Supporting Information for

Tunable Size and Sensitization of ZnO Nanoarrays as Electron Transport Layer for Enhancing Photocurrent of Photovoltaic Devices

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Experimental Section

Synthesis of ZnO NAs

ZnO nanoparticles (NPs) layer fabricated via an easy and convenient *in stiu* method[5] process were covered on indium-tin-oxide-coated glass (ITO, Shenzhen Laibao Hi-Tech Co., Ltd., China) for nucleation. The ZnO nanoarrays (NAs) were hydrothermally grown by suspending the ZnO NPs-coated ITO substrate upside down in an aqueous solution of zinc acetate dihydrate (0.025 M, $Zn(CH_3COO)_2 \cdot 2H_2O$, Aldrich, 99.9%) and hexamethylenetetramine (0.025 M, J&K chemistry, 90%) at 90 °C for different hydrolysis time.

Synthesis of ZnO NAs with different shells

Deposition of Ag_2S, CdS, and CdS/Ag_2S on the ZnO NAs were carried out by successive ion layer adsorption and reaction (SILAR) to form ZnO/Ag_2S NAs (ZA NAs), ZnO/CdS NAs (ZC NAs) and $ZnO/CdS/Ag_2S$ NAs (ZCA NAs). Typically, ZnO NAs were first immersed in 10 mM aqueous solution of $AgNO_3$ (Energy

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Chemical, 95%) or $Cd(NO_3)_2$ (Energy Chemical, 95%) for 30 s and rinsed with water, followed by immersion in 10 mM Na_2S (Meryer, 90%) aqueous solution for 30 s and water-washing, which was referred to as one SILAR cycle. The defined shell thickness (L) was obtained by different SILAR cycle number. Then nanoarrays were dried and stored in ambient conditions for use. Small organic molecules 2-(2-(2-methoxyethoxy) ethoxy) ethyl under-10-enyl malonate C_{60} (C-EMMC, 2mg/ml in dichlorobenzene) was spin-coated on the top of nanoarrays.

Device fabrication

The synthesis process and structure of the device in this work was schematically illustrated in **Scheme 1.** The region regular poly(3-hexylthiophene-2,5-diyl) (P3HT, 20 mg, Mw = 48300 g/mol, head-to-tail, regioregularity > 90%, Rieke Metals, Inc.) and [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$, 20 mg, 99.5% purity, Nano-C) were dissolved in 1,2-dichlorobenzene solution (P3HT:$PC_{61}BM$ 1:1 w/w) or the poly{4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophene-4,6-diyl}eshiou (PTB7, 10 mg, One materials, Inc.) and [6,6]-phenyl-C_{71}-butyric-acid-methyl-ester ($PC_{71}BM$, 15 mg, Nano-C) dissolved in the chlorobenzene solution were spin-coated on the top ZnO NAs or ZA NAs, ZC NAs, ZCA NAs, and then dried in a nitrogen glovebox to get a full infiltration of active layer into the interspaces between nanoarrays. Finally, 6 nm MoO_3 as holes transport layer and Ag electrode were sequently deposited on the top of the active layer in a vacuum atmosphere to form devices with an effective contact area of 6.06 mm^2 (all the areas were tested with an aperture).

Characterizations

Scanning electron microscopy (SEM, FEI Quanta 200F), atomic force microscopy (AFM, Bruker, MultiMode 8), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM, JEOL, JEM-2100F) were carried out to confirm the nanostructure of the bare ZnO NAs and ZnO NAs with different shells. The Philips X'Pert Pro MPD with Cu Kα radiation (λ = 1.54056 Å) was applied to gather the X-ray diffraction (XRD) data. To gain insight on the photophysics and electronic properties of the pure ZnO NAs and ZnO NAs with different shells, photoluminescence spectroscopy (PL, Hitachi F-7000), transmittance spectroscopy, UV-vis-NIR spectroscopy, diffuse reflectance spectroscopy (performed by Perkin-Elmer Lambda 750 with integrating sphere) were utilized. The thicknesses of all the layers were measured by surface profilometer (AMBIOS TECHNOLOGY ltd. XP-2). X-ray photoelectron spectroscopy (XPS) was executed by employing a Kratos AXIS Ultra. Ultraviolet photoelectron spectroscopy (UPS) was carried out by the AXIS-ULTRA DLD spectrometer (Kratos Analytical Ltd.). For the UPS measurements, He I (21.22 eV) radiation line from a discharge lamp was used, with an experimental resolution of 0.15 eV. All the UPS measurements of the onset of photoemission for determining the work function were done using standard procedures with a -5 V bias applied to the sample. The current-voltage (*J-V*) characteristics of the devices under illumination were tested via a Keithley 2400 Source Meter. The light intensity of the simu-lated AM 1.5G illumination (Abet Solar Simulator Sun2000) was 100 mW/cm^2. The incident photon-to-current efficiency (IPCE) was measured by using of an Oriel Corner-stone 260 1/4 m monochromator equipped with an Oriel 70613NS QTH lamp, and the incident light was calibrated with a monocrystalline Si solar cell.

**Space-charge-limited-current (SCLC) mobility measurement**

In order to characterize the carrier mobility of modified device, electron-only devices and hole-only devices were fabricated. The electron-only devices used a diode configuration of ITO/Al/P3HT:PCBM/LiF/Al and the hole-only devices was built as ITO/PEDOT:PSS/P3HT:PCBM/MoO$_3$/Ag. The carrier mobility was measured using the SCLC model at low voltage which is described by (Equation 1):

$$J=9\varepsilon_0\varepsilon_r\mu V^2/8L^3 \text{ (1)}$$

Where ε_0 is the permittivity of free space (8.85×10^{-12}F m^{-1}), ε_r is the dielectric constant of P3HT or PCBM (assumed to 3), μ is the mobility of an electron, V is the applied voltage, and L is the film thickness. The thickness of the BHJ blend for SCLC measurement was about 120 nm. By fitting the results to a space-charge-limited form, $J^{0.5}$ versus V is plotted in **Figure 7**.
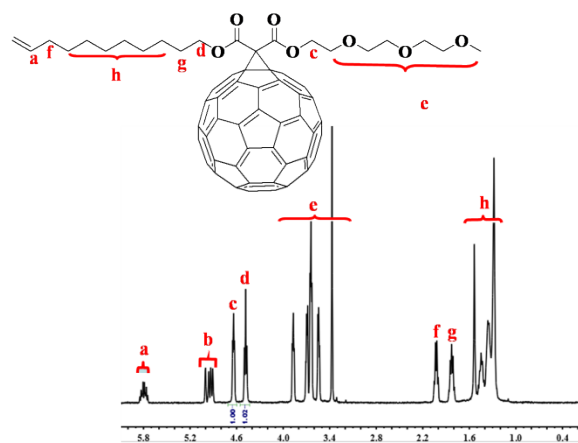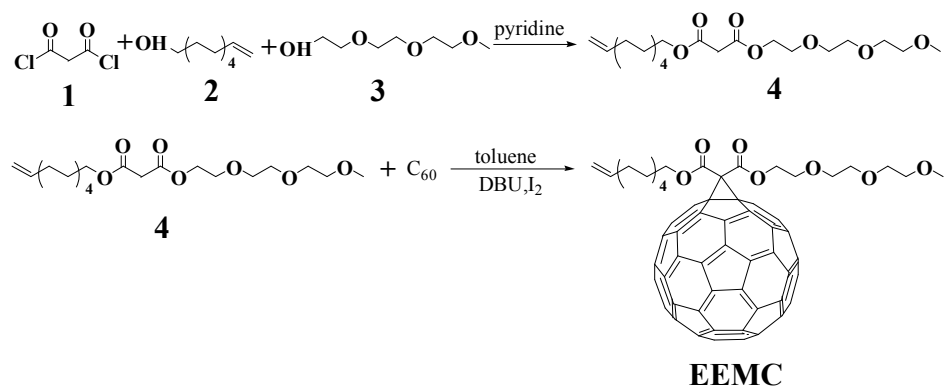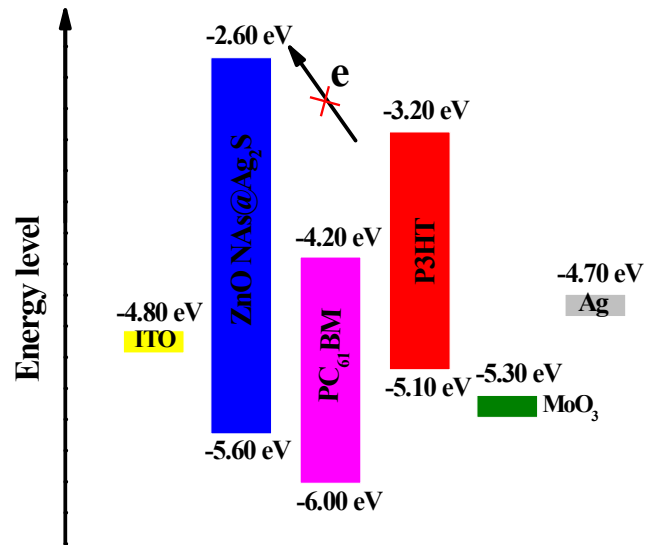
Figure S1. The synthetic process and ^{1}HNMR figure of EEMC.
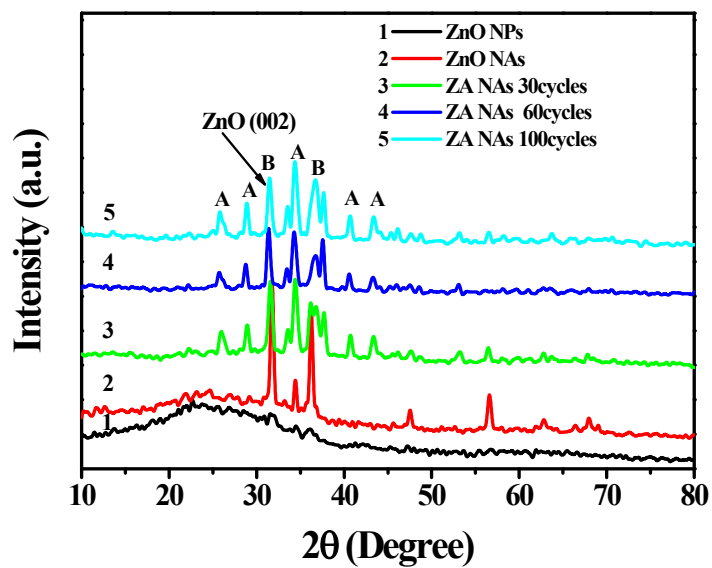
Figure S2. XRD patterns of ZnO NPs, ZnO NAs, and ZA NAs with different thickness of Ag_2S shell, (for the thickness of Ag_2S shell is controlled by the cycles of SILAR).
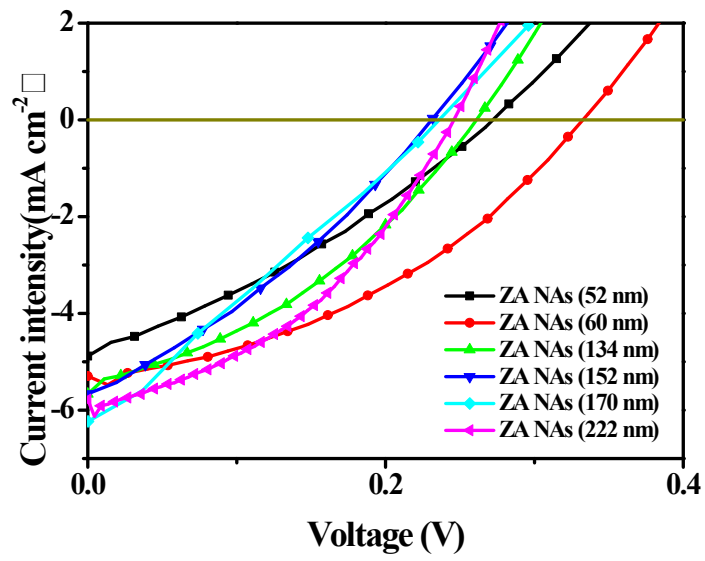
Figure S3. *J-V* curves of the devices based on ZA NAs with different ZnO NAs

length.

Figure S4. The energy band diagram of glass/ITO/ZA NAs/P3HT:PC$_{61}$BM/MoO$_3$/Ag solar cell.

Table S1. Photovoltaic parameters of the devices with ITO/ZA

NAs/P3HT:PC$_{61}$BM/MoO$_3$/Ag structure.

Buffer layer	J_{sc} (mA·cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
ZA NAs (52 nm)	7.13±0.35	0.20±0.02	41.6±2.1	0.6±0.1(0.7)[a]
ZA NAs (60 nm)	7.28±0.40	0.21±0.02	41.8±3.2	0.7±0.2(0.8)[a]
ZA NAs (134 nm)	6.00±0.33	0.18±0.01	46.6±2.3	0.5±0.1(0.6)[a]
ZA NAs (152 nm)	6.48±0.30	0.16±0.02	35.1±2.7	0.4±0.1(0.5)[a]
ZA NAs (170 nm)	6.05±0.31	0.17±0.01	39.1±1.3	0.4±0.1(0.5)[a]
ZA NAs (222 nm)	4.89±0.27	0.11±0.01	31.2±2.0	0.2±0.1(0.3)[a]

*All values represent averages from twelve devices on a single chip. [a] The best device PCE.

Table S2. Electron mobility of the devices based on ZnO NPs/EEMC, ZnO NAs/EEMC, ZA NAs/EEMC, ZC NAs/EEMC and ZCA NAs/EEMC, respectively.

Devices	ZnO NPs /EEMC	ZnO NAs /EEMC	ZA NAs /EEMC	ZC NAs /EEMC	ZCA NAs /EEMC
Electron mobility [$cm^2 V^{-1} s^{-1}$]	8.98×10^{-4}	1.34×10^{-3}	1.31×10^{-3}	1.70×10^{-3}	1.95×10^{-3}