

Supporting Online Material for

**Inverted Hybrid CdSe-Polymer Solar Cells Adopting
PEDOT:PSS/MoO₃ as Dual Hole Transport Layers**

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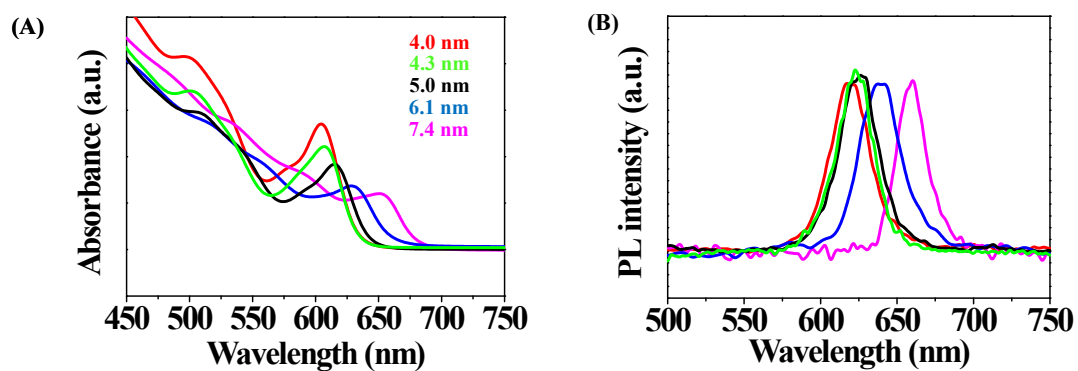


Figure S1 (A) UV-Vis absorption spectra and (B) PL spectra of CdSe QDs synthesized by reacting at 280°C for 2-30 min. The size of CdSe QDs was calculated from the wavelength of the first excitonic absorption peak of the UV-Vis spectra.

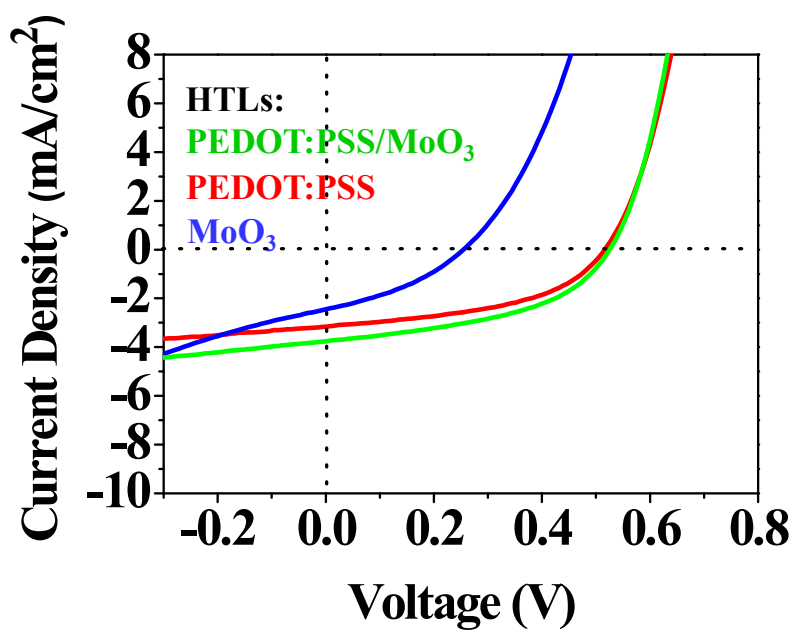


Figure S2 Typical J-V characteristics of the inverted devices under 1 sun AM 1.5G solar illumination. Devices were fabricated with a structure of ITO/ZnO/80 wt% CdSe QDs:P3HT/HTLs/Ag. A MoO₃ only, a PEDOT:PSS only, or a PEDOT:PSS/MoO₃ were used as the HTL. The thickness of PEDOT:PSS and MoO₃ are 40 and 10 nm, respectively.

Table S1 Summary of the performance parameters of inverted hybrid CdSe QDs:P3HT solar cells under AM 1.5G 1-sun illumination. Devices were fabricated with a structure of ITO/ZnO/80 wt% CdSe QDs:P3HT/HTLs/Ag. A MoO₃ only, a PEDOT:PSS only, or a PEDOT:PSS/MoO₃ were used as the HTLs. The thickness of PEDOT:PSS and MoO₃ are 40 and 10 nm, respectively.

HTL	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)	PCE _{MAX} (%)	R _s (Ω)	R _{sh} (Ω)
PEDOT:PSS/ MoO₃	0.53±0.01	3.66±0.11	45.4±1.2	0.94±0.18	1.07	4.67	26764.3
PEDOT:PSS	0.52±0.00	3.16±0.18	46.8±1.6	0.74±0.01	0.75	2.18	25512.7
MoO₃	0.21±0.04	2.62±0.29	31.9±2.8	0.18±0.19	0.34	0.40	1522.5

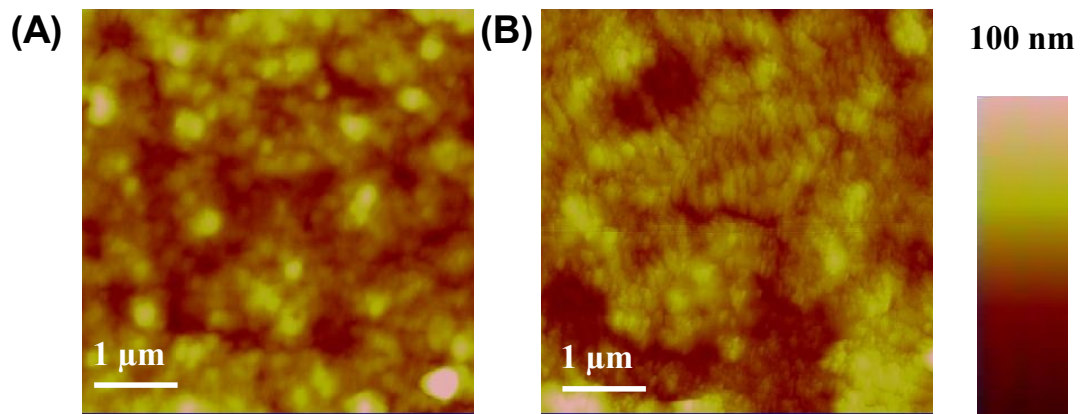


Figure S3 AFM images of 85 wt% (A) and 80 wt% (B) CdSe QDs:P3HT films on ZnO coated ITO glass.

Table S2 Summary of the fitting parameters for the dark J-V characteristics of a hole-only and an electron-only devices using Mott-Gurney's law including the Frenkel effect.

Carrier mobility	β ($\text{m}^{0.5}\text{V}^{-0.5}$)	μ ($\text{cm}^2(\text{V}\cdot\text{s})^{-1}$)
Hole	0.00019	1.8×10^{-6}
Electron	0.00009	1.1×10^{-3}

The permittivity of free space: $\epsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$

The relative permittivity¹: $\epsilon = 6$

The active layer thickness: $L = 1.04 \times 10^{-7} \text{ m}$

Improved Shockley Model Using the Space-Charge Approach⁴⁹ for calculating R_{sh} and R_s

If the charge carrier mobilities are low, space-charge effects become important at higher electric fields because there is a high current level resulting from injection of charges. A modified Shockley model which incorporates the decrease in electric field due to space-charge is used to model the organic/inorganic hybrid solar cells:

$$J = \frac{R_{sh}}{R_s + R_{sh}} \left\{ J_0 \left[\exp\left(\frac{q(V - V_b)}{nk_B T}\right) - 1 \right] + \frac{V}{SR_{sh}} \right\},$$

(S1)

where J is the total current density, V the applied voltage, J_0 the reverse dark saturation current density, n the diode ideality factor, k_B the Boltzmann's constant (1.38×10^{-23} J/K), q the magnitude of the electronic charge, T the temperature, R_{sh} the shunt resistance (Ω), R_s the series resistance (Ω), and S the area of the device. The term V_b accounts for both series resistance and space charge as follows

$$J = AV_b + BV_b^2, \quad (S2)$$

$$V_b = \frac{-A + \sqrt{A^2 + 4JB}}{2B},$$

(S3)

with $A = \frac{1}{SR_s}$ $B = \frac{9}{8L^3} \mu \epsilon \Theta$.

B accounts for the trap density² $\Theta = 1 \times 10^{12} \text{ m}^{-3}$, and the hole mobility $\mu = 1.8 \times 10^{-10} \text{ m}^2(\text{V}\cdot\text{s})^{-1}$ in a thin film with contact area $S = 1.0 \times 10^{-5} \text{ m}^2$, thickness $L = 1.04 \times 10^{-7} \text{ m}$, and permittivity $\epsilon = 5.3 \times 10^{-11} \text{ F m}^{-1}$.

We used Eqs. S1-S3 to fit the dark J-V curves (Fig. 4) at forward bias greater than 0.3 V. The n and J_0 are listed in Table S3 and the R_{sh} and R_s are listed in Table 1.

This model can also be used to describe nanocrystal-polymer devices for nanocrystals of various diameters and aspect ratios.

HTL	85 wt% CdSe		80 wt% CdSe	
	n	J_0 (mA/cm ²)	n	J_0 (mA/cm ²)
PEDOT:PSS/MoO ₃	2.62	0.0006	2.33	0.0007
PEDOT:PSS	2.88	0.002	2.93	0.001
MoO ₃	5.89	0.1	5.14	0.3

Table S3 Summary of the fitting parameters for the dark J-V curves of inverted hybrid CdSe QDs:P3HT solar cells using Eqs. S1-S3. Devices were fabricated with a structure of ITO/ZnO/CdSe QDs:P3HT/HTLs/Ag. The weight ratio of CdSe in the active layer is 85% or 80%. A MoO₃ only, a PEDOT:PSS only, or a PEDOT:PSS/MoO₃ were used as the HTLs. The thickness of PEDOT:PSS and MoO₃ are 40 and 10 nm, respectively.

The relationship between V_{OC} and dark current and the relationship of V_{OC} as a function of light intensity⁵²

The relationship between dark current and V_{OC} as well as V_{OC} as a function of light intensity can be inferred from the current density under illumination,

$$J = \frac{R_{sh}}{R_s + R_{sh}} \left\{ J_0 \left[\exp\left(\frac{q(V - JSR_s)}{nk_B T}\right) - 1 \right] + \frac{V}{SR_{sh}} \right\} - J_{ph}(V),$$

(S4)

where J_{ph} is the photocurrent. Setting $J = 0$,

$$V_{OC} = \frac{nk_B T}{q} \ln \left[\frac{J_{ph}(V_{OC})}{J_0} + 1 - \frac{V_{OC}}{SR_{sh}J_0} \right].$$

(S5)

When $J_{ph}/J_0 \gg 1$,

$$V_{OC} \propto \frac{nk_B T}{q} \ln \left[\frac{J_{ph}(V_{OC})}{J_0} \right].$$

(S6)

This suggests that a large J_0 results in a reduction in V_{OC} . Since J_{ph}/J_0 has a linear relationship with the light intensity, the ideality factor n can be obtained from the slope of the semi-logarithmic plot of V_{OC} vs. light intensity.

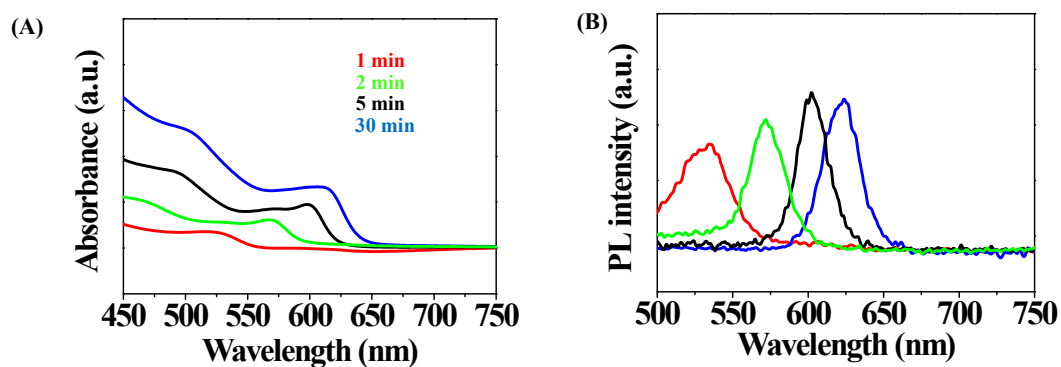


Figure S4 (A) UV-Vis absorption spectra and (B) PL spectra of CdSe NRs synthesized by reacting at 250°C for 1-30 min.

Reference

- 1 J. Yang, A. Tang, R. Zhou and J. Xue, *Sol. Energy Mater. Sol. Cells*, 2011, **95**, 476.
- 2 K. Kumari, S. Chanda, V. Vankar and V. Kumar, *Appl. Phys. Lett.*, 2009, **94**, 213503.