Supplementary Material for "Band Alignment and Enhanced Photocatalytic Activation of α/β-Bi_2O_3 Heterojunction via In Situ Phase Transformation"

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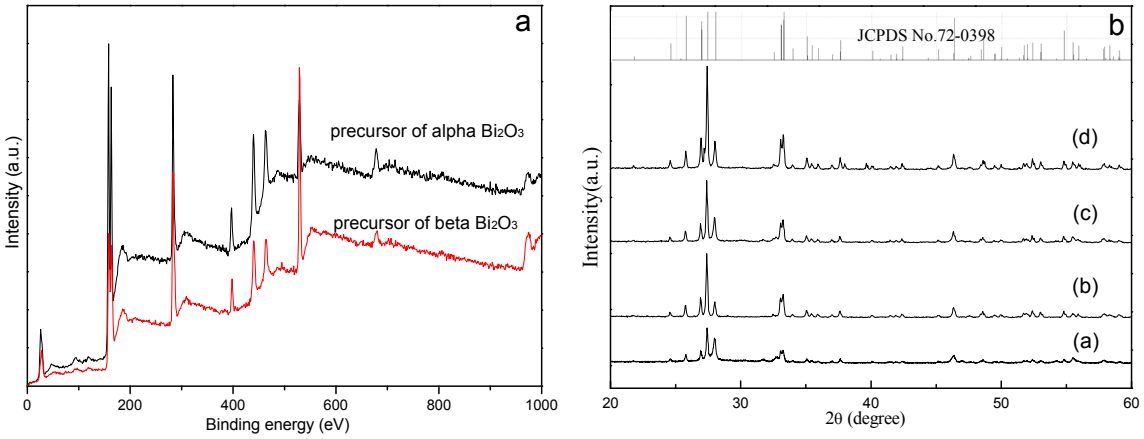

Fig. S1a. Survey XPS of precursors of alpha and beta Bi_2O_3. It was found that there is not Al ions in the precursors of beta Bi_2O_3 (washed with deionized water five times). Its component is characteristic of precursors of alpha Bi_2O_3. There is no typical Al 2s and Al 2p peaks, indicating full removing of Al in precursors of beta Bi_2O_3.

Fig. S1b. XRD patterns of sintered AP at different temperature. (a) 325 °C for 4 h, (b) 350 °C for 4 h, (c) 375 °C for 3 h, (d) 375 °C for 4 h. Peaks of all XRD spectra are matched well with monoclinic Bi_2O_3 (α phase, JCPDS No.72-0398).

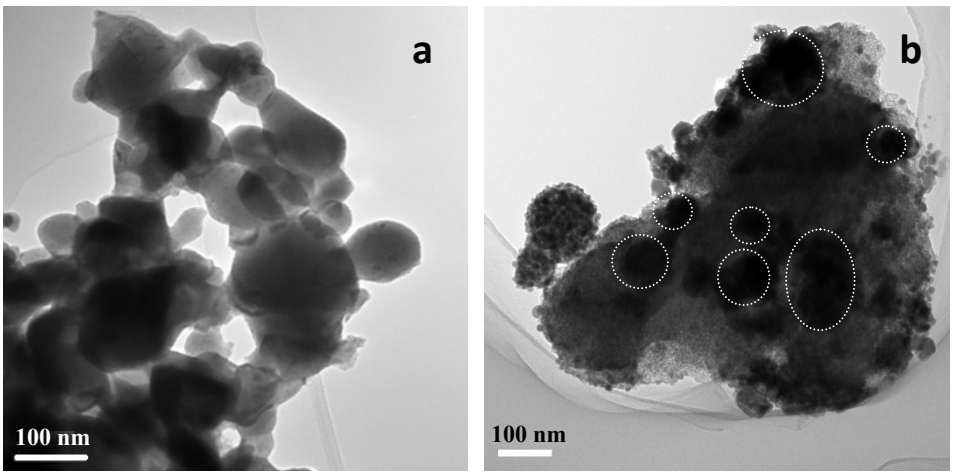

Fig. S2. Typical TEM images of (a) α-Bi_2O_3 (375 °C for 3 h), (b) α/β-Bi_2O_3 heterojunction (375 °C for 2.5 h). Figure S2a illustrates the representative TEM image of α-Bi_2O_3 by heat treating AP powders. Figure S2b shows the TEM image of α/β-Bi_2O_3 heterojunction via thermal treatment for BP powder.

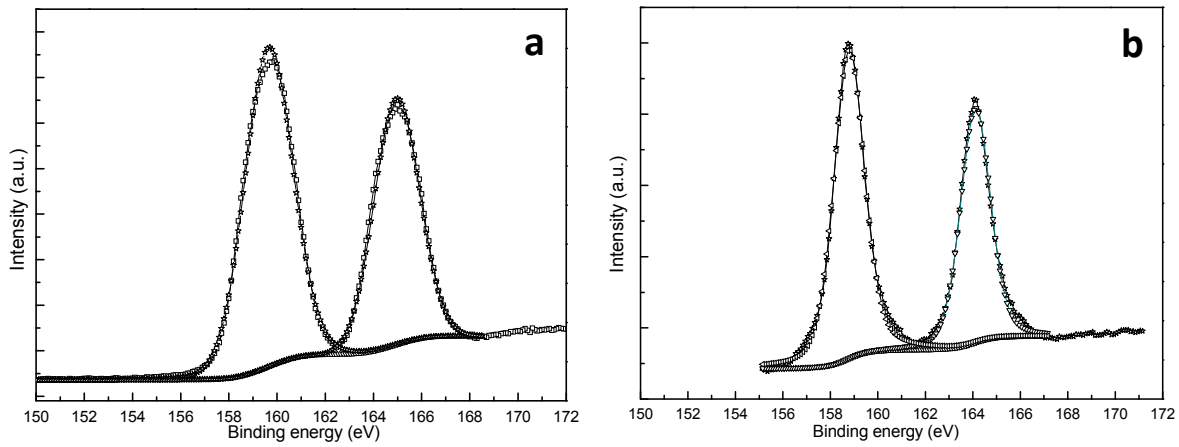

Fig. S3. Core-level Bi 4f spectra recorded on the β-Bi_2O_3 (a), α-Bi_2O_3 (b) and α/β-Bi_2O_3 (c) samples. Raw data shown as star is fitted with the peak shapes derived from phase-pure β-Bi_2O_3 (quadrangles) and α-Bi_2O_3 (triangles). All the CL spectra have been fitted using a Shirley background. The surveys of these samples were shown in the last figure.

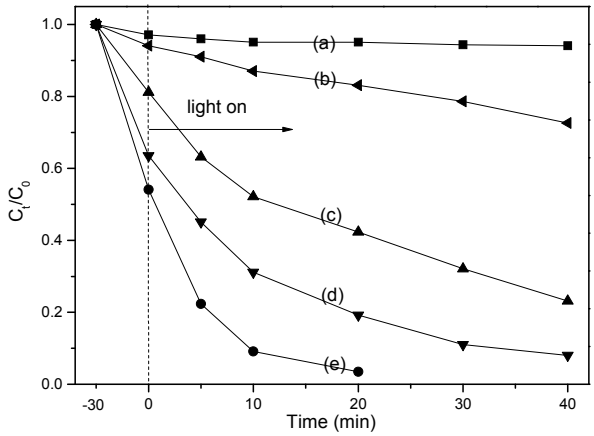

Fig. S4. The C_t/C_0 of MB versus visible-light irradiation time: (a) no pholocatalyst, (b) α-Bi_2O_3, (c) CM2, (d) β-Bi_2O_3, (e) CM1.

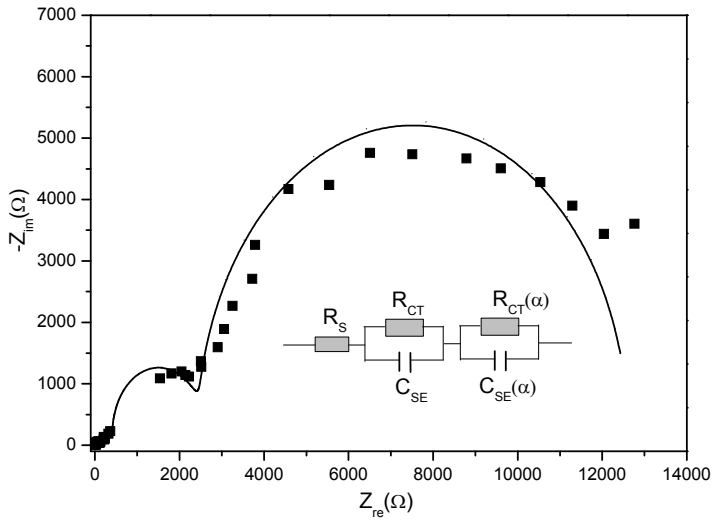

Fig. S5. The Nyquist plot from the impedance measurement of α/β-Bi_2O_3 heterojunction (375 °C for 2.5 h), and the equivalent circuit used to fit the measured data. The Nyquist plot shows a double arc which can be decomposed into semicircles by means of the equivalent electrical circuit, which consists of a resistor, two pairs of parallel-connected capacitors and resistors connected in series. The small semicircle indicates the increasing of bulk impedance which arises from increased α phase as raising calcination temperature.

Table S1. XPS CL spectra fitting results and VBM positions obtained by linear extrapolation of the leading edge to the extended base line of the VB spectra.

Sample	State	Binding energy (eV)
α-Bi_2O_3	Bi4f $_{7/2}$	158.78
	VBM	1.18
β-Bi_2O_3	Bi4f $_{7/2}$	159.67
	VBM	1.44
α/β-Bi_2O_3	Bi4f $_{7/2}$	158.96
	Bi4f $_{7/2}$	159.58