

## Electronic Supplementary Information for Energy & Environmental Science

### Electronic Supplementary Information

#### Efficient Polymer/Nanocrystal Hybrid Solar Cells from Aqueous Materials

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*Materials:* NaBH<sub>4</sub> (99%), tellurium powder (200 mesh, 99.8%), cadmium chloride hemi(pentahydrate) (CdCl<sub>2</sub>, 99%), and 2-mercaptoethylamine (MA, 98%) were purchased from Aldrich. P-xylene dichloride (98%) and tetrahydrothiophene (98%), zinc acetate dihydrate were purchased from Alfa Aesar. All materials were used as received. Methanol was AR grade, and water was deionized.

*Preparation of MA-capped CdTe NCs:* MA-capped aqueous CdTe NCs were prepared according to our previous report [1]. Typically, aqueous precursor of CdTe NCs were obtained by injecting a freshly prepared solution of NaHTe into 12.5 mM N<sub>2</sub>-saturated CdCl<sub>2</sub> solutions in the presence of MA at pH range of 5.5~6.0. The molar ratio of Cd<sup>2+</sup>/MA/HTe<sup>-</sup> was set as 1:2.4:0.2. The resultant precursor solutions were refluxed at 100 °C to maintain the growth of NCs; their sizes increased with the reflux duration. After preparation, the NCs solution was centrifugated at a speed of 6,000 rpm with the addition of isopropanol to remove superfluous salts and MA. Then the precipitated NCs were redissolved in deionized water with a concentration of 47 mg ml<sup>-1</sup>.

*Preparation of PPV precursor and ZnO NCs:* The PPV precursor was prepared following reference [2] (see Scheme S1). Briefly, the monomer *p*-xylene-bis(tetrahydrothiophenium chloride) was prepared by reaction of dichloro-*p*-xylene (3 g) with tetrahydrothiophene (3 ml) at 50 °C in methanol (40 ml) for 24 h. The product was purified by concentrating the

## Electronic Supplementary Information for Energy & Environmental Science

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reaction solution and then precipitating the condensed solution in cold acetone (0 °C). The solid was collected by filtration and dried thoroughly in vacuum oven. After that, 11.6 mL of 0.4 M NaOH solution was added into the *p*-xylene-bis(tetrahydrothiophenium chloride) aqueous solution in 30 min. The reaction proceeded at 0 °C for 30 min and then was terminated by the addition of 0.4 M HCl aqueous solution to neutralize the reaction solution. Then precursor solution was dialyzed in distilled water for a week. The concentration of the polymer was obtained by evaporating known volumes to dryness and weighing. The solution of PPV precursor in this case was measured to be 5 mg ml<sup>-1</sup>. The ZnO NCs of ca. 5 nm in diameter were prepared in methanol according to previous report [3]. ZnO NCs were synthesized by hydrolysis and condensation of zinc acetate dihydrate by potassium hydroxide in methanol using a Zn<sup>2+</sup>:OH<sup>-</sup> ratio of 1:1.7. The resulting ZnO NCs are dispersed in mixing solvents of chloroform and methanol (v/v, 1/9) with the concentration of 7.5 mg ml<sup>-1</sup>.

*Device fabrication and characterization:* For device fabrication, indium tin oxide (ITO) glass was cleaned by ultrasonic in chloroform, acetone, and isopropanol for 10 min each, and rinsed by deionized water before drying in N<sub>2</sub> flow. Active layer was fabricated by spin-coating the blends of CdTe NCs and PPV precursor under air condition. When the active layer was dry, the devices were transferred into a glove box filled with nitrogen atmosphere (H<sub>2</sub>O<1 ppm and O<sub>2</sub><1 ppm) and annealed at 320 °C for 60 min. The back electrode of 70 nm Al was finally evaporated under high vacuum. A buffer layer of conductive polymer, poly(3,4-ethylene dioxylenethiophene):poly(styrene sulfonic acid) (PEDOT:PSS) was spin coated on the cleaned ITO glass. For the cathode modification, a thin film of ZnO NCs was spin coated on the annealed active layer before evaporating Al.

UV-visible absorption spectra were obtained using a Shimadzu 3100 UV-Vis spectrophotometer. Fluorescence spectroscopy was performed with a Shimadzu RF-5301 PC spectrophotometer. TEM was conducted using a Hitachi H-800 electron microscope at an acceleration voltage of 200 kV with a CCD camera. SEM image was taken with a JEOL

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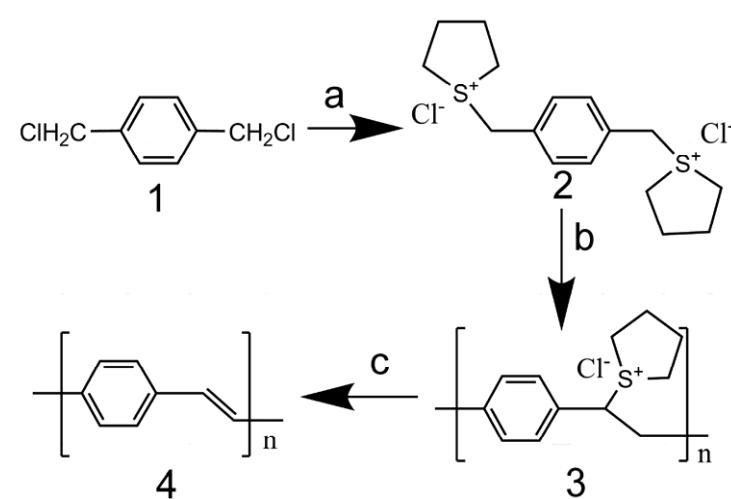
FESEM 6700F electron microscope with primary electron energy of 3 kV. AFM tapping mode measurements were performed on a Nanoscope IIIa scanning probe microscope (Digital Instruments), using a rotated tapping mode etched silicon probe (RTESP) tip. The film thickness was determined using a Dektak150 surface profiler. Thermo-gravimetric Analysis (TGA) was conducted on TGA Q500 from TA instruments. XPS examinations were performed using an ESCALAB 250 spectrometer (VG, Thermo Scientific). The highest occupied molecular orbital (HOMO) levels of PPV and the valence band edge of CdTe NCs were determined by the ultraviolet photoelectron spectroscopy (UPS) measurements of a bulk thin film spin-coated on ITO. Current density–Voltage measurement of the devices was conducted on a computer-controlled Keithley2400 source meter measurement system. AM 1.5G (100 mW cm<sup>-2</sup>) illumination from a Scientech 500 W solar simulator acted as a light source. EQE measurement was measured under illumination of monochromatic light from the xenon lamp using a monochromator (Jobin Yvon, TRIAX 320) and detected by a computer-controlled Stanford SR830 lock-in amplifier with a Stanford SR540 chopper.

## References

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- [2] S. H. Jin, M. S. ang, H. S. Suh, H. N. Cho, J. H. Lee, Y. S. Gal, *Chem. Mater.*, **2002**, *14*, 643-650.
- [3] W. J. E. Beek, M. M. Wienk, M. Kemerink, X. N. Yang, R. A. J. Janssen, *J. Phys. Chem. B*, **2005**, *109*, 9505-9516.

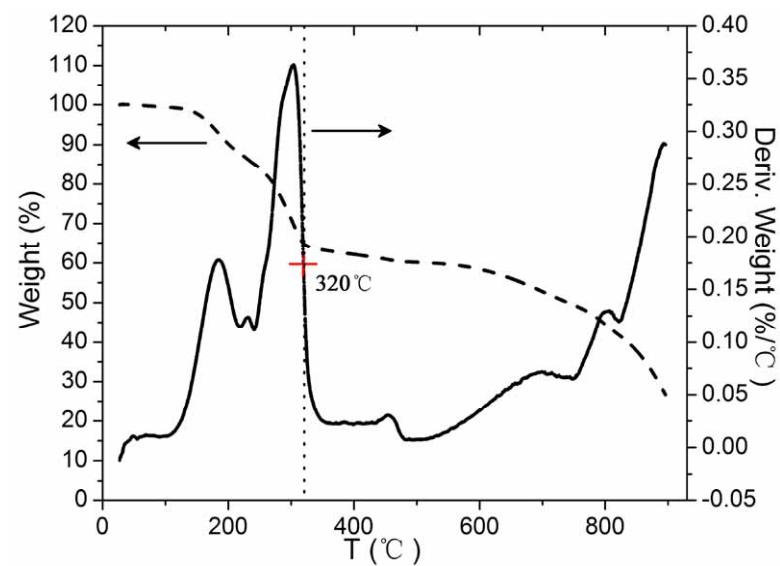
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Scheme S1. Synthesis route of PPV precursor (3) and PPV (4). Materials: (1) dichloro-*p*-xylene; (2) *p*-xylene-bis(tetrahydrothiophenium chloride). (a) tetrahydrothiophene, MeOH, 50 °C, 24 h; (b) NaOH, 0 °C, 30 min; neutralization (HCl); dialysis (water); (c) 320 °C, N<sub>2</sub>.



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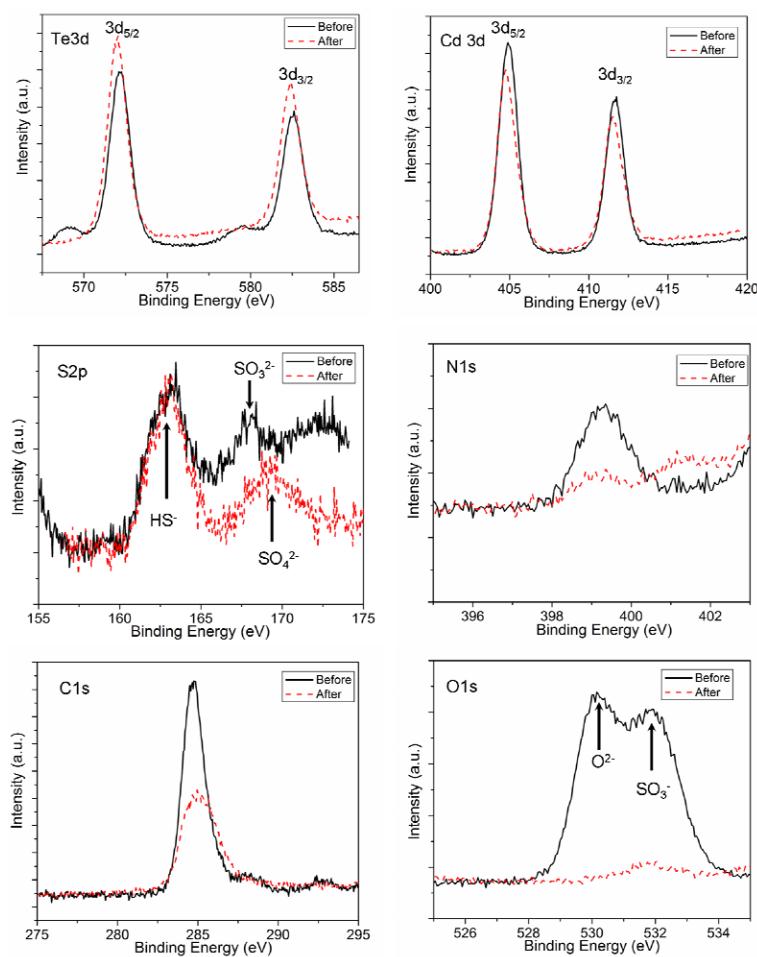
Figure S1. The TGA of MA-capped CdTe NCs.



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**Figure S2.** XPS analysis of CdTe NCs film before and after annealing treatment.

Samples were dip-coated on cleaned silicon substrates. The annealing treatment was carried out in glove box filled with N<sub>2</sub> gas.



The XPS data indicated that annealing treatment removed most of MA covering on NC surface. The remaining S, N, C and O elements corresponded to 42, 18, 43, and 0.03% of original contents, respectively. The S 2p sulfite peak at 168.2 eV was replaced by sulfate at 169.2 eV after annealing treatment. The O 1s contained oxide peak at 530.1 eV and sulfite peak at 532.0 eV before annealing treatment.