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Carbon nanoparticles as an interfacial layer between TiO_2-coated ZnO nanorod arrays and conjugated polymers for high-photocurrent hybrid solar cells

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Experimental

General. All reagents and solvents were used as received without further purification. Indium tin oxide (ITO) coated glass slides with sheet resistance of 8–12 Ω/square was purchased from Delta Technologies. SEM images were taken using a Philips SEM 515 scanning electron microscope or a Tescan Vega3 scanning electron microscope. Crystal structure characterization was carried out by X-ray diffraction measurements on a Rigaku Miniflex automated powder X-ray diffractometer (Cu Kα, 35 kV 15 mA, Ni filter). FTIR spectra were measured with a Shimadzu IRAffinity-1 Fourier transform infrared spectrophotometer. UV-vis absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Fluorescence spectra were recorded with a Shimadzu RF-5301PC spectrofluorophotometer.

Preparation of CNPs: Graphite powders (< 20 μm, Sigma-Aldrich) were placed into a stainless steel vial together with milling balls of different diameters (4–12 mm) in glove box. The powder-to-ball mass ratio was set to 1:10. The vial was then sealed and the ball milling was carried out for 40 h. The as-milled powders were placed in 5 M HNO_3 (15 mL) followed by reflux for 18 h in N_2. The reaction mixture was then centrifuged at 3000 rpm for 10 min. The top clear dark brown-colored solution was collected, to which 5 M NaOH solution was added dropwise until pH reached 7~8. The mixture was passed through a 0.45 μm filter. After adjusting the pH of the filtrate to 3~4 with 1 M HCl, dialysis was then performed on the solution with a Float-A-Lyzer G2 dialysis device (approximate molecular weight cut off 100–500 Daltons) to remove the salt(s). The resulting solution was evaporated under reduced pressure to yield water-soluble CNPs as black powders.

Cyclic Voltammetry (CV) Measurements. CV studies were carried out under argon using BAS Epsilon EC electrochemical station employing a 1 mm^2 Pt disk as the working electrode, $Ag/AgNO_3$ as the reference electrode and a Pt wire as the counter electrode. For the thin film measurement, a 2 mg mL^{-1} CNP aqueous solution was drop-casted on the surface of Pt disk and the film was dried in air. A 0.1 M tetra-n-butylammonium hexafluorophosphate solution in acetonitrile was used as the supporting electrolyte. Its potential was internally calibrated using a ferrocene/ferrocenium (Fc/Fc^+) redox couple whose absolute energy was assigned as −4.80 eV vs vacuum. Same with electrochemically synthesized graphene quantum dots,[S1] there are no obvious redox peaks observed during CV scans for the CNP film. For the solution measurement, a 0.2 M KNO_3 solution in DI water was used as supporting electrolyte and the scan rate was 20 mV s^{-1}. CNPs were dissolved in DI water (~0.4 mg mL^{-1}). $K_4Fe(CN)_6$ was used as reference for the measurements and assigned an absolute energy of −4.80 eV vs vacuum.[S2]

Fabrication and Characterization of HSCs: TiO_2-ZnO films were prepared following our previously published procedure.[S3] The TiO_2-ZnO films were heated to 80 °C, immersed into a CNP solution [0.5 mg mL^{-1} in H_2O/EtOH (1/1, v/v)] and kept at r.t. overnight. The films were taken out, flushed with H_2O/EtOH mixture (1/1, v/v) and dried by compressed air and then under vacuum at 50 °C for 6 h. P3HT (with number average molecular weight of 16.2 KDa and polydispersity index of 1.2) solution (30 mg mL^{-1}) in 1,2-dichlorobenzene was heated at 50 °C with stirring for 14 h and then passed through a 0.45 μm filter. The P3HT film was deposited by spin coating the P3HT solution onto the TiO_2-ZnO-CNP substrate at 600 rpm for 1 min. The films were annealed at 140 °C for 1 h under nitrogen atmosphere. Finally, a 120-nm thick Au layer was deposited onto the P3HT layer by thermal evaporation under high vacuum (< 2×10^{-6}

MB). For comparison, corresponding CNP-free devices were also fabricated following the same procedures. Current–voltage characteristics of the devices were measured using a Keithley 2400 source meter. The devices were illuminated with an Oriel xenon arc lamp solar simulator with an AM1.5 filter at an intensity of ~100 mW cm^{-2}. J_{SC}, V_{OC}, and maximum output power density ($J_{max}V_{max}$) were derived from the $J-V$ curves. The PCE was calculated by $\eta = J_{SC}V_{OC}FF/P_{in}$, where P_{in} is the incident power density and FF is given by $J_{max}V_{max}/J_{SC}V_{OC}$.

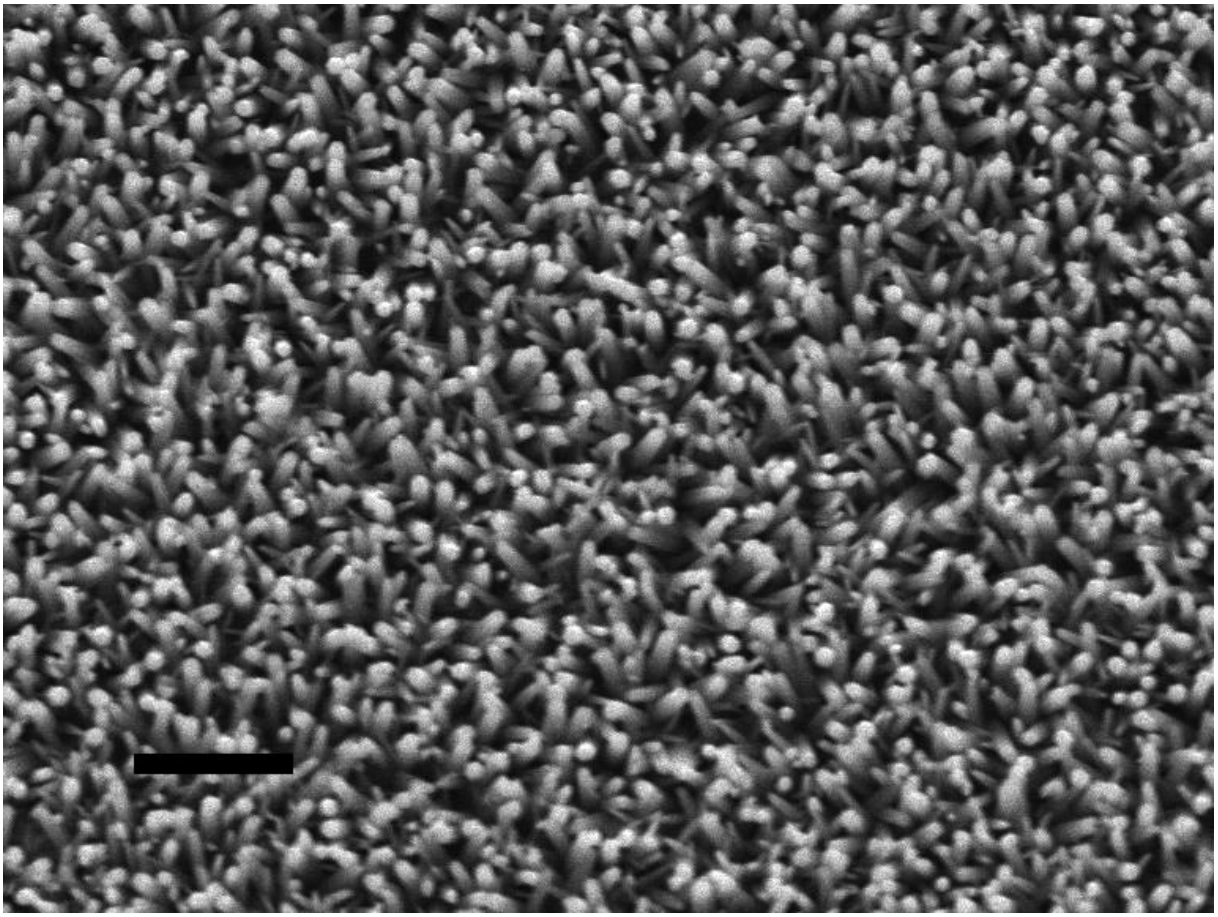

Fig. S1 SEM image of ZnO nanorods. Scale bar: 2 μm.

[S1] Y. Li, Y. Hu, Y. Zhao, G. Shi, L. Deng, Y. Hou and L. Qu, *Adv. Mater.*, 2011, **23**, 776.

[S2] K. E. Heusler and W. J. Lorenz, in *Standard Potentials in Aqueous Solution*, ed. A. J. Bard, R. Parsons, J. Jordan, Marcel Dekker, New York, USA, 1985, ch. 14.

[S3] Y. Li, P. Lu, M. Jiang, R. Dhakal, P. Thapaliya, Z. Peng, B. Jha and X. Yan, *J. Phys. Chem. C*, 2012, **116**, 25248.