Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2019

Supplementary information

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

Zuping Wu^{a,b}, Huangzhong Yu^{a,d*}, Shengwei Shi^{c*}, Yanping Li^e

^aSchool of Physics and Optoelectronics, South China University of Technology, 510640 Guangzhou, China

^bSchool of Materials Science & Engineering, South China University of Technology, 510640 Guangzhou, China

^cSchool of Materials Science and Engineering, Wuhan Institute of Technology, 430205 Wuhan, China

^dSouth China Institute of Collaborative Innovation, 523808 Dongguan, China

eWuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, 430074

Wuhan, China

Corresponding author. E-mail address: hzhyu@scut.edu.cn (H.Z. Yu), shisw@wit.edu.cn (S.W. Shi)



Fig. S1 (a) TEM images of Bi₂O₂S nanoparticles. (b) XRD spectra of pure Bi₂O₂S powder.

Figure S1 (a) shows that our synthetic Bi_2O_2S material is the nanoparticles with diameter of more than 10 nanometers. Clear lattice fringe of an individual Bi_2O_2S nanoparticle is observed in Figure S1 (a), which indicates that the prepared Bi_2O_2S nanoparticle has good crystallinity. The interplanar spacing of 3.77 Å is observed which corresponds to the (110) planes of orthorhombic Bi_2O_2S . The inset of Figure S1 (a) is the SEAD of the Bi_2O_2S nanoparticle, indicating the monocrystalline structure of prepared Bi_2O_2S nanoparticle. The XRD spectrum in figure S1 (b) confines the structure and phase purity of Bi_2O_2S particles. The orthorhombic phase of Bi_2O_2S (JCPDS no.34-1493) contributes to the appearance of diffraction peaks in Figure S1 (b), which is indexed to the Pnnm space group.¹ Diffraction peaks of Bi_2O_2S nanoparticles at 20 = 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_2O_2S , respectively, which shows the high purity of the Bi_2O_2S powder. It means that our method can prepare pure Bi_2O_2S sample, in contrast with the previously reported methods. ^{2,3}



Fig. S2 (a) UV-vis spectra of Bi_2O_2S . (b) CV measurement of Bi_2O_2S powder. (c) UV-vis spectra of ZnO NRAs and ZnO NRAs/ Bi_2O_2S with different concentrations, respectively. (d) The plot of $(\alpha hv)^2$ versus hv of ZnO NRAs,

and ZnO NRAs/2%Bi $_2O_2S$ composite.

Figure S2 (a) shows the UV-vis absorption spectra of bare Bi₂O₂S, 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_2O_2S is ca. 1.31 eV. Figure S2(b) is the cyclic voltammetry measurement of Bi₂O₂S, according to the formula $E_{HOMO} = -(E_{onset}+4.8+E_{Fc/Fc+})$.^{4,5} The highest occupied molecular orbital (HOMO) of Bi₂O₂S is -5.54 eV, with Eg ca. 1.31 eV. Therefore, the corresponding lowest unoccupied molecular orbital (LUMO) level of Bi₂O₂S is calculated to -4.23 eV. Figure S2 (c) gives the UV-vis absorption spectra of bare ZnO NRAs and ZnO NRAs/Bi₂O₂S 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. ⁶ The absorption spectra of the prepared films demonstrate a high absorbance and sharp peak between 300 and 400 nm after Bi₂O₂S coating. As known for the quantum-confinement effect, Bi₂O₂S nanoparticles may be responsible for the red shift of the absorption edge.⁷ The weak visible light absorption at 587 nm shows a slight increase, which can be attributed to the Bi₂O₂S coating. From figure S2 (d), E_g of bare ZnO NRAs and ZnO NRAs/2% Bi2O2S composites locate at ca. 3.17 eV and 3.00 eV, respectively. So ZnO NRAs/Bi₂O₂S 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. ^{8,9} 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. ¹⁰ From figure S3, we can see that the intensity of S peaks becomes stronger with the

increase of the Bi₂O₂S 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 Bi₂O₂S.

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. ¹¹ Figure S4 (c, e and g) are TEM images of ZnO NRAs/Bi₂O₂S composites with different concentrations, respectively. After Bi₂O₂S 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 Bi₂O₂S. Moreover, we can see from HRTEM images in Figure S4 (d, f and h) that all films show two different regions, 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 Bi₂O₂S. ¹² 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_2O_2S nanoparticles of light region. Further increasing the Bi_2O_2S 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_2O_2S are precipitated on the ZnO NRAs. This demonstrates the successful formation of ZnO/Bi_2O_2S core-shell structure.





Figure S4 (a)-(h) TEM images of bare ZnO NPs and ZnO NRAs/Bi₂O₂S. (b), (d), (f) and (h) HRTEM images of



ZnO NPs with d-spacing of 2.60 Å and Bi₂O₂S of 0.20 Å.

Figure S5 XRD spectra of bare ZnO NRAs and ZnO NRAs/Bi₂O₂S.

Figure S5 displays XRD patterns of bare ZnO NRAs and ZnO NRAs/Bi₂O₂S. 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. ¹³ 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% Bi₂O₂S, the peak of ZnO (002) becomes the most dominant. So 2% Bi₂O₂S 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 Bi₂O₂S does not alter the crystal structure of ZnO NRAs. However, the Bi₂O₂S signal is too weak in ZnO NRAs/Bi₂O₂S composites (maximum 3%) to be detected, therefore, Bi₂O₂S brown powder is also measured by XRD (Fig. S1 (b)) alone.

The water contact angles (WCAs) of the ZnO NRAs (Bi₂O₂S)/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% Bi₂O₂S 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 Bi₂O₂S 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% Bi₂O₂S 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 Bi₂O₂S 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%) Bi₂O₂S/P3HT:PCBM, (e) ZnO NRAs/2%

Bi₂O₂S/PCBM, (f) ZnO NRAs/2% Bi₂O₂S/P3HT.

Reference

1 X. Zhang, Y.F. Liu, G.H. Zhang, Y.Q. Wang, H. Zhang and F.Q. Huang, ACS Appl. Mater. Interfaces 2015, 7, 4442–4448.

2 I. A. Kariper, Spectrochim. Acta. A 2016, 163, 102-107.

3 E. Koyama, I. Nakai and K. Nagashima, Acta Crystallogr. 1984, 40, 105-109.

4 J. Kim and M. Kang, Int. J. Hydrogen Energ. 2012, 37, 8249-8256.

5 C. F. Zhang, T. M. Higgins, S. H. Park, S. E. O'Brien, D. H. Long and J. V. Coleman, Nano Energy 2016, 28, 495-505.

6 M. D. R. Peralta, U. Pal and R. S. Zeferino, ACS Appl. Mater. Interfaces 2012, 4, 4807-4816.

7 P. Lv, W. Fu, H. Yang, H. Sun, Y. Chen, J. Ma, X. Zhou, L. Tian, W. Zhang and M. Li, Crystengcomm 2013,

- 15, 7548-7555.
- 8 S. Bera, S. Ghosh and R. N. Basu, New J. Chem. 2018, 42, 541-554.
- 9 E. B. Díaz-Cruz, O. A. Castelo-González, C. Martínez-Alonso, Z. Montiel-González, M. C. Arenas-Arrocena and H. Hu, Sci. Semicond. Process. 2018, 75, 311-318.
- 10 M. Han and J. Jia, J. Power Sources 2016, 329, 23-30.
- 11 B. Liu and H. C. Zeng, J. Am. Chem. Soc. 2003, 125, 4430-4431.
- 12 P. Ruankham, S. Yoshikawa and T. Sagawa, Phys. Chem. Chem. Phys. 2013, 15, 9516-9522.
- 13 P. R. Nikam, P. K. Baviskar, J. V. Sali, K. V. Gurav, H. K. Jin and B. R. Sankapal, Ceram. Int. 2015, 41,

10394-10399.