

## Supplementary Material

### Direct Z-scheme $\alpha$ -MnO<sub>2</sub>@MnIn<sub>2</sub>S<sub>4</sub> Hierarchical Photocatalysts with Atomically Defined Junction for Improved Photocatalytic Activities

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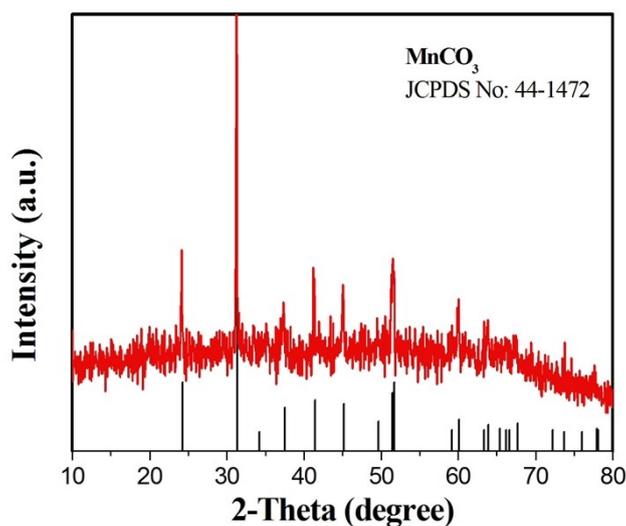


Fig. S1. XRD pattern of MnCO<sub>3</sub> nanocubes.

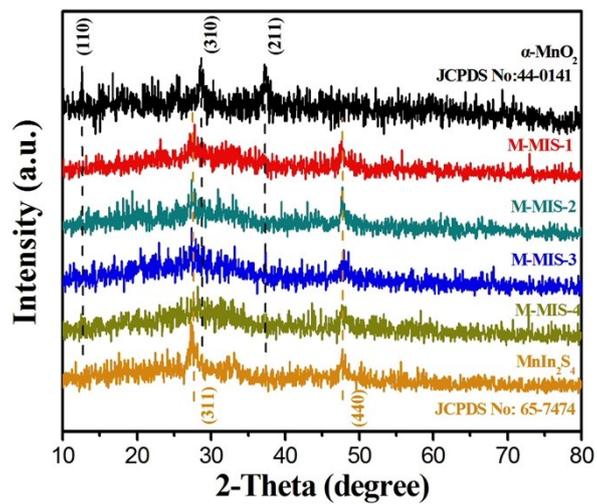


Fig. S2. XRD patterns of pure  $\alpha$ -MnO<sub>2</sub>, MnIn<sub>2</sub>S<sub>4</sub> and M-MIS-x (x=1, 2, 3, 4).

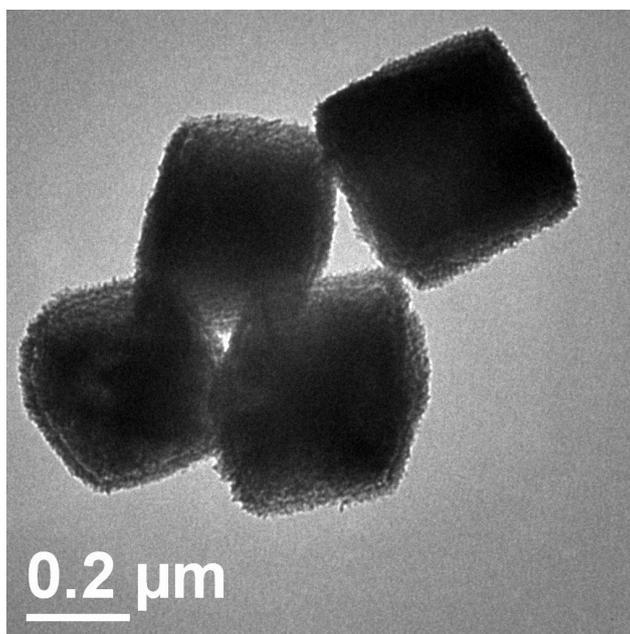


Fig. S3. The TEM image of  $\delta$ -MnO<sub>2</sub> precursor.

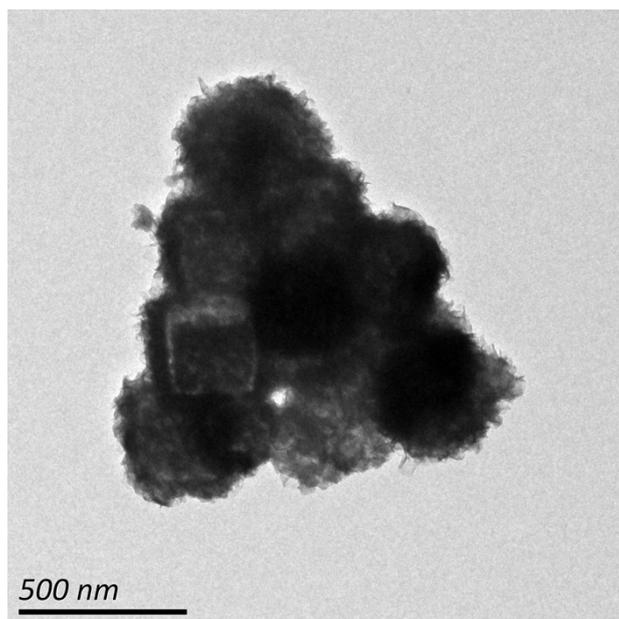


Fig S4. TEM images of M-MIS-2 at interface.

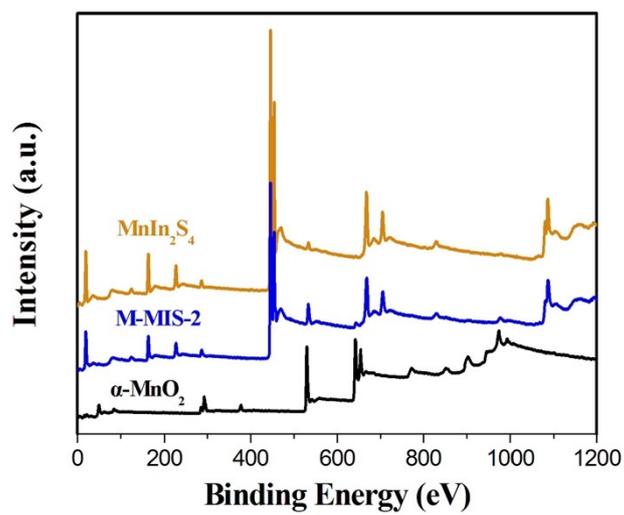
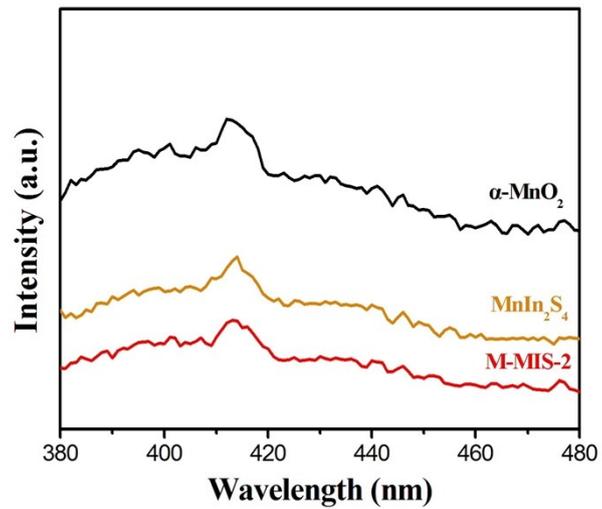
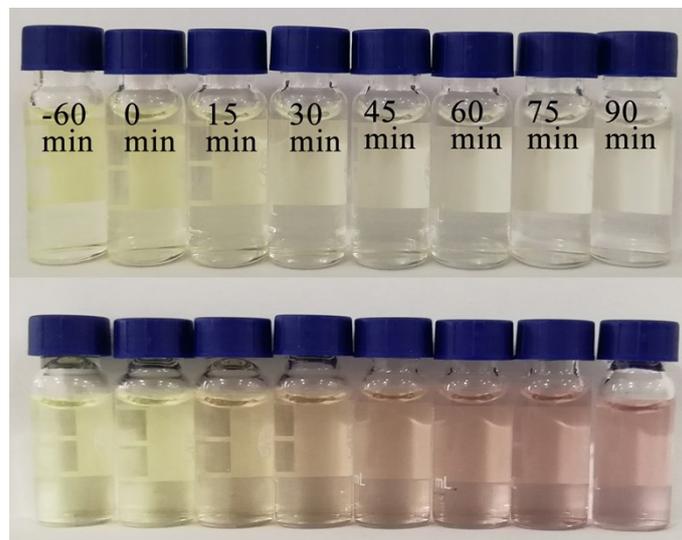


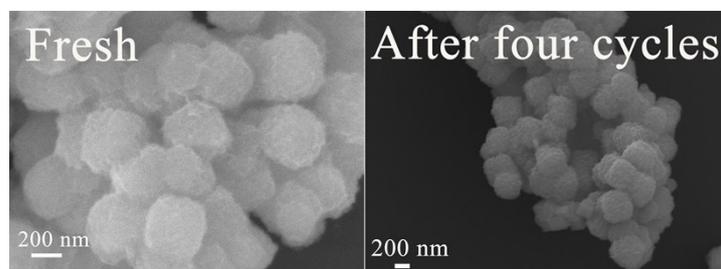
Fig. S5. The full-scale XPS spectra for the  $\alpha$ -MnO<sub>2</sub>@MnIn<sub>2</sub>S<sub>4</sub> (M-MIS-2) and pure  $\alpha$ -MnO<sub>2</sub>, MnIn<sub>2</sub>S<sub>4</sub>.



**Fig. S6.** Solid state PL emission spectra of  $\alpha$ -MnO<sub>2</sub>, MnIn<sub>2</sub>S<sub>4</sub> and M-MIS-2.



**Fig. S7.** The color variation of 4-NA during photocatalytic reaction and corresponding color change when the catalysate was oxidized used M-MIS-2 as the catalyst.



**Fig. S8.** The SEM images M-MIS-2 catalyst before and after the reaction.

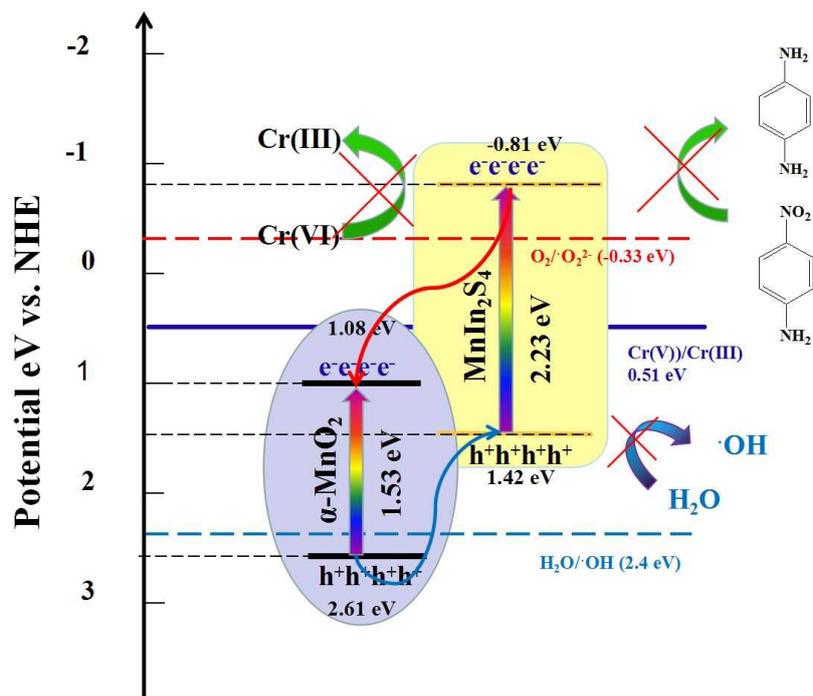


Fig S9. Type II heterojunction photocatalytic mechanism.