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Supplementary Information

ZnO&GeSe composite electron transport layer for organic solar cells

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The preparation of materials

Poly[(2,6-(4,8-bis(5-(2-ethylhexyl) thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene))-co-(1,3-di(5-thiophene-2-yl)-5,7-bis(2-ethylhexyl)benzo[1,2-c:4,5-c′]dithiophene-4,8-dione)] (PBDB-T) and 9-bis(2-methylene(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl) dithieno-[2,3-d:2′,3′-d′]-s-indaceno [1,2-b:5,6- b′] dithiophene (ITIC) were bought form Luminescent Technology. Poly[(2,6-(4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene))-co-(1,3-di(5-thiophene-2-yl)-5,7-bis(2-ethylhexyl)-benzo[1,2-c:4,5-c′]dithiophene-4,8-dione))] (PM6) and poly[(2,6-(4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene))-co-(1,3-di(5-thiophene-2-yl)-5,7-bis(2-ethylhexyl)-benzo[1,2-c:4,5-c′]dithiophene-4,8-dione))] (Y6) were supplied by Solarmer Materials Inc. Chlorobenzene (CB), chloroform (CF), 1-chlorobenzene (CN) and 1,8-diiodooctane (DIO) were supported by Sigma-Aldrich. Bulk GeSe was bought form Nanjing MKNANO Tech..

Production of 2D GeSe nanosheets

Liquid-phase Exfoliated (LPE) method was used to obtain the 2D GeSe. Briefly, 40 mg bulk GeSe was directly added to 4 ml IPA solvent. In this procedure, 80 mg bulk GeSe was added to the 4 ml IPA solvent and the configured suspension was ultrasonicated at 5°C for 5 hours. The suspension was centrifuged at 2000 rpm for 30 min to remove blocky GeSe, and then further centrifuged at 8000 rpm for 10 min to obtain fewer layered GeSe nanosheets in the supernatant.

Device Fabrication

All OSCs devices were made on indium tin oxide (ITO) substrates and the structure of the inverted OSCs was ITO/ZnO/GeSe/active-layer/MoO_3/Ag from bottom to top. Ultrasonic cleaning agent, deionized water, acetone, ethanol and isopropyl alcohol were used to clean the surface of ITO glass for 20 min. The ITO glass was dried in a drying oven at 80°C for 8 hours, and then treated with ultraviolet ozone for 15 min. Next, we spin coated ZnO sol-gel solution on ITO substrate and annealed it at 200 °C for 60 min to obtain a 30 nm thick electron transport layer. Then the exfoliated GeSe colloidal solution was applied to the ZnO surface at a rotational speed of 1000/2000/3000/4000 rpm respectively, and then annealed at 200 °C for 20 minutes to construct the 2D GeSe electron transport layer. As the spin-coating speed increases, the thickness of the GeSe layer decreases, the thickness of the GeSe layer with 2000 rpm/s rotational speed is about 15 nm, and the result is measured by JS100A- High precision step meter. PM6 and Y6 (1:1.2 by weight, 16 mg/ml) were dissolved in the mixture of CF and CN (99.5:0.5 by volume). The PM6:Y6 solution was spun on the surface of 2D GeSe electron transport layer with a thickness of 150 nm to obtain PM6:Y6 active layer. PBDB-T and ITIC (1:1 by weight, 20 mg/ml) were dissolved in the mixture of CB and DIO (99.5:0.5 by volume). The PBDB-T:ITIC solution was spun on the surface of 2D GeSe electron transport layer with a thickness of 100 nm to obtain PBDB-T:ITIC active layer. At last, we used MoO_3 and Ag to form the hole transport layer (2 nm) and metallic anode (100 nm) respectively in the vacuum evaporation. The size of ITO glass substrate is 1.5 cm × 1.5 cm, each ITO glass contains 5 sub devices, and the effective area of each device was 0.15 cm^2.

Characterization and measurement

The surface morphology, size and thickness of 2D GeSe were demonstrated by atomic force microscope (AFM). Transmission electron microscopy (TEM) images were taken using the JEOL-2100F electron microscope. X-ray diffraction (XRD) spectrum was taken by using bruker advance diffractometer. JEOL-2100F electron microscope was used to take the transmission electron microscopy (TEM) images. X-ray photoelectron spectroscopy (XPS) was measured by Al Kα X-ray source. The Renishaw InVia Raman microscope, excited by 532 nm wavelength laser was used to obtain the Raman spectra of 2D GeSe. SPEX 1681 automatic fluorescence spectrometer was used to obtain Photoluminescence (PL) spectra. Keithley 2400 source meter was used to measure the *J-V* curves under AM 1.5 G, 100 mW/cm^2 and SRF50 system was used to measure the external quantum efficiency (EQE) of OSCs. The water contact angle (WCA) was measured by DSA100, and the functional groups of zinc oxide and three biophenolic acid small molecules were determined by Fourier Transform infrared spectroscopy (FTIR, Bruker ERTEEX 70). The film thickness was measured by using a step meter (KP Technology SKP5050).

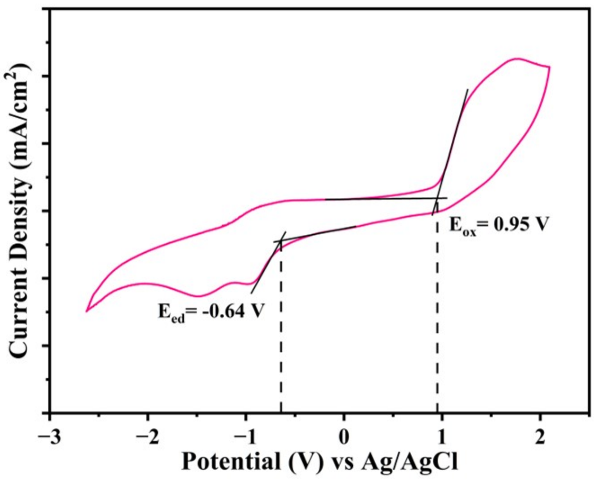

Figure S1. Cyclic voltammogram (vs. Ag/AgCl) of 2D GeSe.

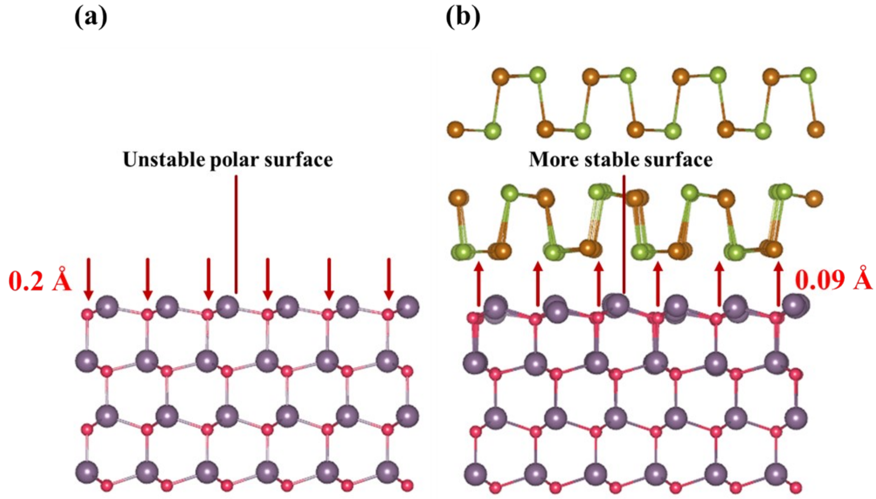

Figure S2. The change of ZnO polar surface structure (a) before and (b) after 2D GeSe modification.

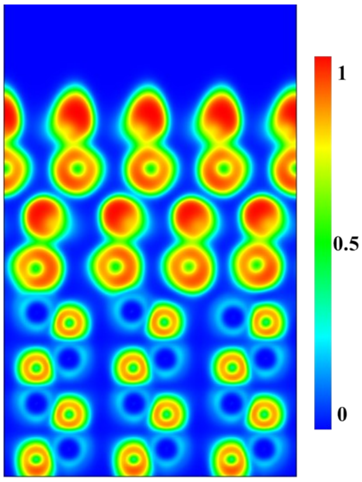

Figure S3. Electron localization function (ELF) of ZnO&GeSe ETL

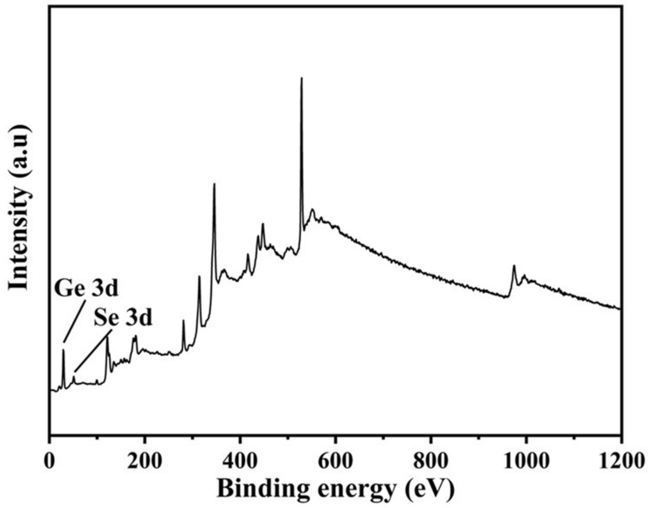

Figure S4. Full XPS spectrum of GeSe

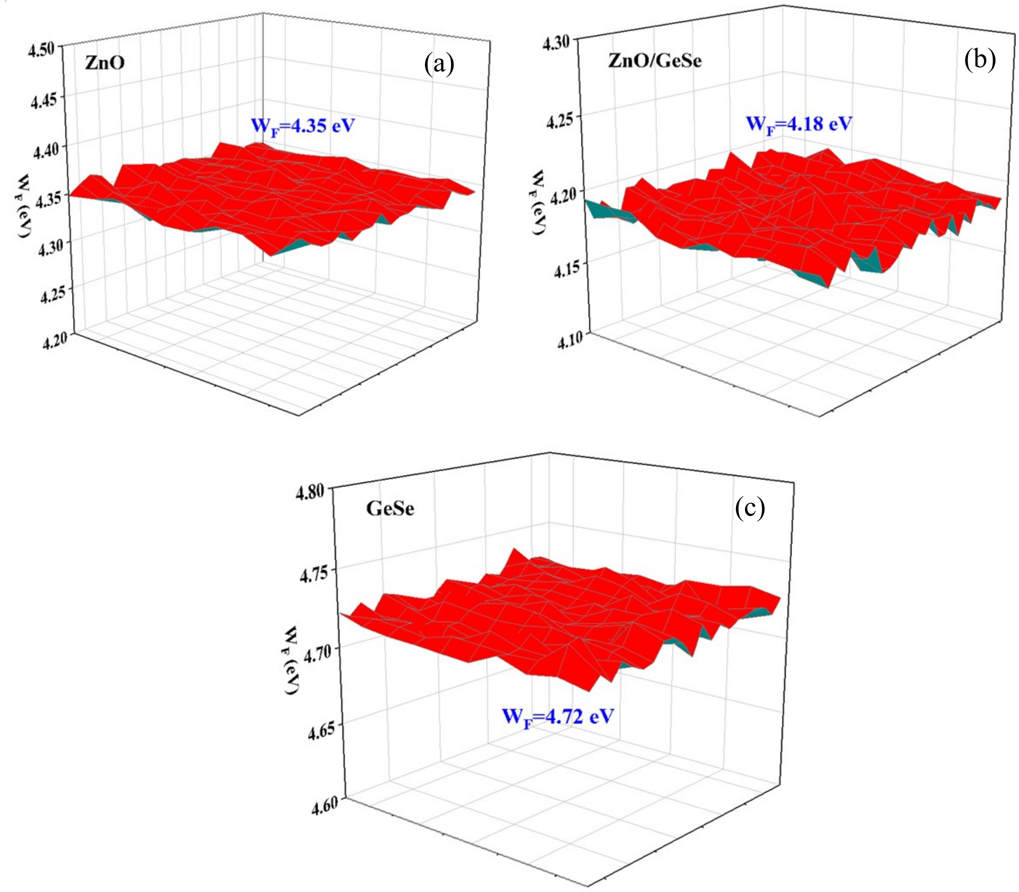

Figure S5. The work functions of ZnO (a), ZnO/GeSe (b), GeSe (c) by Kelvin probe to measure.

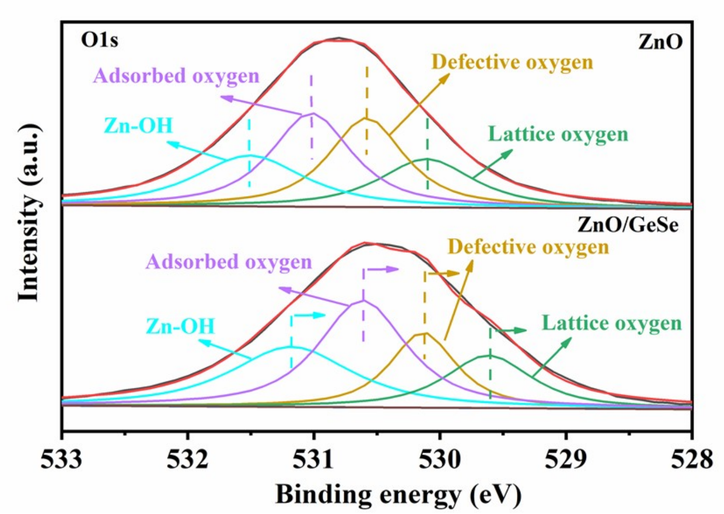

Figure S6. XPS images of O1s in ZnO and ZnO/GeSe.

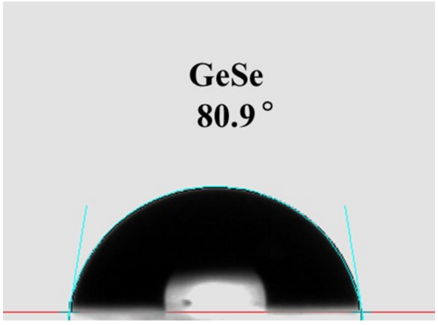

Figure S7. Water contact angle on GeSe

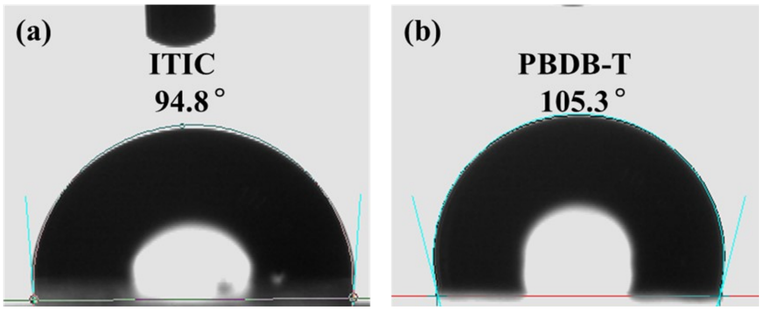

Figure S8. (a) Water contact angle on ITIC and (b) PBDB-T.

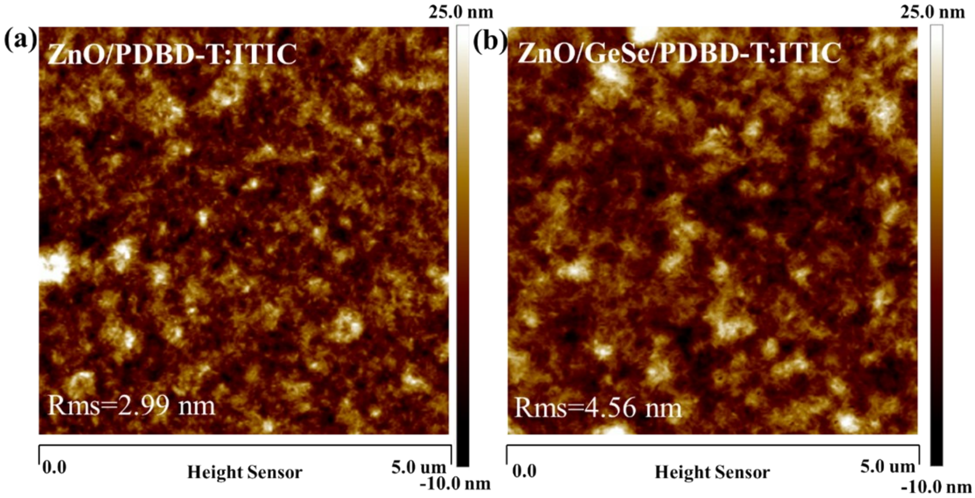

Figure S9. AFM surface images of ZnO/PDBD-T:ITIC (a), and ZnO/GeSe/PDBD-T:ITIC (b).

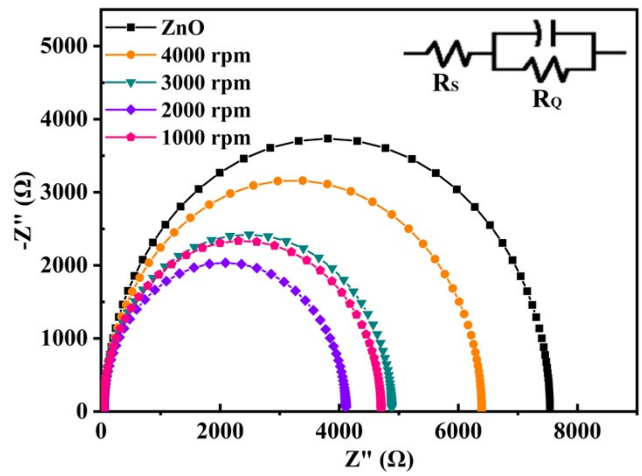

Figure S10. Electrochemical impedance spectroscopy (EIS) of OSCs based on PBDB-T:ITIC with ZnO ETL and ZnO&GeSe composite ETL.

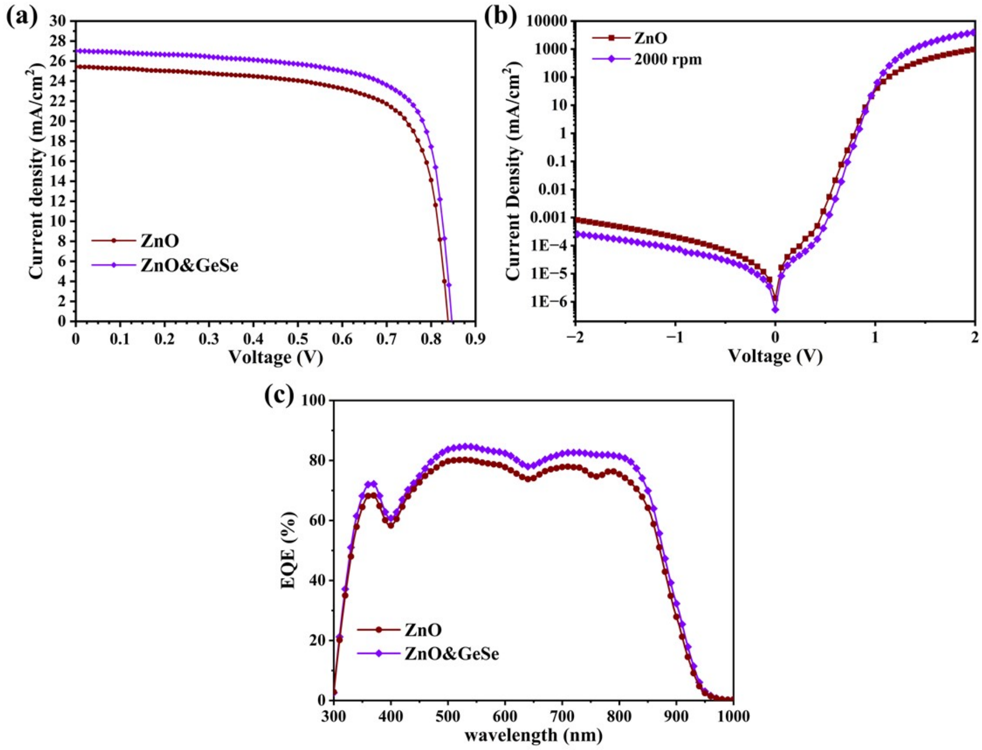

Figure S11. (a) *J–V* curves of OSCs based on PM6:Y6 with ZnO ETL and ZnO&GeSe composite ETL. (b) *J–V* curves under darkness. (c) EQE spectra of OSCs based on PM6:Y6 with ZnO ETL and ZnO&GeSe composite ETL.

Table S1 The fitted details from the O1s XPS spectra for ZnO and ZnO/GeSe films.

Samples	Chemical state	Position (eV)	Intensity (a.u.)	Area ratio (%)	$\sum X^2$
ZnO	lattice oxygen	530.1	62497.6	18.170	13.353
	defective oxygen	530.6	95126.9	27.656	
	adsorbed oxygen	531.0	107446.1	31.238	
	Zn-OH	531.5	78891.1	22.936	
ZnO/GeSe	lattice oxygen	529.6	68790.6	17.348	18.415
	defective oxygen	530.1	75006.3	18.916	
	adsorbed oxygen	530.6	141876.5	35.780	
	Zn-OH	531.2	110849.8	27.956	

Table S2. Fitting results of equivalent circuit parameters

ETL type	$\boldsymbol{R_S}$ **(Ω)**	$\boldsymbol{R_Q}$ **(kΩ)**
Pure ZnO	23.8	7.49
ZnO&GeSe (4000 rpm)	16.8	6.36
ZnO&GeSe (3000 rpm)	15.8	4.86
ZnO&GeSe (2000 rpm)	15.1	4.04
ZnO&GeSe (1000 rpm)	15.5	4.66