

Supporting Information

Improvement of Power Conversion Efficiency of P3HT:CdSe Hybrid Solar Cells by Enhanced Interconnection of CdSe Nanorods via Decomposable Selenourea

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Experimental Section

Synthesis of CdSe nanorods

Cadmium oxide (CdO $\geq 99.99\%$), TOPO (technical-grade, 90%), trioctylphosphine (TOP, 97%), and SeU (Se=C(NH₂)₂, 98%) was purchased from Sigma-Aldrich. Octylphosphonic acid (OPA) and dodecylphosphonic acid (DDPA) were purchased from PCI Synthesis. All reagents and chemicals were used without further purification. CdSe nanorods were synthesized according to the literature.^{R1} CdO (0.1926 g, 1.5 mmol), OPA (0.1942 g, 1.0 mmol), DDPA (0.5006 g, 2.0 mmol), and 1.5 g TOPO were loaded into a flask and heated up to 310 °C under nitrogen flow to dissolve CdO in the OPA/DDPA/TOPO solution. After an optically clear solution was obtained, it was cooled to 120 °C and kept under vacuum for 2 h. The solution was then heated to 315 °C and TOP-selenium complex (TOP-Se, 0.1777 g, 2.25 mmol in 1.0 g TOP) was quickly injected into the flask. This solution was kept at 315 °C for 20 min and the reaction stopped by removing the heating mantle. Hexane (10 ml) was added into the flask to dissolve the nanocrystals at 50 °C. Methanol (80 ml) was used to separate the CdSe nanorods from organic surfactants by centrifugation and decantation three times, and then the solution was dried and stored in vacuum.

Pyridine treatment of CdSe nanorods

The CdSe nanorods were put in anhydrous pyridine (30 ml) and refluxed at 120 °C for 24 h under nitrogen flow. After pyridine treatment, the CdSe nanorods were centrifuged with hexanes (120 ml) and redissolved into chloroform (10 ml). The CdSe/chloroform solution was sonicated for 30 min and then filtrated using 5 μm PTFE filter. The filtrated solution was dried and kept under vacuum.

P3HT: Allyl-end functionalized P3HT (the number average molecular weight =29400 and the polydispersity index =1.13) was synthesized at this laboratory^{R2,R3} and used without further purification.

Fabrication of P3HT:CdSe hybrid solar cells

All devices were fabricated on an indium-tin oxide (ITO)-coated glass. The ITO was sequentially cleaned using acetone, ethanol, mucasol detergent diluted in deionized water, acetone, and ethanol in an ultrasonic bath. Next, the ITO glass was exposed to ozone under UV irradiation for 20 min and coated with PEDOT:PSS (CLEVIOS P VP AI 4083) at 4000 rpm for 60 s. Then, the samples were annealed for 20 min at 150 °C. The P3HT (3 mg) and CdSe (30 mg) in mixed solvent of dichlorobenzene (0.90 ml) and pyridine (0.05ml) were prepared, while SeU in pyridine (0.05 ml) were also prepared. The two solutions were combined and stirred at 55 °C for 12 h. The solution was spin-coated onto the PEDOT:PSS-coated ITO substrates at 800 rpm for 90 s and then annealed at three different temperatures (150, 180, and 215 °C) for 10 min and then transferred to a high-vacuum chamber for Al deposition with a thickness of 100 nm at rates of about 1.0 Å/s up to 20 nm and 3.0 Å/s for the rest on top of the P3HT:CdSe-SeU blend films. An active area is 0.0314 cm².

Characterization of P3HT:CdSe hybrid solar cells

J-V characteristics of the devices were measured under 100mW/cm² illumination from an AM 1.5 G solar simulator. Hitachi 7600 transmission electron microscopy (TEM) operated at 80 kV, JEOL JEM-2100F (with Cs Corrector on STEM) operated at 200kV, and Fourier-transform infrared spectrometer (ABB MB3000) were used. XPS analysis was performed with a VG ESCALAB 220 iXL system with mono-chromated Al K α (1486.6 eV) X-ray source. Sheet resistance was measured using a Keithley model 2400 source meter and four point probe system. Optical properties of CdSe nanorod films were characterized by using Carry 5000 UV-Vis-NIR spectrophotometer.

Table S1. Calculated shunt and series resistance of P3HT:CdSe hybrid solar cells with various amounts of SeU annealed at 215 °C. The device performance was obtained under AM 1.5 G illumination from a calibrated solar simulator with an incident light intensity of 100 mW cm⁻².

SeU ratio	0	0.033	0.1
Shunt resistance ($\Omega \text{ cm}^2$)	5.22×10^2	3.57×10^2	3.7×10^2
Series resistance ($\Omega \text{ cm}^2$)	19.5	11.5	22.9
Sheet resistance (M Ω)	~ 810	~ 590	-

Table S2. Device performance of the P3HT:CdSe hybrid solar cells with various amounts of SeU at a fixed annealing temperature of 215 °C.

SeU ratio	J _{sc} (mA cm ⁻²)	V _{oc} (V)	Fill Factor (%)	PCE (%)
0	5.0	0.640	53.3	1.71
0.008	7.6	0.610	53.5	2.48
0.012	7.8	0.611	52.2	2.49
0.016	8.0	0.611	51.7	2.53
0.033	8.4	0.613	51.0	2.63
0.05	8.0	0.622	51.3	2.55
0.1	5.4	0.573	46.7	1.44

Table S3. Device performance for P3HT:CdSe hybrid solar cells without and with an SeU ratio of 0.033 after thermal annealing at three different temperatures.

Annealing temperature (°C)	J _{sc} (mA cm ⁻²)	V _{oc} (V)	Fill Factor (%)	PCE (%)
150	6.5	0.680	48.0	2.12
180	7.5	0.620	49.5	2.30
215	8.4	0.613	51.0	2.63

Figure S1 shows UV-Vis absorption spectra of CdSe nanorod films with various SeU ratios (0, 0.033, and 0.1). It is seen that the absorption spectrum of a CdSe nanorod film without SeU gives essentially the same as that of CdSe films with SeU ratios of 0.033 and 0.1. Thus, the band gap (or energy level) of CdSe would not change with the addition of SeU.

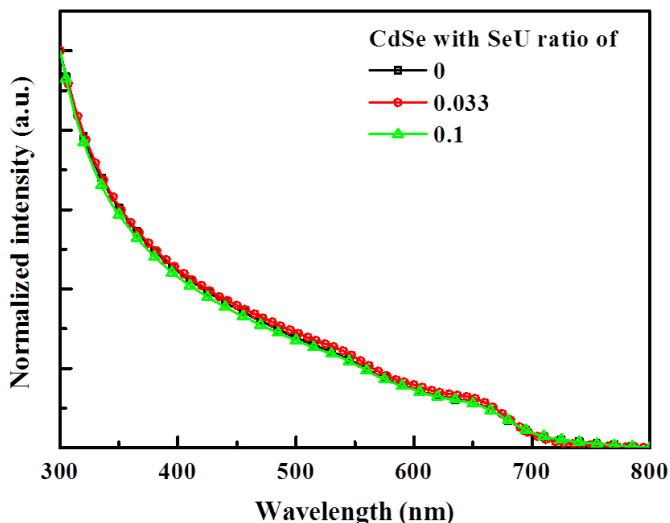


Fig. S1. UV-Vis absorption spectra of CdSe nanorod films with various SeU ratios (0, 0.033, and 0.1).

Figure S2 gives the curves of incident-photon-to-current conversion efficiency (IPCE) of P3HT:CdSe hybrid solar cells with various SeU ratios (0, 0.012, 0.033, and 0.1). The IPCE at the entire excitation spectral ranges increases as increasing SeU ratio up to 0.033, then it decreases. The maximum IPCE of P3HT:CdSe hybrid solar cell with an SeU ratio of 0.033 is 58.5 % at 460 nm. The trend of IPCE with the change of the amount of SeU is same as that of J_{SC} and PCE.

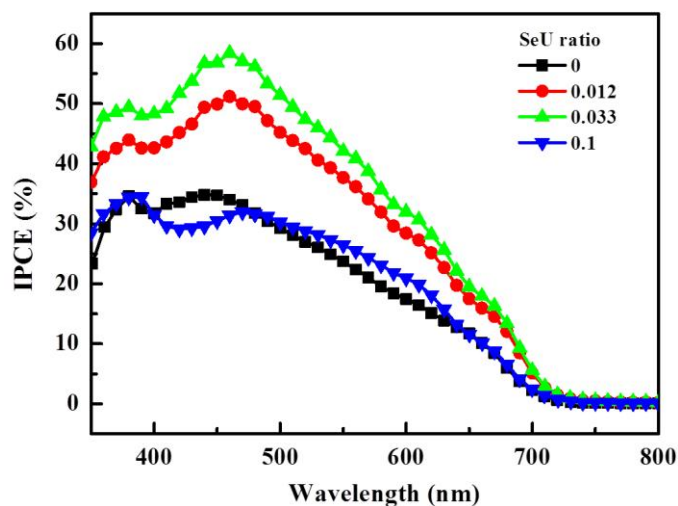


Fig. S2. IPCE curves of P3HT:CdSe hybrid solar cells with various SeU ratios (0, 0.012, 0.033, and 0.1).

Figure S3 gives TEM images of the films of 1:1 (w/w) P3HT:CdSe nanorods with three different SeU ratios after thermal annealing at 215 °C. CdSe nanorods (dark) without SeU are uniformly dispersed in P3HT (bright), suggesting that CdSe nanorods are not connected themselves (Figure S3(a)). On the other hand, P3HT:CdSe with an SeU ratio of 0.033 shows interconnection of CdSe nanorods in nanoscale without severe aggregation (Figure S3(b)). However, P3HT:CdSe with an SeU ratio of 0.1 shows that CdSe nanorods are severely aggregated (Figure S3(c)).

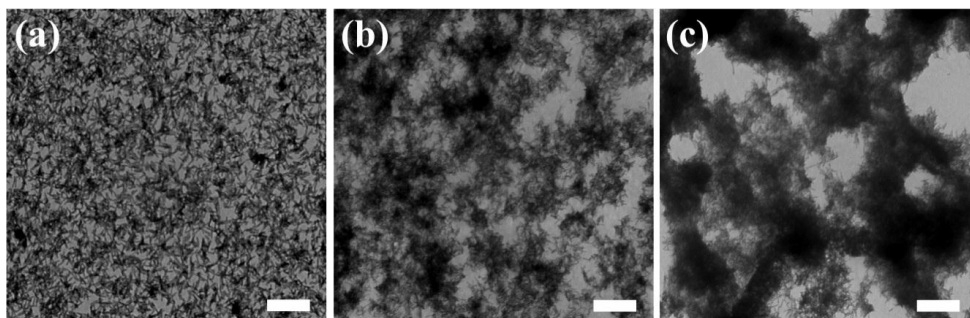


Fig. S3. TEM images of 1:1 (wt/wt) P3HT:CdSe nanorods with SeU ratio of (a) 0, (b) 0.033, and (c) 0.1 after annealing at 215 °C (scale bar = 200 nm).

Figure S4 gives FT-IR spectra of the film of CdSe nanorods without and with an SeU ratio of 0.033 before thermal annealing. The absorption bands of C-N (1410 cm^{-1}) and N-H (1640 cm^{-1} and $3000\sim 3500\text{ cm}^{-1}$) belonging to urea are clearly seen in the film with an SeU ratio of 0.033. Also, the absorbance at a band of P=O (1100 cm^{-1}) belonging to TOPO groups, of CdSe nanorod film with an SeU ratio of 0.033 is slightly lower than that of CdSe nanorod film without SeU. This means that SeU was successfully attached to CdSe nanorods by replacing TOPO groups. These peaks were maintained even after the film was washed with ethanol, indicating that SeU is chemically linked to CdSe nanorods.

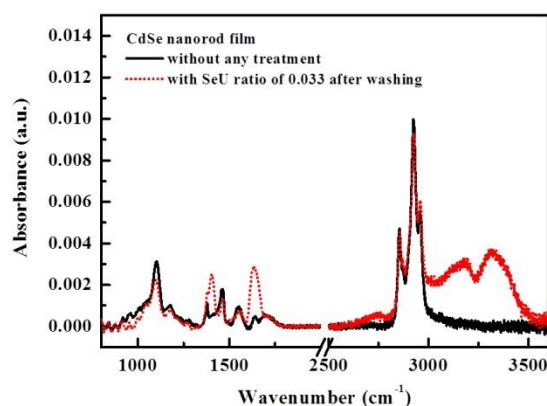


Fig. S4. FT-IR spectra of CdSe nanorod films without and with an SeU ratio of 0.033 before thermal annealing.

Figure S5 gives thermogravimetric analysis (TGA, TA Instruments TGA 2050) thermogram of SeU during heating at a rate of 0.5 °C/min. A large decrease in the weight of SeU is first observed at ~ 185 °C, and SeU is completely decomposed at ~ 205 °C. The final weight loss (37 wt %) of SeU is the essentially the same as the amount urea (36 wt %) in SeU.

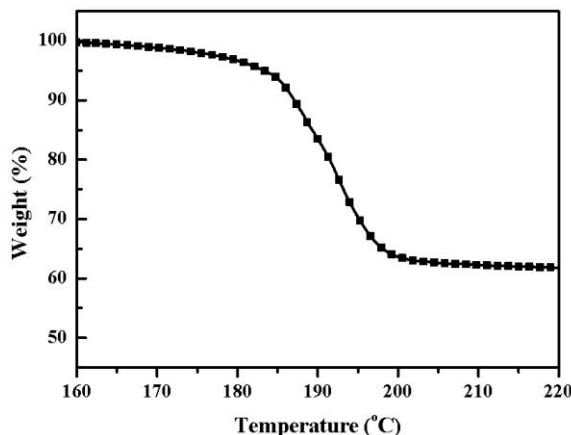


Fig. S5. TGA thermogram of SeU during heating at a rate of 0.5 °C/min under nitrogen atmosphere.

Figure S6 gives J - V characteristics of P3HT:CdSe hybrid solar cells with an SeU ratio of 0.033 annealed at 215 °C, 230 °C, and 250 °C. When annealed at higher temperatures (for instance, 230 °C or 250 °C), J_{SC} and V_{OC} (and thus PCE) are lower than those of another device annealed at 215 °C. The decrease in J_{SC} and V_{OC} might be because the grain sizes of the P3HT crystals of a sample crystallized at a constant temperature lower than the melting temperature of P3HT ($T_m \sim 230$ °C) are different from those of another prepared by the cooling from higher temperatures than T_m .^{R4,R5}

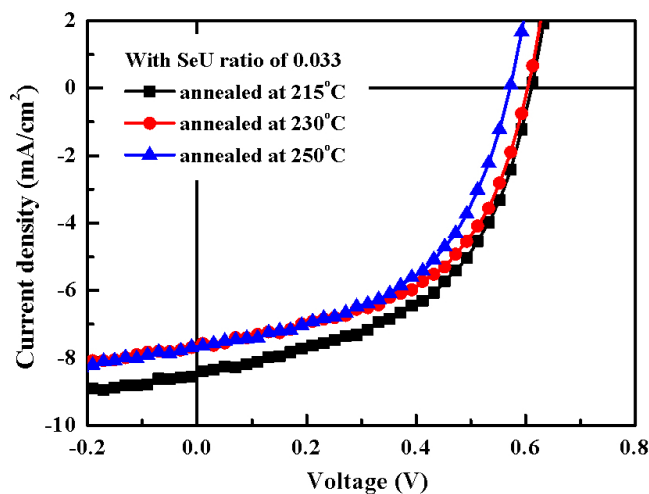


Fig. S6. J - V characteristics of P3HT:CdSe hybrid solar cells with an SeU ratio of 0.033 annealed at 215 °C, 230 °C, and 250 °C.

Figure S7 gives Se 3d XPS spectra of CdSe nanorod films without and with SeU ratios of 0.033 and 0.1 after annealing at 215 °C for 10 min. CdSe nanorod film with SeU shows a peak at 53.8 eV, which is the same as that of single component of CdSe. Since the peak at 55.5 eV corresponding to selenium peak, was not observed, similar to the film without SeU,^{R6} selenium (Se-Se linkage) was not formed in CdSe nanorods, namely, all of Se in SeU was converted to selenide form (for instance, CdSe).

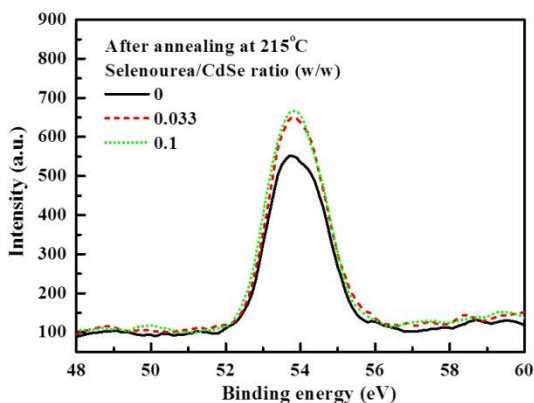


Fig. S7. Se 3d XPS spectra of CdSe nanorod films without and with SeU ratios of 0.033 and 0.1 after thermal annealing at 215 °C.

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