Supporting Information

BiOBr nanoplate-wrapped ZnO nanorod arrays for high performance photoelectrocatalytic application

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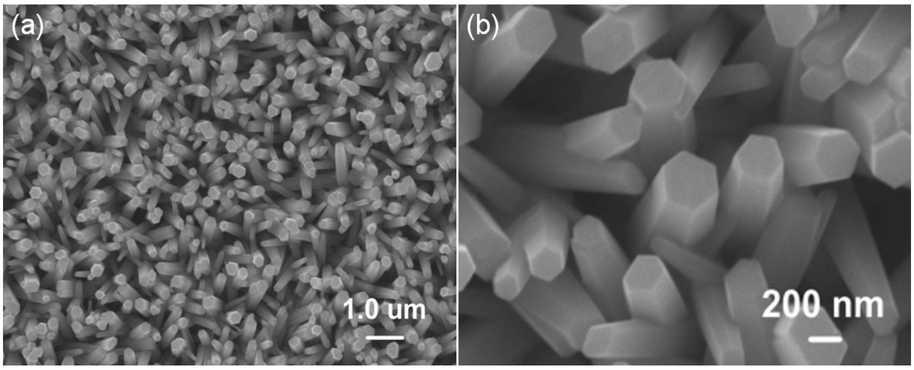


Fig. S1 SEM images of the ZnO NRAs.

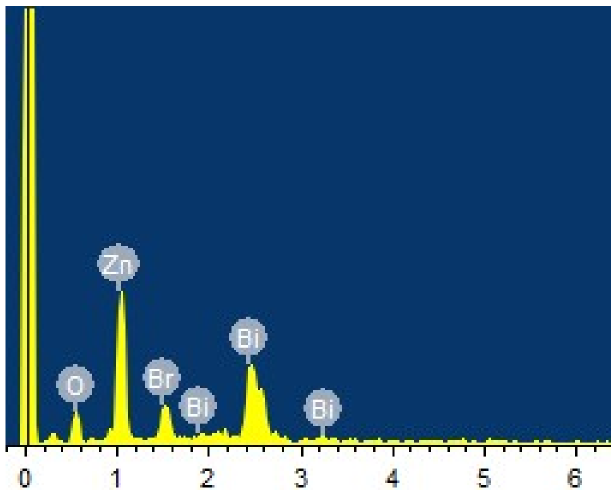


Fig. S2 EDS spectrum of the ZnO/BiOBr heterostructure.

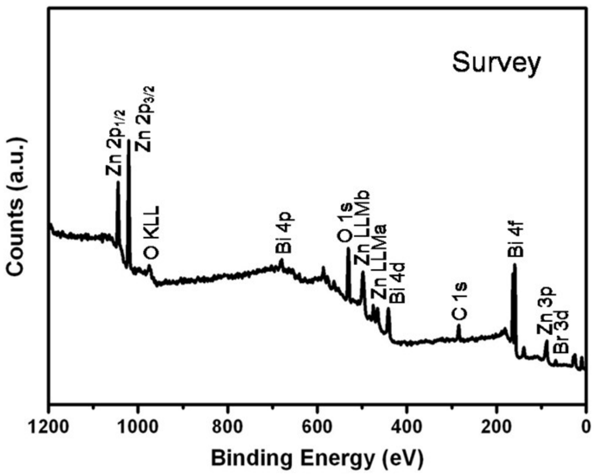


Fig. S3 XPS survey spectrum of the ZnO/BiOBr heterostructure.

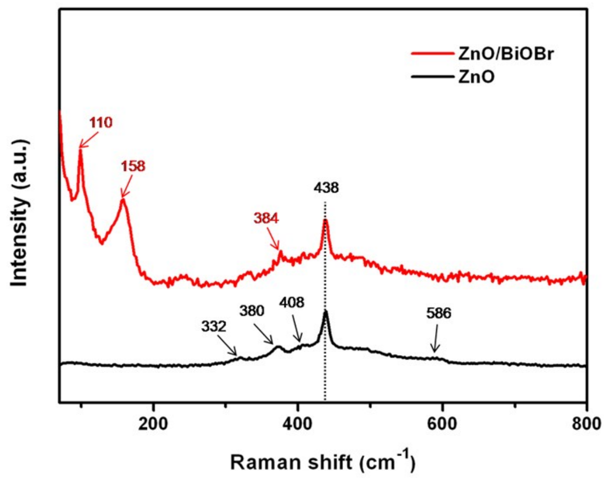


Fig. S4 Raman spectra of pure ZnO and ZnO/BiOBr heterostructure.

Fig. S4 exhibits the Raman spectra of pure ZnO and ZnO/BiOBr heterostructure. The strong peak at 438 cm^{-1} and other four weak peaks at 332, 380, 408 and 586 cm^{-1} are correspondent to the E_2(high), A_1(TO), A_1(TO), E_1(TO) and E_1(LO) mode in wurtzite structured ZnO.[S1,S2] The strong band observed at 110 cm^{-1} for ZnO/BiOBr could be attributed to A_{1g} internal Bi-Br stretching mode, and the band at 158 cm^{-1} could be ascribed to E_g internal Bi-Br stretching mode.[S3] Moreover, the weak band at 384 cm^{-1} that generated by the motion of oxygen atoms is belongs to the B_{1g} mode.[S4] The above results can be regarded as the combination of ZnO and BiOBr in the products.

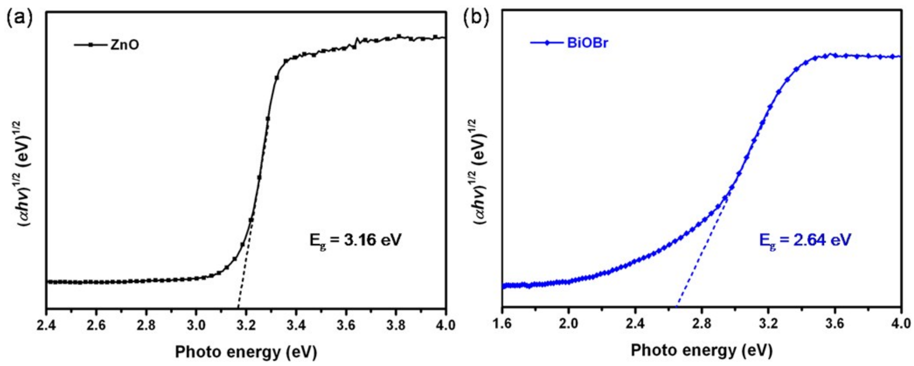


Fig. S5 Plots of $(\alpha hv)^{1/2}$ versus energy (hv) for the band gap energy of the (a) ZnO and (b) BiOBr.

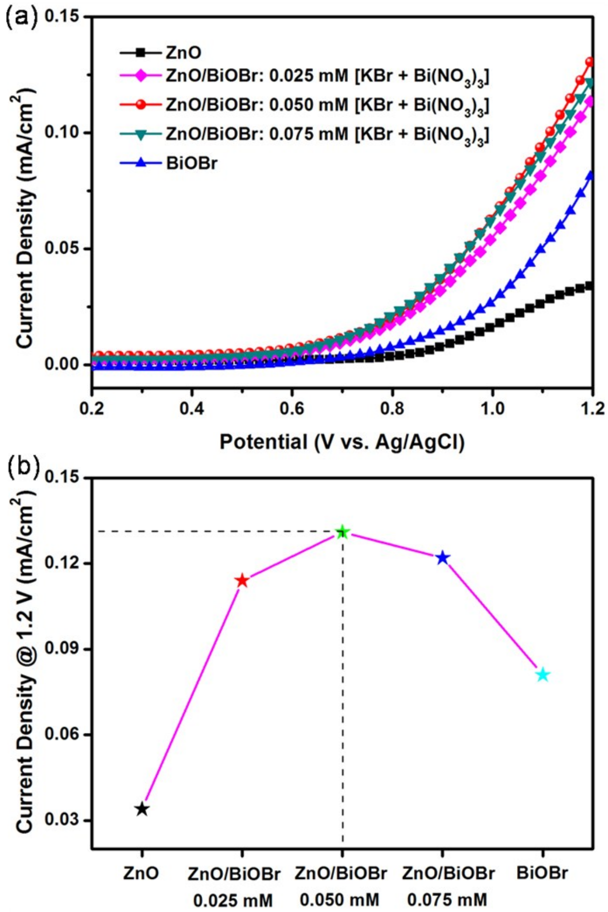


Fig. S6 (a) Current-potential (*I-V*) curves of ZnO/BiOBr samples with different BiOBr NPs content, (b) optimization curve.

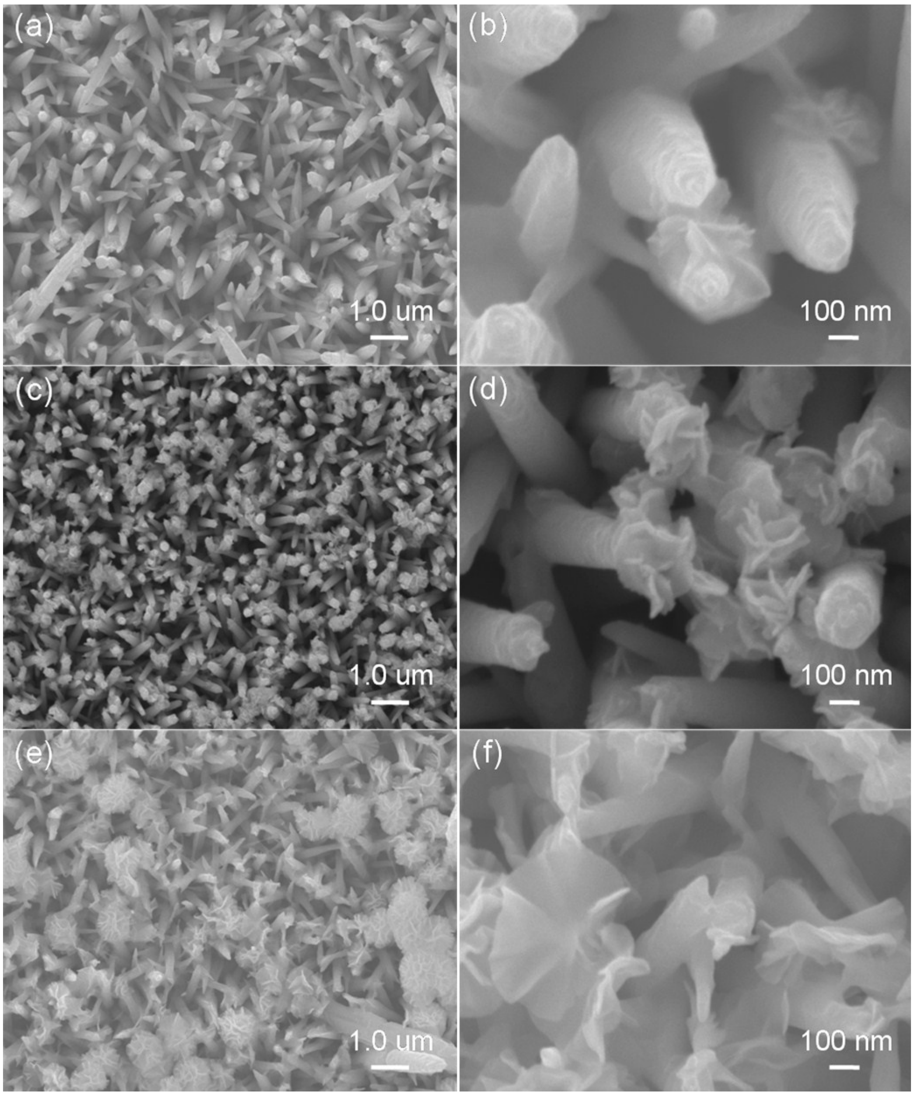


Fig. S7 SEM images of ZnO/BiOBr samples with different BiOBr NPs content: (a-b) 0.025 mM [KBr + Bi$(NO_3)_3$], (c-d) 0.05 mM [KBr + Bi$(NO_3)_3$], and (e-f) 0.075 mM [KBr + Bi$(NO_3)_3$].

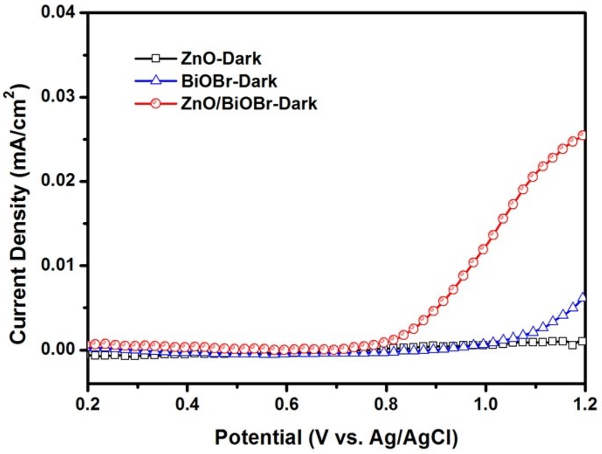


Fig. S8 Current density versus applied potential curves for the pure ZnO, BiOBr and ZnO/BiOBr photoanodes in dark condition.

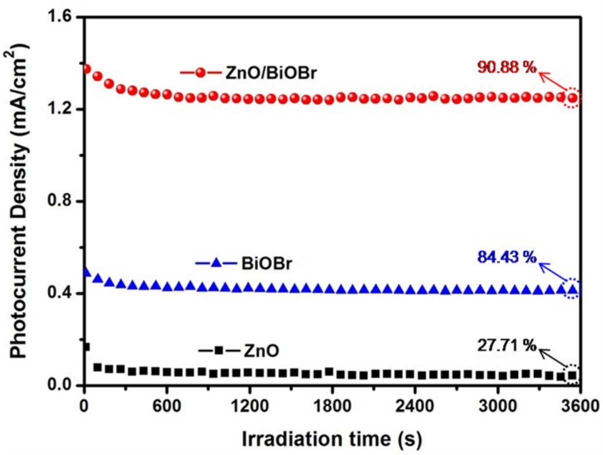


Fig. S9 Photocurrent density stability test of the as-prepared photoanodes under visible light illumination for 1 h with the applied bias of 0.5 V.

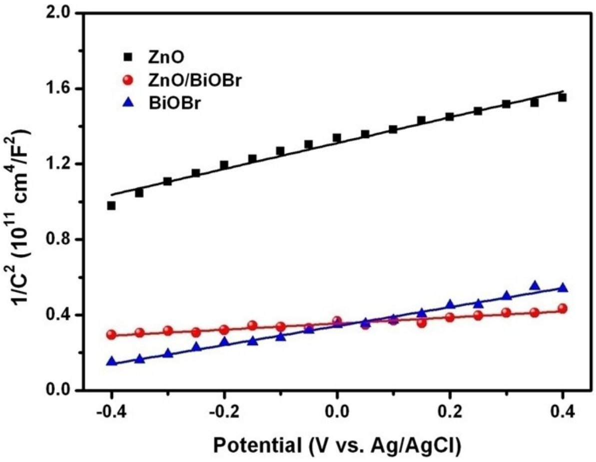


Fig. S10. Mott-Schottky plots of the ZnO, BiOBr and ZnO/BiOBr heterostructure in dark at a frequency of 10 KHz and a current of 5 mV with a three-electrode system.

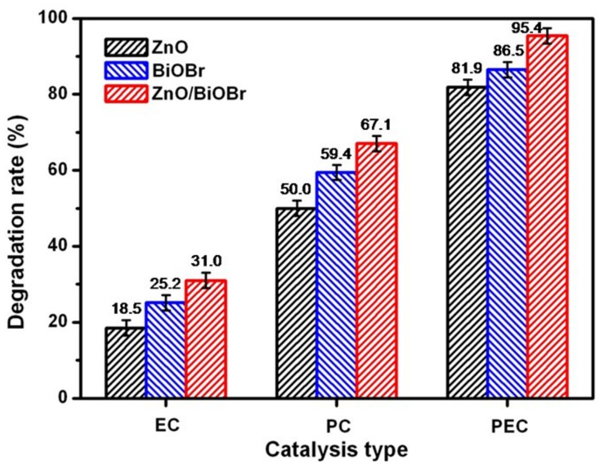


Fig. S11. Degradation rates for RhB solution by different catalysis type of ZnO, BiOBr and ZnO/BiOBr photoelectrodes.

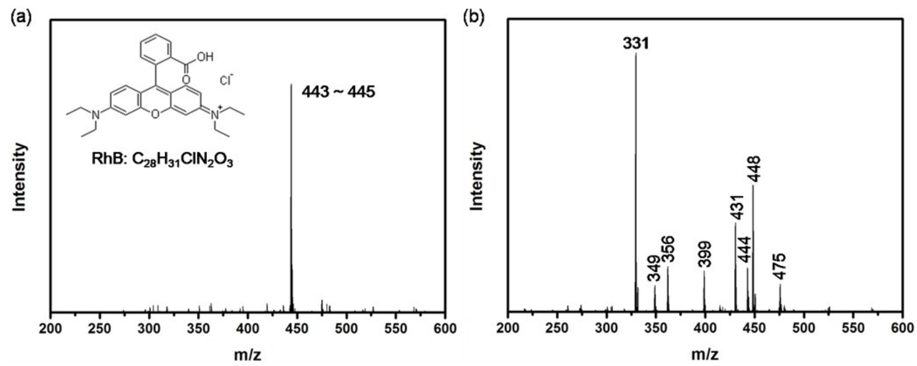


Fig. S12. ESI-MS spectra of the RhB solution in the degradation process (a) before and (b) after the light illumiantion for 100 min.

These peaks may be ascribed to the following decomposition products:

peaks at 443 ~ 445, 448: characteristic of RhB molecule.

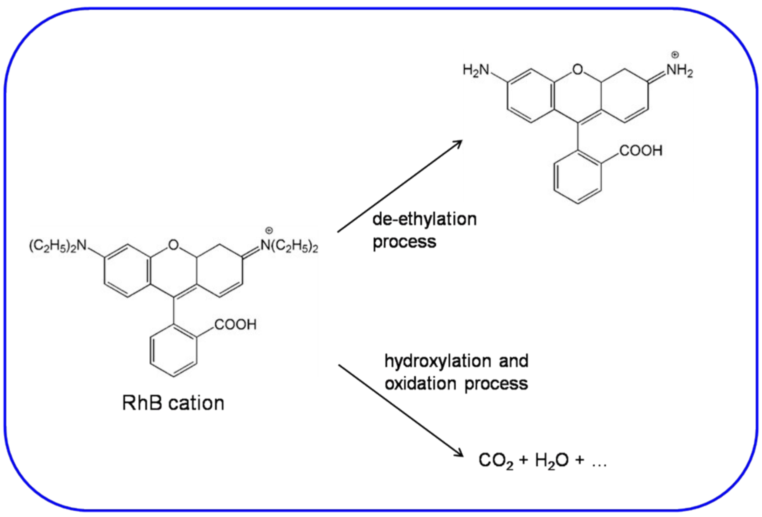
peaks at 331, 356: fragments which resulted from severing ethyl group from RhB molecule.

peaks at 349, 431: fragments which resulted from de-ethylation and hydroxylation process.

peaks at 399: fragments which resulted from severing one carboxyl group from RhB molecule.

peaks at 475: fragments which resulted from hydroxylation process by two hydroxyl radicals.

Moreover, these above degradation processes can be conclued to the following two aspects:



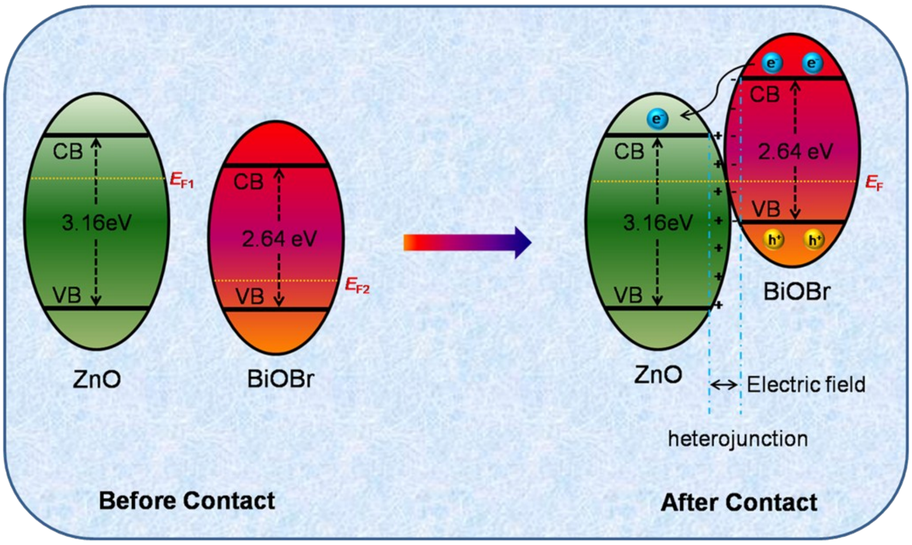


Fig. S13. The band structures variation of the two semiconductors before and after contact.

Table S1 Pseudo-first-order rate constants of RhB solution degradation by different catalysis types.

Serie	Catalysis type		The first order Kinetic equation	$k(min^{-1})$	R^2
1	EC	ZnO	$-\ln(C_t/C_0)=0.0021\ t$	0.0021	0.9812
2		BiOBr	$-\ln(C_t/C_0)=0.0030\ t$	0.0030	0.9876
3		ZnO/BiOBr	$-\ln(C_t/C_0)=0.0038\ t$	0.0038	0.9877
4	PC	ZnO	$-\ln(C_t/C_0)=0.0070\ t$	0.0070	0.9782
5		BiOBr	$-\ln(C_t/C_0)=0.0089\ t$	0.0089	0.9885
6		ZnO/BiOBr	$-\ln(C_t/C_0)=0.0112\ t$	0.0112	0.9899
7	PEC	ZnO	$-\ln(C_t/C_0)=0.0166\ t$	0.0166	0.9951
8		BiOBr	$-\ln(C_t/C_0)=0.0197\ t$	0.0197	0.9985
9		ZnO/BiOBr	$-\ln(C_t/C_0)=0.0290\ t$	0.0290	0.9641

References

[S1] K. Kim, K. L. Kim and K. S. Shin, *Phys. Chem. Chem. Phys.,* 2013, **15**, 9288-9294.

[S2] X. D. Xue, T. Wang, X. D. Jiang, J. Jiang, C. X. Pan and Y. C. Wu, *CrystEngComm*, 2014 , **16**, 1207-1216.

[S3] D. Zhang, J. Li, Q. G. Wang and Q. S. Wu, *J. Mater. Chem. A*, 2013, **1**, 8622-8629.

[S4] Y. Lei, G. Wang, S. Song, W. Fan and H. Zhang, *CrystEngComm*, 2009, **11**, 1857-1862.