Supplementary information

**Bismuth Oxysulfide Modified ZnO Nanorod Arrays as an Efficient Electron Transport Layer for Inverted Polymer Solar Cells**

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Fig. S1 (a) TEM images of Bi$_2$O$_2$S nanoparticles. (b) XRD spectra of pure Bi$_2$O$_2$S powder.

Figure S1 (a) shows that our synthetic Bi$_2$O$_2$S material is the nanoparticles with diameter of more than 10 nanometers. Clear lattice fringe of an individual Bi$_2$O$_2$S nanoparticle is observed in Figure S1 (a), which indicates that the prepared Bi$_2$O$_2$S nanoparticle has good crystallinity. The interplanar spacing of 3.77 Å is observed which corresponds to the (110) planes of orthorhombic Bi$_2$O$_2$S. The inset of Figure S1 (a) is the SEAD of the Bi$_2$O$_2$S nanoparticle, indicating the
monocrystalline structure of prepared Bi$_2$O$_2$S nanoparticle. The XRD spectrum in figure S1 (b) confines the structure and phase purity of Bi$_2$O$_2$S particles. The orthorhombic phase of Bi$_2$O$_2$S (JCPDS no.34-1493) contributes to the appearance of diffraction peaks in Figure S1 (b), which is indexed to the Pnnm space group. Diffraction peaks of Bi$_2$O$_2$S nanoparticles at 2θ = 14.9, 24.2, 27.4, 30.0, 32.3, 32.7, 33.7, 45.0, 45.6, 47.4, 50.9, 53.8, 55.3, 57.3, 58.3, 59.2, 61.6, 62.3, 69.2, and 72.4° match (020), (110), (120), (040), (130), (101), (111), (141), (060), (002), (151), (112), (221), (161), (132), (170), (250), (080), (212), and (261) planes of the orthorhombic structure of Bi$_2$O$_2$S, respectively, which shows the high purity of the Bi$_2$O$_2$S powder. It means that our method can prepare pure Bi$_2$O$_2$S sample, in contrast with the previously reported methods. 2,3

![Graphs showing UV-vis spectra, CV measurement, and absorption spectra](image)

**Fig. S2** (a) UV-vis spectra of Bi$_2$O$_2$S. (b) CV measurement of Bi$_2$O$_2$S powder. (c) UV-vis spectra of ZnO NRAs and ZnO NRAs/Bi$_2$O$_2$S with different concentrations, respectively. (d) The plot of $(\alpha h\nu)^2$ versus $h\nu$ of ZnO NRAs,
Figure S2 (a) shows the UV-vis absorption spectra of bare Bi$_2$O$_2$S, and the intrinsic absorption peak is at 580 nm. Optical band gap can be calculated by $(\alpha h\nu)^2 = A(h\nu - E_g)$, while A is proportionality constant and $E_g$ is the band gap. Therefore, we calculate the $E_g$ of Bi$_2$O$_2$S is ca. 1.31 eV. Figure S2(b) is the cyclic voltammetry measurement of Bi$_2$O$_2$S, according to the formula $E_{\text{HOMO}} = -(E_{\text{onset}} + 4.8 + E_{\text{Fc/Fc}^-})$. The highest occupied molecular orbital (HOMO) of Bi$_2$O$_2$S is $-5.54$ eV, with $E_g$ ca. 1.31 eV. Therefore, the corresponding lowest unoccupied molecular orbital (LUMO) level of Bi$_2$O$_2$S is calculated to -4.23 eV. Figure S2 (c) gives the UV-vis absorption spectra of bare ZnO NRAs and ZnO NRAs/Bi$_2$O$_2$S composites. The intrinsic wide band-gap of ZnO leads to a strong UV light absorption of bare ZnO NRAs and the weak visible light absorption at 587 nm corresponds to the surface defects in the ZnO NRAs. The absorption spectra of the prepared films demonstrate a high absorbance and sharp peak between 300 and 400 nm after Bi$_2$O$_2$S coating. As known for the quantum-confinement effect, Bi$_2$O$_2$S nanoparticles may be responsible for the red shift of the absorption edge. The weak visible light absorption at 587 nm shows a slight increase, which can be attributed to the Bi$_2$O$_2$S coating. From figure S2 (d), $E_g$ of bare ZnO NRAs and ZnO NRAs/2% Bi$_2$O$_2$S composites locate at ca. 3.17 eV and 3.00 eV, respectively. So ZnO NRAs/Bi$_2$O$_2$S composites possess nice transmittance in the visible light section.

Figure S3 shows the strong peaks at binding energy at 158.8 eV and 164.1 eV with typical doublet splitting of 5.32 eV, which correspond to the Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$, respectively. The peaks found between Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$ at 161.0 eV and 162.2 eV are assigned to S 2p$_{1/2}$ and S 2p$_{3/2}$, respectively. In addition, the presence of shoulders at 159.9 and 165.2 eV is associated to the Bi-O bonds. From figure S3, we can see that the intensity of S peaks becomes stronger with the
increase of the Bi$_2$O$_2$S concentration, showing the formation of Zn-S bonding on ZnO surface.

Figure S3 Bi 4f XPS spectra of modified ZnO NRAs with different concentrations of Bi$_2$O$_2$S.

Figure S4 (a) is the bare ZnO TEM image, and the inset is selected area electron diffraction (SAED) pattern. Figure S4 (b) is a HRTEM image with the lattice fringes of 0.26 nm, corresponding to the interplanar spacing of the (002) plane of wurtzite-type ZnO. Figure S4 (c, e and g) are TEM images of ZnO NRAs/Bi$_2$O$_2$S composites with different concentrations, respectively. After Bi$_2$O$_2$S coating, all ZnO NRAs show almost the same image with more homogeneous surfaces. The phenomenon occurs as the increased compactness. The indexing of the SAED patterns shows a crystal two-dimensional lattice and polycrystal diffraction rings, representing ZnO polycrystalline nanorods and single crystal coating Bi$_2$O$_2$S, which shows the selected area is the combination of polycrystalline ZnO and single crystalline Bi$_2$O$_2$S. Moreover, we can see from HRTEM images in Figure S4 (d, f and h) that all films show two different regions, the core of darkish region and shell of light region. The lattice fringe of 0.26 nm corresponds to the interplanar spacing of the (002) plane of wurtzite-type ZnO in core regions and the lattice fringe of 0.20 nm corresponds to the (141) plane of orthorhombic phase Bi$_2$O$_2$S. The thickness of the light region is about 5-10 nm, which shows ZnO NRAs of darkish region are covered with 5-10 nm
Bi$_2$O$_2$S nanoparticles of light region. Further increasing the Bi$_2$O$_2$S concentration to 3%, the shell of light region is detected to be darker, and it can be verified by the SEM images before that some Bi$_2$O$_2$S are precipitated on the ZnO NRAs. This demonstrates the successful formation of ZnO/Bi$_2$O$_2$S core-shell structure.
Figure S4 (a)-(h) TEM images of bare ZnO NPs and ZnO NRAs/Bi$_2$O$_2$S. (b), (d), (f) and (h) HRTEM images of ZnO NPs with d-spacing of 2.60 Å and Bi$_2$O$_2$S of 0.20 Å.

Figure S5 XRD spectra of bare ZnO NRAs and ZnO NRAs/Bi$_2$O$_2$S.

Figure S5 displays XRD patterns of bare ZnO NRAs and ZnO NRAs/Bi$_2$O$_2$S. The substrates are ITO and its corresponding peaks are marked with asterisk. In XRD pattern of bare ZnO NRAs, all the diffraction peaks can be accurately assigned to the hexagonal structure of ZnO (JCPDS Card no. 36-1451) with a relatively strong orientation along (002) plane for ZnO NRAs. Most of the growth of the ZnO NRAs are perpendicular to the substrate surface which is c-axis oriented. We can clearly observe that after coated with 2% Bi$_2$O$_2$S, the peak of ZnO (002) becomes the most dominant. So 2% Bi$_2$O$_2$S coated ZnO NRAs possess the better crystallinity, which will ultimately
increase the charge transfer in solar cells. In addition to the peaks of ZnO, no other characteristic peaks corresponding to any kind of impurity are measured, and Bi$_2$O$_2$S does not alter the crystal structure of ZnO NRAs. However, the Bi$_2$O$_2$S signal is too weak in ZnO NRAs/Bi$_2$O$_2$S composites (maximum 3%) to be detected, therefore, Bi$_2$O$_2$S brown powder is also measured by XRD (Fig. S1 (b)) alone.

The water contact angles (WCAs) of the ZnO NRAs (Bi$_2$O$_2$S)/P3HT:PCBM are measured in figure S6 (a, b, c and d). We can see from figure S6 (a) that WCA of P3HT:PCBM on bare ZnO NRAs is 120.77°, and the WCA of P3HT:PCBM on coated ZnO NRAs/1%, 2% and 3% Bi$_2$O$_2$S increase to 134.13° (Figure S6 (b)), 135.20° (Figure S6 (c)) and 135.19° (Figure S6 (d)), respectively. The increase of WCAs after coated with Bi$_2$O$_2$S shows that ETLs play an influence on active layer. Besides, WCAs of pure PCBM (Figure S 6 (e)), pure P3HT (Figure S 6 (f)) and P3HT:PCBM blend films (Figure S6 (c)) on ZnO NRAs/2% Bi$_2$O$_2$S are 110.73°, 137.01° and 135.20°, respectively. Obviously, the WCAs of P3HT:PCBM are very close to that of the pure P3HT film, which clearly elucidates that the surface of blend films is governed by the P3HT film and the vertical phase-separation occurs between P3HT and PCBM within the Bi$_2$O$_2$S coating. When P3HT and PCBM are vertical phase separation, the active layer near ZnO NRAs side will be PCBM rich region. Consequently, the efficient electron transfer will be induced, increasing the $J_{sc}$ of the devices.
Figure S6 Water contact angle of (a)-(d) ZnO NRAs/(0%, 1%, 2%, 3%) Bi$_2$O$_2$S/P3HT:PCBM, (e) ZnO NRAs/2% Bi$_2$O$_2$S/PCBM, (f) ZnO NRAs/2% Bi$_2$O$_2$S/P3HT.

Reference


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