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Supporting Information

In-Situ Formation of $CsPbBr_3$/ZnO Bulk Heterojunctions Towards Photodetector with Ultrahigh Responsivity

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Experimental section

Preparation of colloidal ZnO: All chemicals were purchased from Aladdin and used without further purification. ZnO was prepared according to the previously reported procedures with some modification.[1,2] 30 mL DMSO of 3 mmol zinc acetate hydrate and 10 mL ethanol of 7.5 mmol TMAH were mixed into a flask under vigorous stirring. Keep continuous stirring for 12 h. Then ethyl acetate was added into the solution until the milk white colloidal ZnO were precipitated. The obtained ZnO were washed two times with ethyl acetate and redispersed in 5 mL DMSO finally.

Preparation of $CsPbBr_3$/ZnO precursor solution: Typically, the as-prepared ZnO was dissolved in dimethyl-sulfoxide (DMSO) to form a colloidal solution. Sequentially, CsBr (0.5 mmol) and $PbBr_2$ (0.5 mmol) were added into 1.6 mL of ZnO solution under vigorous stirring for 1.0 h. The $CsPbBr_3$/ZnO bulk heterojunctions in-situ formed in solution without further operating in this hybrid system. The hybrid solution was treated by a slight ultrasound before further using. Pristine $CsPbBr_3$ precursor solution was prepared by adding CsBr (0.5 mmol) and $PbBr_2$ (0.5 mmol) into 1.6 mL of DMSO, followed by a 1.0 h vigorous stirring.

Device fabrication: Commercial Au electrodes deposited on Si substrates covered with 300 nm SiO_2 layer were purchased from professional manufacturer for use. The electrodes were used after cleaning by ultrasonication in acetone and isopropanol, followed by treating in ultraviolet/ozone to remove residues. The active-layer was deposited on the cleaned electrode by drop-coating the above hybrid solution, and then transferred into vacuum oven at 100 °C for 30 min. After solvent evaporation, the PD was sent for further characterizations.

Charaterizations: XRD measurements were carried out with a Bruker D8 Advanced XRD system. The absorption spectra were measured by using a Shimadzu 3600 UV/Vis spectrophotometer. Photoluminescence spectra were obtained via Varian Cary Eclipse instrument. The PL lifetime was measured by an Optronics streak camera system with optimized temporal resolution of $\approx$ 50 ps. The morphology and microstructures were obtained using SEM (FEI Quanta 250F), TEM (FEI Tecnai G20) and HRTEM (FEI Tecnai G20). UPS was measured by ESCALAB 250XI instrument. The responsivity and external quantum efficiency (EQE) of PDs were measured by a Zolix DSR101detector spectral responsivity measurement system with a silicon photodetector as the reference. *I-V* (current-voltage) and *I-T* (current-time) characteristic curves were measured by using a Keithley 6487 testing system. All the device characterizations were conducted at room temperature under ambient air.

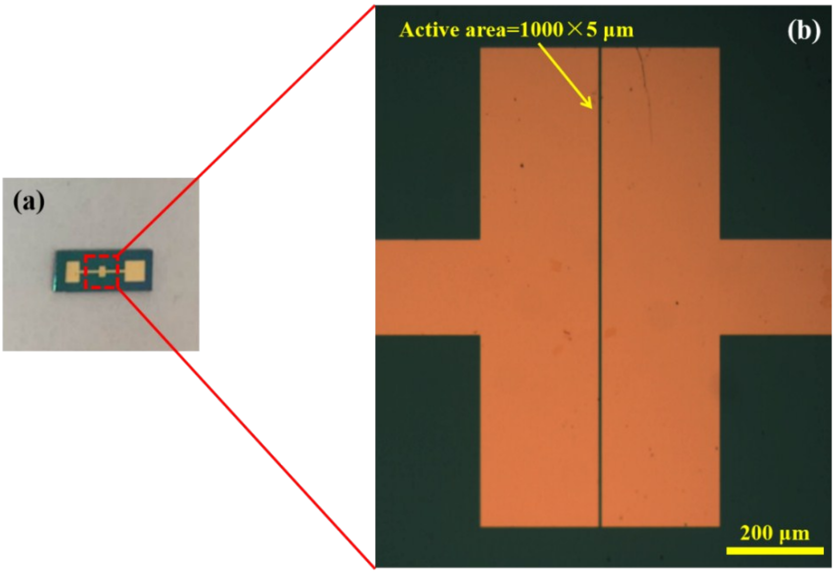


Figure S1. (a) The photograph of the PD. (b) The corresponding optical microscope image of the Au electrodes with channel width of 5 μm.

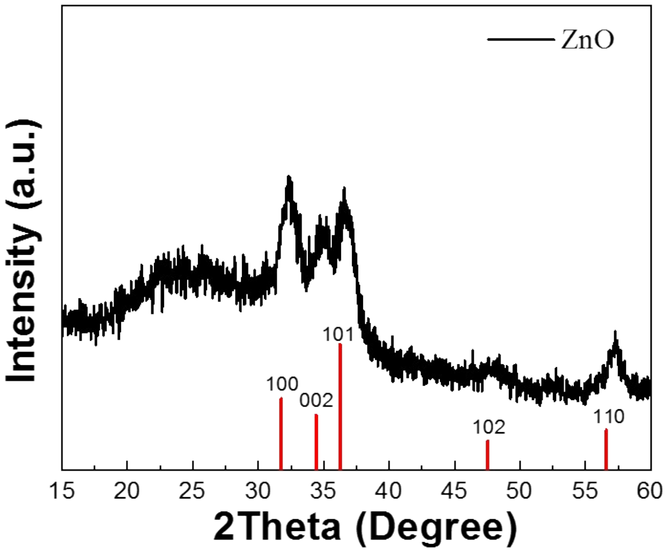


Figure S2. The XRD pattern of the as-prepared colloidal ZnO.

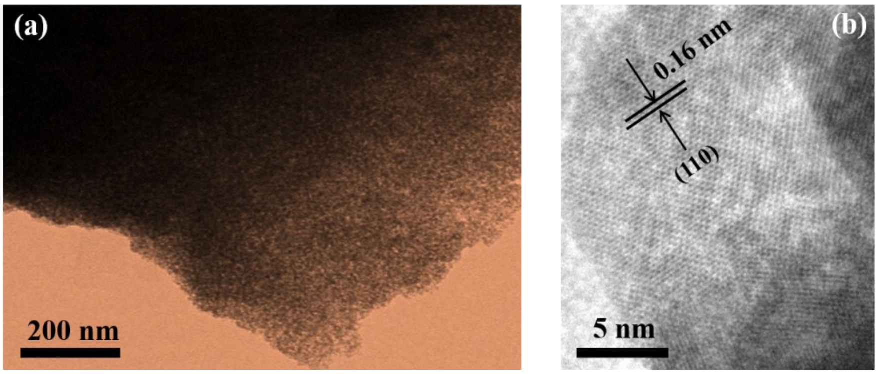


Figure S3. (a) TEM and (b) corresponding HRTEM image of colloidal ZnO.

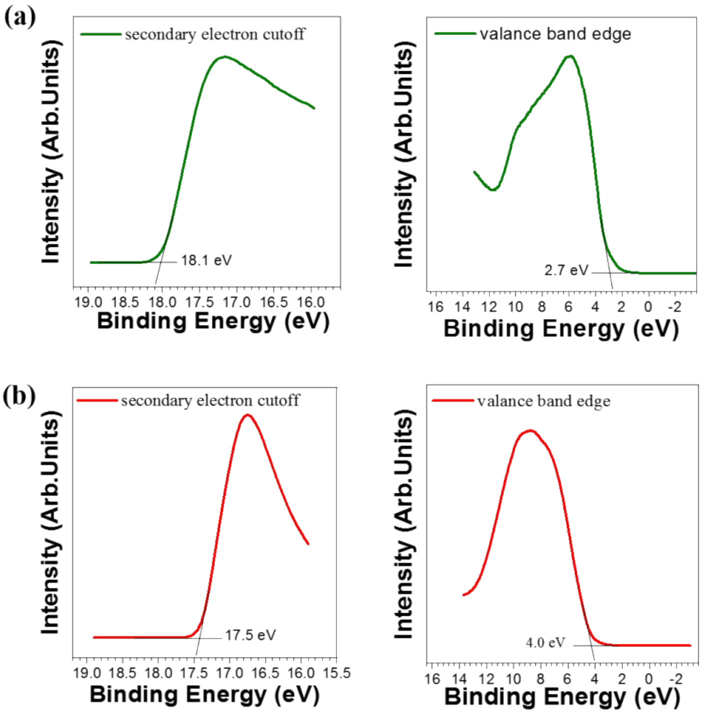


Figure S4. UPS spectrums of (a) perovskite $CsPbBr_3$ and (b) colloidal ZnO. The valence band maximum (VBM) is estimated according to equation: $E_v = hv + E_{cutoff} - E_{Feimi}$. As for the $CsPbBr_3$, the hv is 21.2 eV, the E_{Feimi} and E_{cutoff} extracted from the results are 18.1 eV and 2.7 eV, respectively. The E_v of $CsPbBr_3$ is calculated to be 5.8 eV, and the E_v value of ZnO is 7.7 eV through the same method. Combined with the absorption spectra of the $CsPbBr_3$ (Fig 1c) and the ZnO (Figure S5), the E_g were estimated to be 2.4 eV and 3.3 eV, respectively. The conduction band minimum (CBM) could be obtained finally.

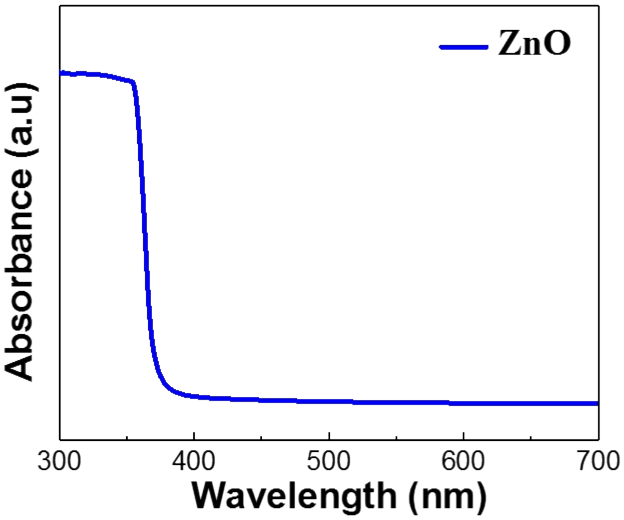


Figure S5. Absorption spectra of colloidal ZnO film.

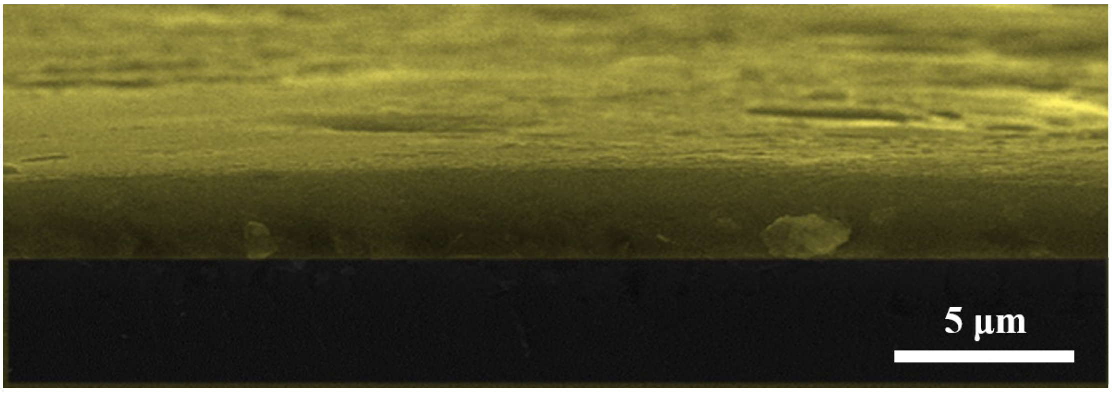
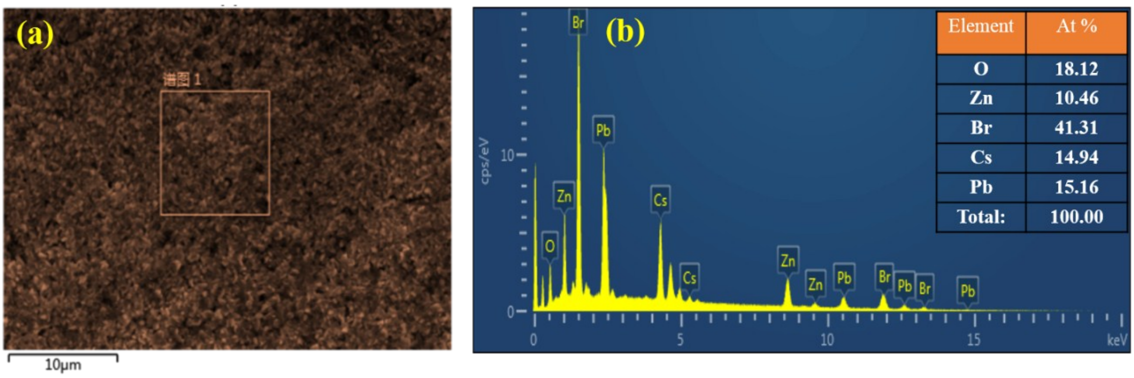


Figure S6. Cross-section SEM image of the hybrid $CsPbBr_3$/ZnO film.



Element	At %
O	18.12
Zn	10.46
Br	41.31
Cs	14.94
Pb	15.16
Total:	100.00

Figure S7. The EDX elemental analysis of the hybrid $CsPbBr_3$/ZnO film.

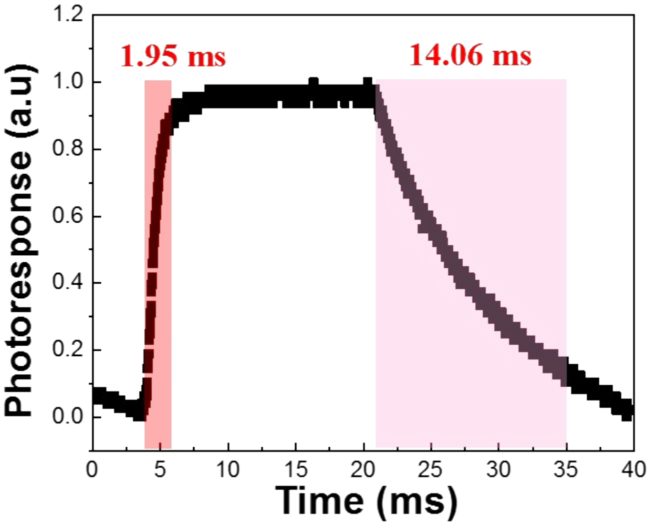


Figure S8. Normalized photoresponse for the rise and decay time of the pristine $CsPbBr_3$ PD.

References

1. L. Qian, Y. Zheng, K. R. Choudhury, D. Bera, F. So, J. Xue and P. H. Holloway, *Nano Today*, 2010, **5**, 384-389.
2. X. Dai, Z. Zhang, Y. Jin, Y. Niu, H. Cao, X. Liang, L. Chen, J. Wang and X. Peng, *Nature*, 2014, **515**, 96-99.