## **Supplementary Information**

In situ construction and composition engineering of PbBiO<sub>2</sub>Br/metal halide perovskite heterojunctions for enhanced interfacial charge transfer and photocatalytic activity

Qi Qin,<sup>a,b</sup> Wei-Qi Liu,<sup>a</sup> Zhi-Hua Xia,<sup>a</sup> Hong-Yan Chen, \*<sup>a</sup> and Dai-Bin Kuang\*<sup>a</sup>

<sup>a</sup>Key Laboratory of Bioinorganic and Synthetic Chemistry of Ministry of Education, LIFM, GBRCE for Functional Molecular Engineering, School of Chemistry, IGCME, Sun Yat-Sen University, Guangzhou 510006, China

<sup>b</sup>School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai 519082, China E-mail: chenhy33@mail.sysu.edu.cn (H. Y. Chen); kuangdb@mail.sysu.edu.cn (D. B. Kuang)



**Fig. S1.** Optical photos of heterojunctions prepared with different volumes of the HBr: 0, 0.5, 0.8, 1.0, 1.4, 1.8 and 2.5  $\mu$ L of the HBr was added from left to right, respectively.



Fig. S2. Element mapping of PbBiO<sub>2</sub>Br/MHPs (1.0).



Fig. S3. Low-magnified TEM images of PbBiO<sub>2</sub>Br/MHPs(1.4) and PbBiO<sub>2</sub>Br/MHPs(2.5).



**Fig. S4.** *In situ* XPS spectra of PbBiO<sub>2</sub>Br and PbBiO<sub>2</sub>Br/Bi-CsPbBr<sub>3</sub>:(a) survey spectra; (b) Pb 4f; (c) Bi 4f; (d) Br 3d.



**Fig. S5.** Photocatalytic recycling tests of PbBiO<sub>2</sub>Br/Bi-CsPbBr<sub>3</sub> heterojunction with the reaction system refreshed every 3 h.



**Fig. S6.** Photocatalytic CO<sub>2</sub> reduction performances of PbBiO<sub>2</sub>Br/Bi-CsPbBr<sub>3</sub>/ZIF-67 heterojunction prepared by different ZIF-67 precursor concentration after irradiation for 3 h.



Fig. S7. Optical photos of PbBiO<sub>2</sub>Br/Bi-CsPbBr<sub>3</sub> and PbBiO<sub>2</sub>Br/Bi-CsPbBr<sub>3</sub>/ZIF-67 sample.



**Fig. S8.** XRD patterns of ZIF-67, PbBiO<sub>2</sub>Br/Bi-CsPbBr<sub>3</sub> and PbBiO<sub>2</sub>Br/Bi-CsPbBr<sub>3</sub>/ZIF-67 samples.



Fig. S9. (a) *I*-*t* curves and (b) Nyquist plots of PbBiO<sub>2</sub>Br/Bi-CsPbBr<sub>3</sub>/ZIF-67 film.



Fig. S10. The XRD patterns of  $PbBiO_2Br/Bi-CsPbBr_3/ZIF-67$  heterojunction before and after five consecutive cycles of photocatalytic  $CO_2$  reduction.