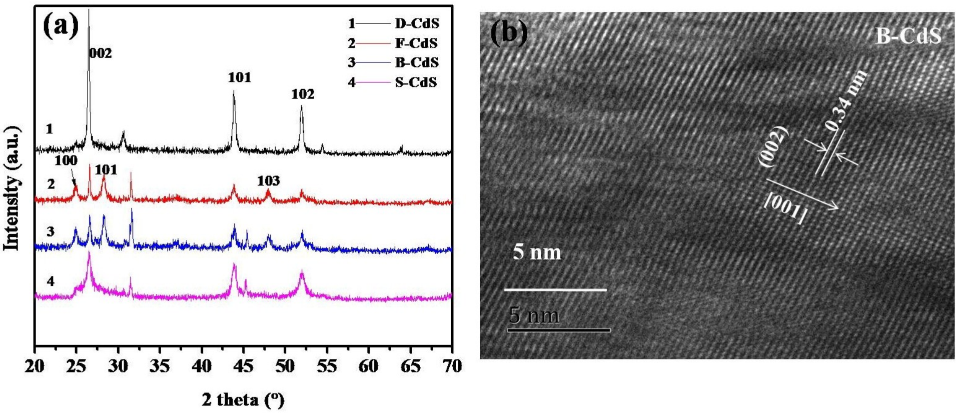

Figure S1. (a) X-ray diffraction (XRD) of D-CdS, F-CdS, B-CdS and S-CdS nanocrystals, (b) HRTEM of B-CdS.

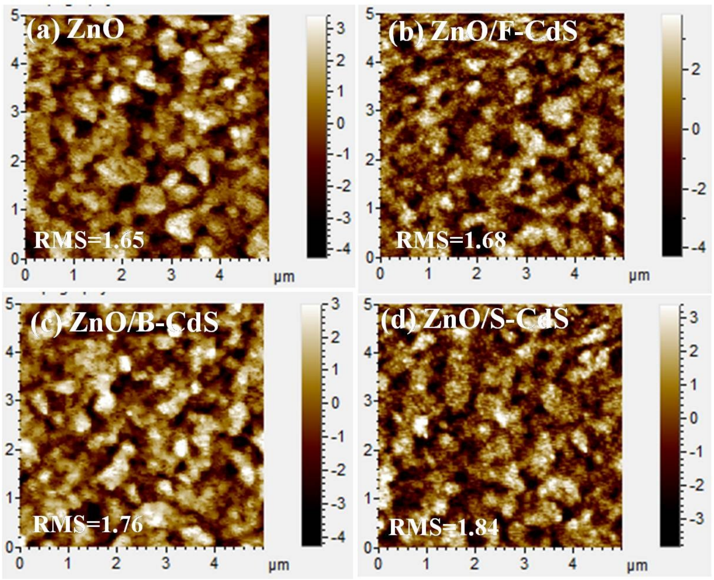

Figure S2. Atomic force microscopy (AFM) images of ZnO, ZnO/F-CdS, ZnO/B-CdS and ZnO/S-CdS nanocrystals.

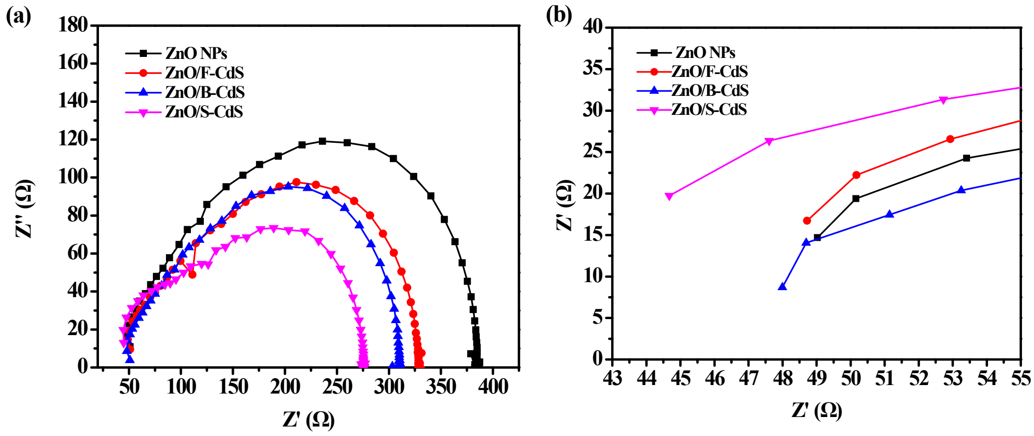

Figure S3. (a) Cole-Cole plots of the device (ITO/ETLs/P3HT:$PC_{61}BM/MoO_3$/Ag) in the dark under AM 1.5 G illumination (100 mW cm^{-2}), (b) the partial of (a).

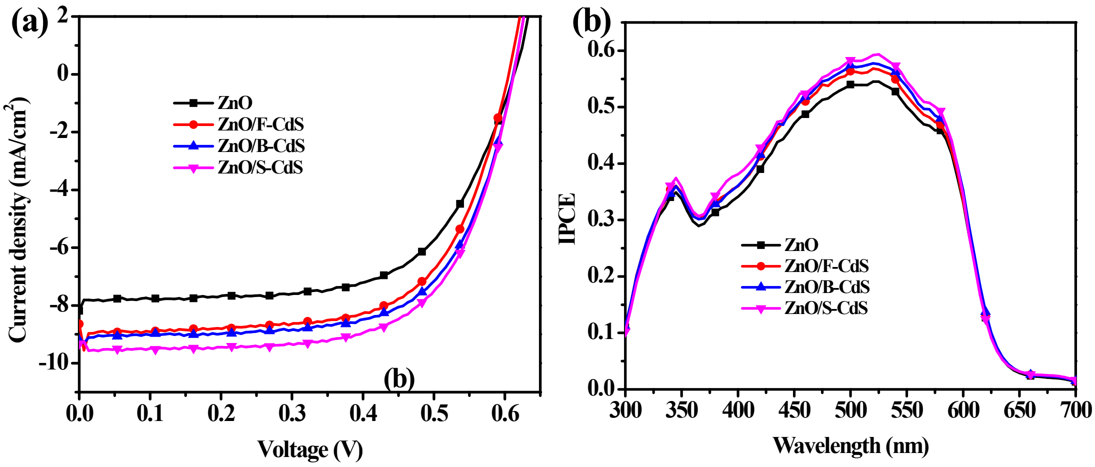

Figure S4. Photovoltaic performance of the devices with different ETLs under simulated AM 1.5 G (100 mW cm^{-2}) illumination: (a) current density-voltage (*J*-*V*) characteristics, (b) incident photon-to-current efficiency (IPCE) spectra based on the active layer of P3HT:$PC_{61}BM$.

Table S1. The impedance parameters from fitting with the equivalent circuit model for the device ITO/ETLs/P3HT:$PC_{61}BM/MoO_3$/Ag in the dark under AM 1.5 G illumination (at 100 mW/cm^2).

Devices with different ETLs	ZnO	ZnO/F-CdS	ZnO/B-CdS	ZnO/S-CdS
R_s (Ω/cm^2)	49	48.5	48	44

Table S2. Photovoltaic parameters of devices with ITO/different ETLs/P3HT:$PC_{61}BM/MoO_3$/Ag.

Devices with different ETLs	J_{sc} ($mA\cdot cm^{-2}$)	V_{oc} (V)	FF (%)	PCE (%)
ZnO	8.19±0.22	0.61±0.01	60.8±1.2	3.0±0.2(3.2)[a]
ZnO/F-CdS	8.64±0.21	0.60±0.01	67.4±1.3	3.5±0.3(3.8)[a]
ZnO/B-CdS	9.20±0.20	0.61±0.01	65.3±1.5	3.7±0.3(4.0)[a]
ZnO/S-CdS	9.38±0.19	0.61±0.01	67.5±1.6	3.9±0.3(4.2)[a]

The active area is 0.06 cm^2 of single chip, all values represent averages from twelve devices on a single chip.

[a] The best device PCE.

Reference

1. F. Chen, R. Zhou, L. Yang, N. Liu, M. Wang and H. Chen, *J. Phys. Chem. C*, 2008, **112**, 1001-1007.

2. Y. Sun, J. H. Seo, C. J. Takacs, J. Seifter and A. J. Heeger, *Adv. Mater.*, 2011, **23**, 1679-1683.