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COMMUNICATION

Low Temperature Solution Processed Planar Heterojunction Perovskite Solar Cells with CdSe Nanocrystal as Electron Transport/Extraction Layer

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Cadmium selenide (CdSe) nanocrystal was used as electron transport/extraction layer for perovskite solar cells due to its high electron mobility and solution-processing ability at low temperature. Power conversion efficiency (PCE) up to 11.7% was achieved under standard AM1.5G conditions in air.

Since T. Miyasaka and co-workers reported the first perovskite-sensitized solar cell in 2009,¹ the perovskite has become one of the hottest solar cell materials. Over the last few years, we have witnessed an unexpected breakthrough and rapid evolution in the field of the emerging photovoltaics, with the realization of highly efficient solid-state hybrid solar cells based on organometal trihalide perovskite absorbers.²⁻⁹ It is likely that the solar research in the coming years will advance this technology to the highest efficiencies while retaining the lowest cost and embodied energy.^{10,11}

At present, most of the highly efficient perovskite-based devices utilize a mesoporous metal-oxide scaffold on which the perovskite crystal grows, while acting as an electron-transport/extraction layer at the same time. However, the mesoporous films such as TiO₂ always require sintering at high temperature (450-550°C) prior to use, rendering them incompatible with the flexible substrates and easy fabrication.⁷ Since the pronounced work by Snaith *et al.*, who demonstrated that a simple planar heterojunction solar cell incorporating vapour-deposited perovskite as the absorbing layer can have a power conversion efficiency (PCE) over 15%,³ many highly efficient planar heterojunction perovskite-based devices have been demonstrated very recently.¹²⁻¹⁴ Subsequently, motivated by the desire to simplify further the processing method, low-temperature solution processed planar heterojunction solar cells were achieved by several groups.^{6,12,15-17} Kelly *et al.* reported a PCE of 15.7% by using a layer of ZnO nanoparticles as an electron-transport layer in CH₃NH₃PbI₃ based solar cells, where the CH₃NH₃PbI₃ layer was grown by a two-step process.⁶ Another promising type of low temperature solution processed perovskite solar cells with an 'inverted' device structure of Indium-Tin-Oxide (ITO)/ poly (3, 4-ethylenedioxythiophene)-polystyrenesulfonic acid (PEDOT-

PSS)/Perovskite/[6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM)/Al have also achieved a high PCE up to 15.4%.¹²

CdSe nanocrystal has been one of the most successful n-type materials for polymer/nanocrystal hybrid solar cells due to its high electron mobility, mature synthesis and tunable band gap.¹⁸⁻²¹ Here we investigated the use of CdSe nanoparticles replacing the widely used TiO₂ as the electron transport/extraction layer for the conventional planar heterojunction perovskite solar cells. Compared to TiO₂ (4-20 cm² V⁻¹ s⁻¹), the much higher electron mobility of CdSe (450-900 cm² V⁻¹ s⁻¹) makes it an ideal choice for an electron-selective contact.^{22,23} In addition, the CdSe nanocrystal films can be solution processed and only low temperature annealing (<150°C) is needed, which renders it possible for deposition on flexible substrates. Devices with CdSe nanoparticles acting as electron transport/extraction layer performed well, with a highest PCE reaching 11.7% when illuminated and tested under standard AM1.5G conditions in air.

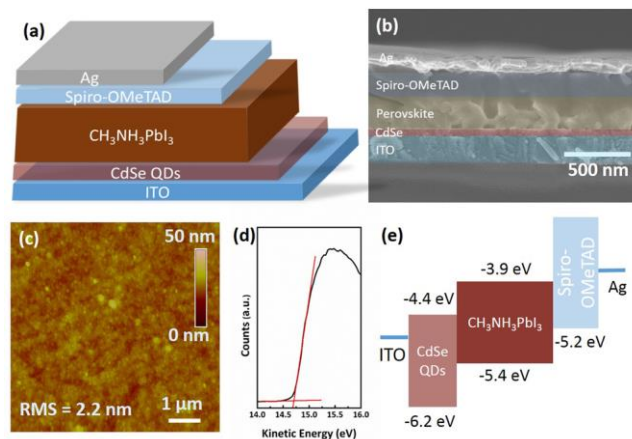


Figure 1. Schematic (a) and cross-sectional SEM image (b) of the perovskite-based solar cell structure used in this study. AFM image (c) and UPS spectrum (d) of the CdSe nanocrystals film. (e) Energy levels of the various device components.

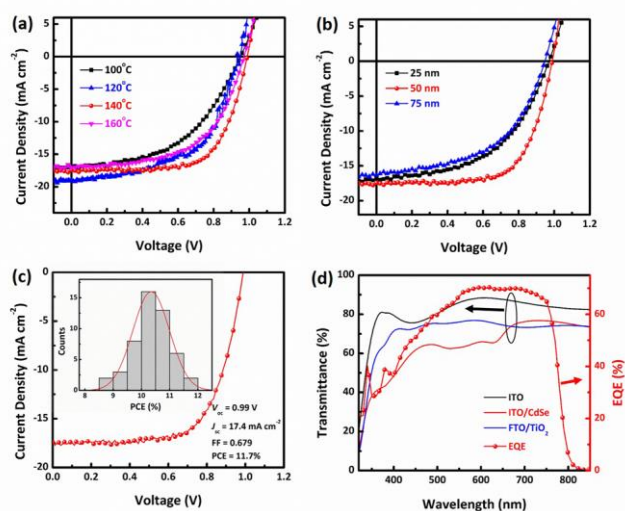


Figure 2. *J-V* characteristics of the ITO/CdSe/CH₃NH₃PbI₃/spiro-OMeTAD/Ag device with CdSe layer treated at different annealing temperatures (a) and in different thicknesses (b). *J-V* characteristics (c), EQE and the corresponding transmittance spectra of various substrates (d) for the best device. Inset in (c) shows histogram of PCEs for 50 devices. *J-V* characteristics were measured under simulated 1 sun AM 1.5 solar illumination in air.

Table 1. Summary of photovoltaic performance of perovskite solar cells with various thicknesses of CdSe nanocrystals layer and annealing temperatures, which represent statistical averages of over 10 devices for each configuration.

ETL	Thickness [nm]	Annealing Temp. [°C]	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF [%]	PCE [%]
CdSe	50	100	0.95±0.01	16.7±1.3	0.50±0.02	7.9±0.6
	50	120	0.95±0.01	18.3±0.6	0.56±0.02	9.7±0.3
	50	140	0.99±0.01	17.6±0.5	0.62±0.03	10.7±0.5 ^a
	50	160	0.96±0.01	16.7±1.0	0.56±0.02	9.0±0.7
	25	140	0.95±0.01	16.5±0.8	0.46±0.03	7.3±0.6
	75	140	0.95±0.01	16.2±0.6	0.47±0.02	7.3±0.5
TiO ₂	50	500	0.85	18.9	0.56	9.0 ^b
/	/	/	0.11	5.08	0.27	0.15 ^b

^a Averaged from 50 devices; ^b Best performance among 10 devices.

The CdSe nanoparticles were prepared by a hot-injection method followed by the ligand exchange with pyridine reported previously.^{20, 24-26} The pyridine exchange process was demonstrated to replace the long chain surfactant on the surface of CdSe (Figure S1) and thus can enhance the electron mobility of CdSe film.^{20, 24} The as-prepared CdSe nanoparticles are approximately 6 nm in diameter, as determined by transmission electron microscopy (TEM) (Figure S2). The CdSe nanoparticles are dispersed in chlorobenzene/pyridine mixed solvent. After spin coated onto the indium tin oxide (ITO) substrate, a relatively compact layer was formed (Figure 1c, also Figure 1b). The work function of the CdSe nanocrystal film is about 4.6 eV, which was determined by the ultraviolet photoemission spectroscopy (UPS) shown in Figure 1d. The suitable energy level is favorable for electron extraction. The CH₃NH₃PbI₃ perovskite absorber film was formed on the top of the CdSe layer by spin coating a N,N-Dimethylformamide (DMF) solution of CH₃NH₃I and PbI₂ and then annealed at 90°C for 30 min. Spin-coating of 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9'-bifluorene (spiro-OMeTAD) acting as the hole-transport layer and thermal

evaporation of the Ag top electrode completes the device fabrication (Figure 1a, Figure 1b). The corresponding energy level alignment was shown in Figure 1e. Free charges generated in CH₃NH₃PbI₃ are supposed to be extracted by transferring electrons to the underlying CdSe layer and holes to the spiro-OMeTAD.

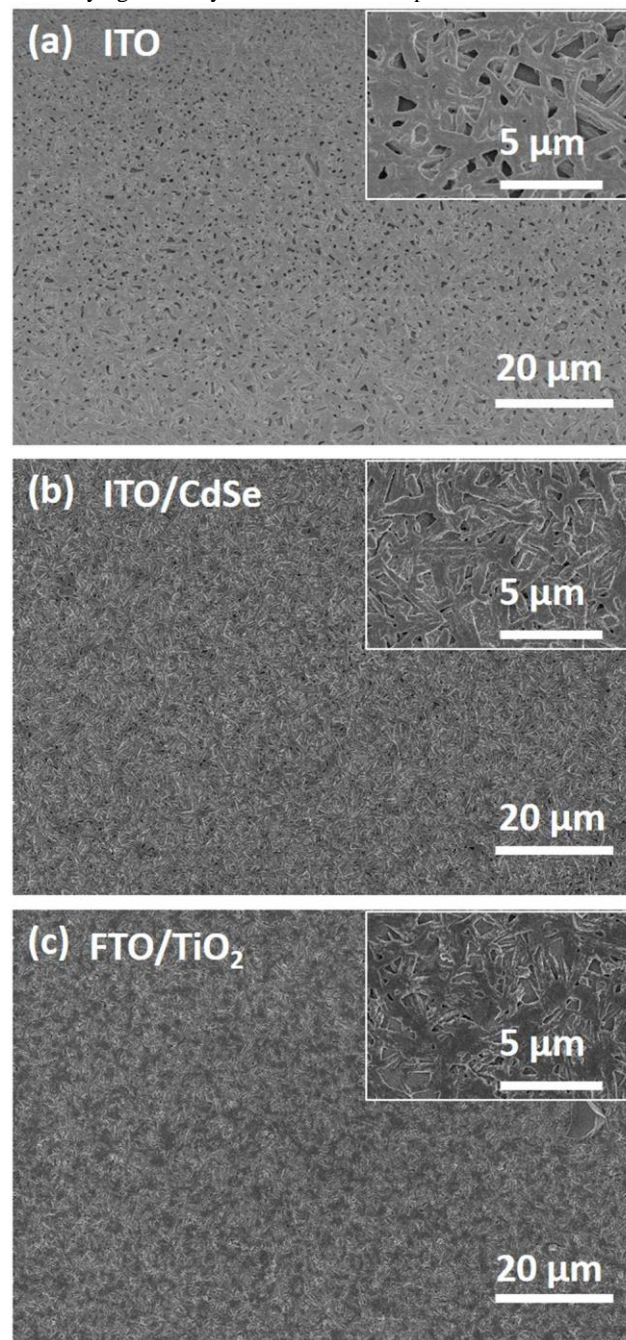


Figure 3. SEM images of the CH₃NH₃PbI₃ layer on the top of different substrates: ITO (a), ITO/CdSe (b), FTO/TiO₂ (c). Inset shows the higher magnification SEM images.

To optimize the performance of perovskite solar cells, devices were prepared by spin coating one, two, or three layers of CdSe nanoparticles and annealed at different temperatures (Figure 2a,b and Table 1). As can be seen from Table 1, incorporating a layer of 50 nm CdSe nanocrystal and annealing at 140°C leads to the best performance, with an average PCE nearly 11%. Thermal annealing can efficiently reduce the traps and enhance the electron mobility of

CdSe films, which contributes to the improvement of devices when increasing the annealing temperature from 100 to 140 °C.^{18, 27} However, further increasing the temperature can not result in any improvements in device performance. Effects of CdSe nanocrystal thickness were also investigated. As we can see, incorporating a thin layer of CdSe (25 nm) into the device significantly improves the performance. When the thickness of CdSe layer is 50 nm, PCEs in excess of 11% were obtained. Further increasing the thickness was harmful to the devices. Thick CdSe film absorbs much incident light but contribute little to current, and it also may introduce large series resistance, thus reducing J_{sc} and FF.^{6, 28}

The current density-voltage (J - V) characteristics and external quantum efficiency (EQE) spectrum of the best device is shown in **Figure 2c,d**. From the J - V curve measured under standard AM1.5G illumination, the short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and PCE were determined as 17.4 mA cm⁻², 0.99 V, 67.9% and 11.7%, respectively. Histogram of efficiencies measured from 50 devices shows an average PCE of 10.7%, which is much higher than that (9.0%) of the devices with TiO₂ as electron transport/extraction layer. The improvement mainly by FF can be attributed to the excellent electron transport/extraction ability of CdSe. These encouraging results demonstrate CdSe is an efficient electron transport/extraction material to obtain reproducible high-performance perovskite solar cell. In **Figure 2d**, the EQE spectrum is shown for the best device, exhibiting spectral sensitivity spanning from the visible to the near-IR (400 to 800 nm) with a peak IPCE of >70%. However, there is an obvious EQE loss below 550 nm as we can see from the EQE spectrum due to the low transmittance of CdSe below 650 nm comparing to the anatase TiO₂. The low EQE values in this range result in low current for CdSe based devices. The hysteresis issue when changed the electron transport layer from TiO₂ to CdSe was studied, and the preliminary results showed no obvious difference for the two electron transport layers. They both showed the obvious hysteresis (**Figure S3**).

The origin of the high performance observed in the perovskite solar cells with CdSe nanocrystals as the electron transport/extraction material was investigated further by studying the electron mobility of CdSe and TiO₂ films, the morphology of perovskite and the electron transfer process between perovskite and CdSe nanocrystal. First, the electron mobilities of CdSe nanoparticles and TiO₂ were studied by space charged limited current (SCLC) method using electron-only devices: ITO/CdSe/poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN)/Al or FTO/TiO₂/PFN/Al. The electron mobility of 1.2×10^{-5} cm² V⁻¹s⁻¹ and 4.1×10^{-7} cm² V⁻¹s⁻¹ has been determined for the devices with CdSe nanoparticle or TiO₂ film, respectively (**Figure S4**). Obviously, the electron mobility in the CdSe nanoparticle film is much higher than that in the TiO₂ film, which indicates that the electrons can be effectively transported in the CdSe nanoparticle films. Then, we studied the surface coverage of the crystallized perovskite that was previously proved to significantly affect the device performance.²⁹ To investigate the surface morphology of the perovskite film on the different substrates, scanning electron microscope (SEM) was conducted. The images are shown in **Figure 3**. CdSe and TiO₂ obviously improve the formation and growth of perovskite film, leading to homogenous and nearly full surface coverage, compared to the bare ITO. However, there are still some voids observed in the films, which need to be further tuned to achieving higher performance.

CdSe nanocrystals and spiro-OMeTAD are supposed to act as the electron transport layer and the hole transport layer, respectively. We measured the charge generation of the perovskite solar cells using photoluminescence (PL) characterization. The PL spectra of

CH₃NH₃PbI₃, CdSe/CH₃NH₃PbI₃, and CdSe/CH₃NH₃PbI₃/spiro-OMeTAD films on glass substrates were measured. The excitation light of 600 nm entered the sample from the glass substrate side, and the PL emission was collected.³⁰ As shown in **Figure 4**, when CH₃NH₃PbI₃ was deposited onto the inert glass substrate, strong PL emission was observed centered at around 780 nm. In contrast, we observed a significant PL quenching effect when perovskite layer established contact with the CdSe nanocrystals. After spiro-OMeTAD was spin-coated on the CdSe/CH₃NH₃PbI₃ layer, the PL was completely quenched. These results indicate that electrons/holes can be efficiently extracted by CdSe and spiro-OMeTAD respectively, which is prerequisite for the high efficient perovskite solar cells.^{30, 31}

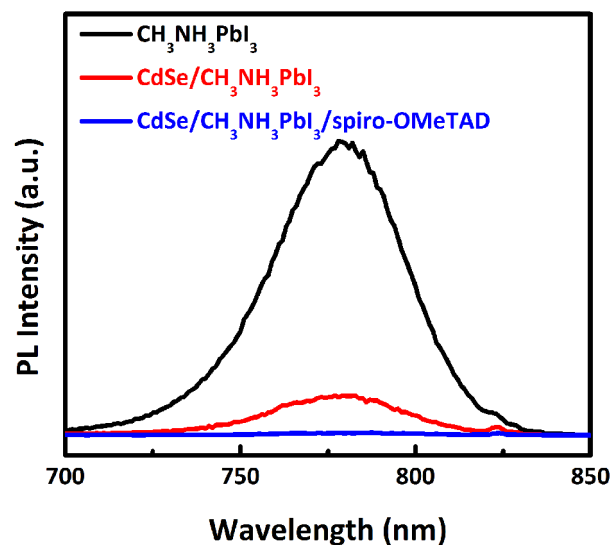


Figure 4. The PL spectra of CH₃NH₃PbI₃, CdSe/CH₃NH₃PbI₃, CdSe/CH₃NH₃PbI₃/spiro-OMeTAD on glass substrates. The excited wavelength is 600 nm.

In conclusion, we successfully demonstrated the ITO/CdSe/CH₃NH₃PbI₃/spiro-OMeTAD/Ag planar heterojunction solar cell with CdSe nanocrystals as the electron transport/extraction layer. High power conversion efficiency of 11.7% was achieved through low temperature solution processing. The results indicate that CdSe nanocrystal is an efficient electron transport/extraction material, which provides varieties for perovskite-based solar cell design.

Notes and references

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Acknowledgement

This work was supported by the Major State Basic Research Development Program (2014CB643503) and the National Natural Science Foundation of China (Grants 91233114, 51261130582, and 50990063).

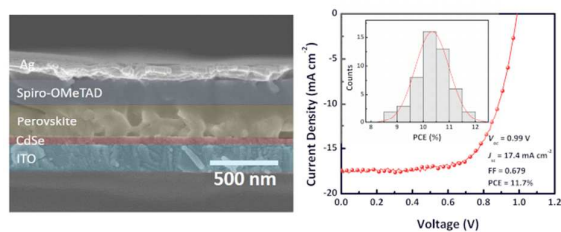
† Electronic Supplementary Information (ESI) available: [CdSe nanocrystal synthesis, material characterization, device fabrication and characterization; TEM images of CdSe nanocrystal]. See DOI: 10.1039/c000000x/

‡These authors contributed equally.

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Power conversion efficiency up to 11.7% was achieved with CdSe nanocrystal acting as electron extraction layer for perovskite solar cells under standard AM1.5G conditions in air.