Supplementary Information:

m-$BiVO_4$@γ-Bi_2O_3 core-shell p-n heterogeneous nanostructure for enhanced visible-light photocatalytic performance

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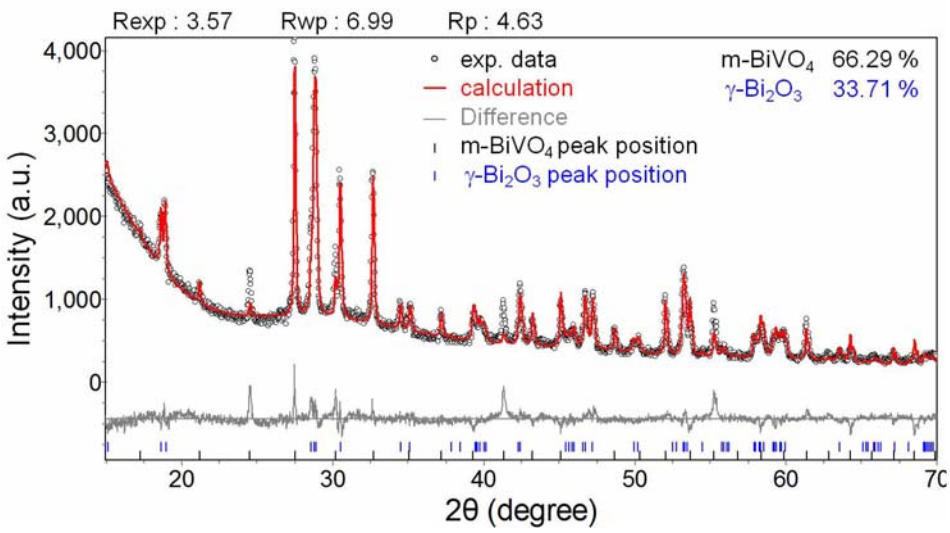
Part 1 XRD refinement

Rietveld refinement details (BB03 as an example):

The Rietveld analysis of BB03 XRD data was conducted by using TOPAS (Version 3, Bruker). Prior to the structural refinement, the X-ray emission profile, instrument parameters and Lorentz-Polarisation factor were corrected according to the instrument conditions, and there parameters were fixed without further refinement. Then, a Chebychev polynomial of 7th order was used to fit the XRD curve background, and the zero point error correction was selected in the latter global curve refinement. For the quantitative analysis, the structure files (.cif) of *m*-$BiVO_4$ and γ-Bi_2O_3 were imported to the software. The structure details are listed in Table S1. Then the quantitative profile refinement was conducted in which the unit cell parameters (*a*, *b*, *c* and *β* for *m*-$BiVO_4$ and *a* for γ-Bi_2O_3), phase scales, crystal size, background, preferred orientation ((004) for *m*-$BiVO_4$ and (222) for γ-Bi_2O_3) were refined together to give the final agreement factors of Rp = 4.63%, Rwp = 6.99%, and Rexp = 3.57%. The atomic coordinates for both crystal phases were not further refined. The resultant phase ratio of BB03 was 66.29% of *m*-$BiVO_4$ and 33.71% of γ-Bi_2O_3 as list in SI Table 1 in the text. The Rietveld refined pattern was shown in SI Figure 1.

SI Table 1 The crystal structure of *m*-$BiVO_4$ and γ-Bi_2O_3.

	m-$BiVO_4$ [1]	γ-Bi_2O_3 [2]
Space Group	I112/b	I23
Crystal System	monoclinic	Cubic
Unit Cell	a = 5.197 Å b = 11.702 Å c = 5.096 Å β = 90.4°	a = 10.267 Å
Cell Volume	309.91 $Å^3$	1082.57 $Å^3$
Z	4	13



SI Figure 1 Rietveld refinement of sample BB03.

Part 2 Diffuse reflectance spectrum (DRS) study and band structure estimation.

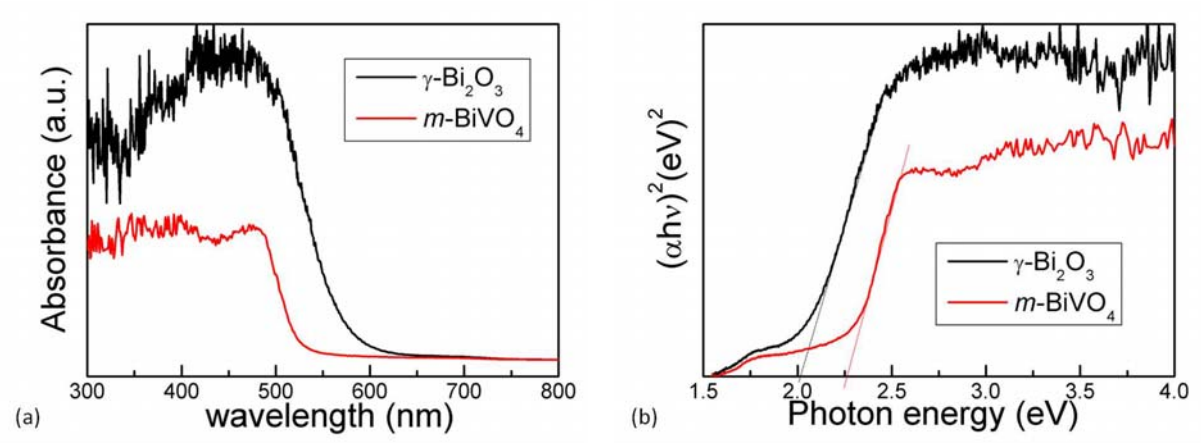
For the two pure oxides, the band edge positions of their conduction band (CB) and valence band (VB) at the point of zero charge (pH_{zpc}) can be predicted by the empirical equation:

$E_{CB}^0 = X - E^c - 1/2\ E_g$

where E_{CB}^0 is the CB edge potential; X is the absolute electronegativity of the semiconductor, which is the geometric mean of the absolute electronegativity of the constituent atoms (X values for $BiVO_4$ and Bi_2O_3 are 6.04 and 5.95 eV, respectively); E^c is the energy of free electrons on the hydrogen scale (about 4.5 eV); and Eg is the band gap of the semiconductor. So the predicted band edge positions of Bi_2O_3 and $BiVO_4$ by the above equation are shown in below SI Table 2, and schematically illustrated in Figure 6 (a).

SI Table 2 Absolute electronegativity, estimated band gap, calculated energy levels of conduction band edge and valence band edge at the zero-charge point for *m*-$BiVO_4$ and γ-Bi_2O_3.

Oxide Material	X, Absolute Electronegativity	Estimated Band Gap (eV)	Calculated CB (eV)	Calculated VB (eV)
$BiVO_4$	6.04	2.26	0.41	2.67
Bi_2O_3	5.95	2.04	0.43	2.47



SI Figure 2 (a) UV-Vis diffuse reflectance spectrum of the as prepared *m*-$BiVO_4$ and γ-Bi_2O_3 samples, and (b) plots of $(\alpha h\nu)^2$ versus hν, by which the values of the energy band gaps of the samples, corresponding to those in (a).

Part 3 Surface photovoltage (SPV) measurement:

The CPD is defined as:

$e \cdot CPD = Ws - Wm$

where Ws is the surface work function of sample powders and Wm is Kelvin probe work function, which was calibrated on Au surface. The ΔCPD is defined as:

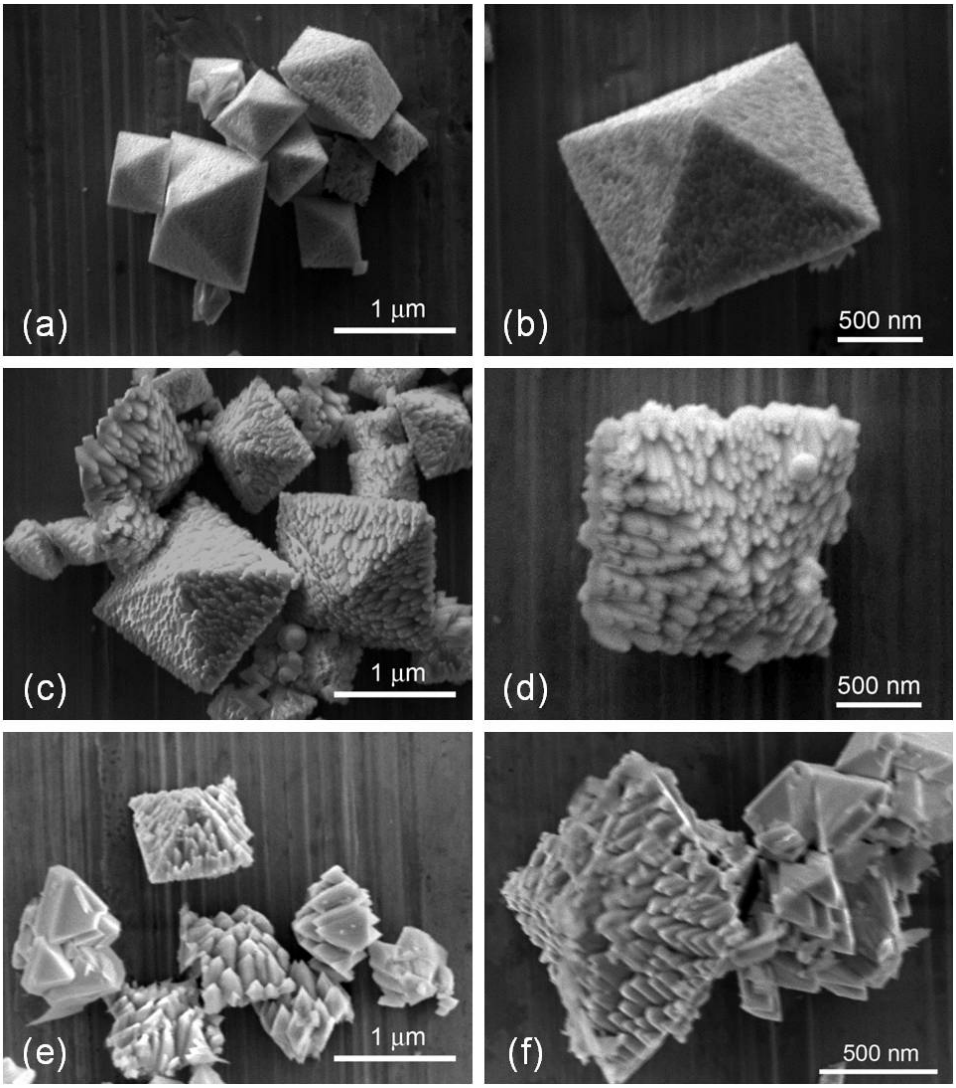
$\Delta CPD = CPD_{\text{in dark}} - CPD_{\text{under illumination}}$

Since the work function of the probe does not change under illumination, it is assumed that

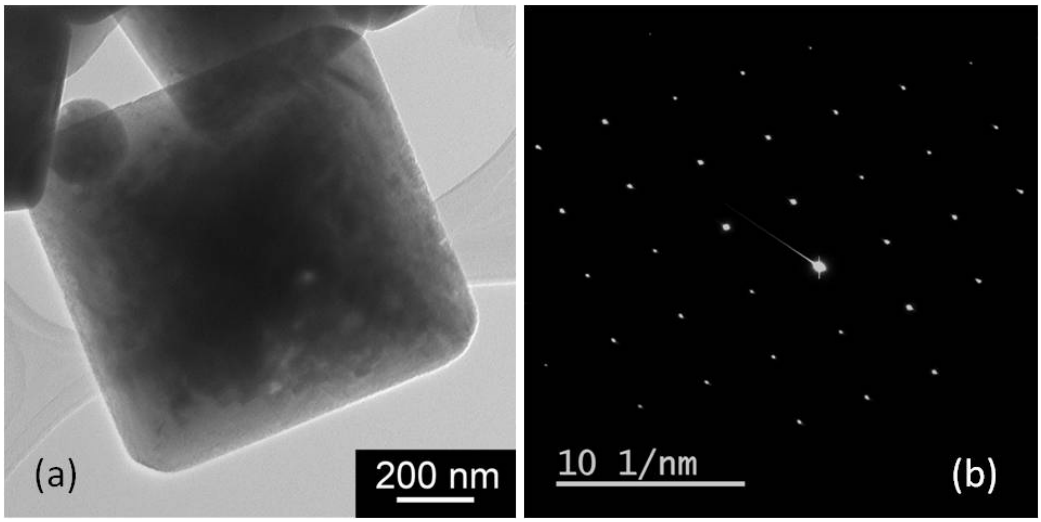
$e \cdot \Delta CPD = \Delta Ws = -e\,\Delta Vs = -e \cdot SPV,$

where ΔVs is the change of surface potential, which is the surface photovoltage (SPV) measured in the Kelvin probe system.

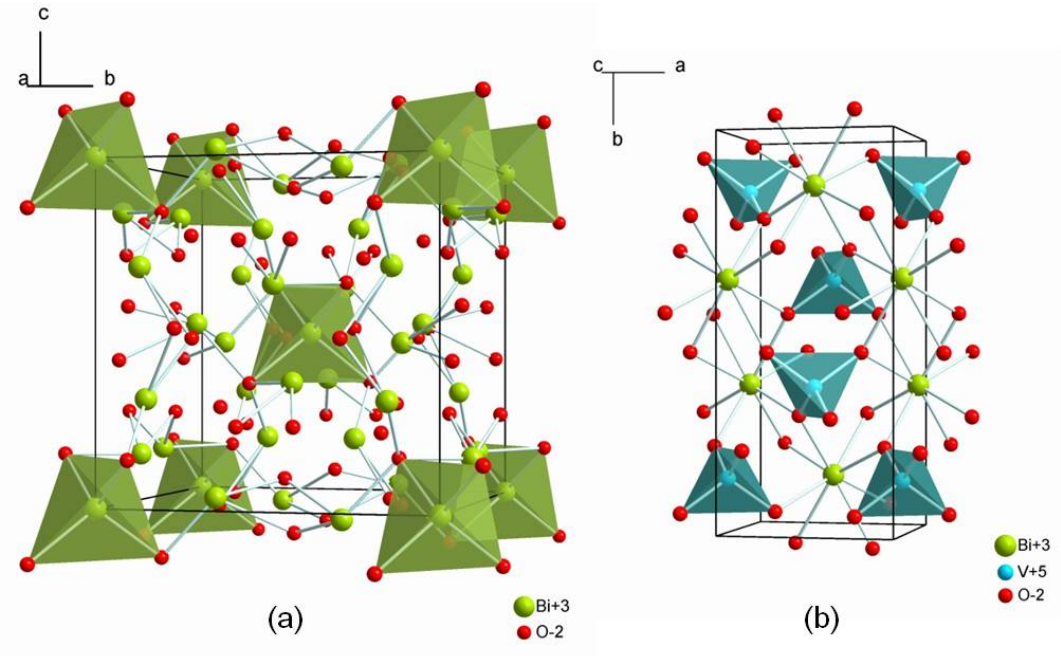
Part 4 Other Figures



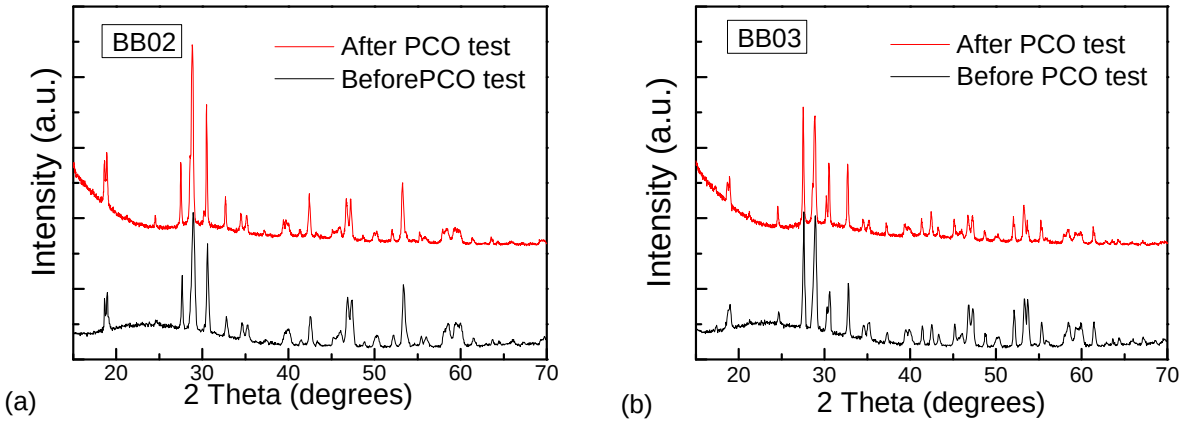
SI Figure 3 SEM images of as-prepared *m*-$BiVO_4$@γ-Bi_2O_3 particles fabricated under different alkaline concentrations, (a) & (b) 0.1 M BB01, (c) & (d) 0.2 M BB03, (e) & (f) 0.3 M BB04.



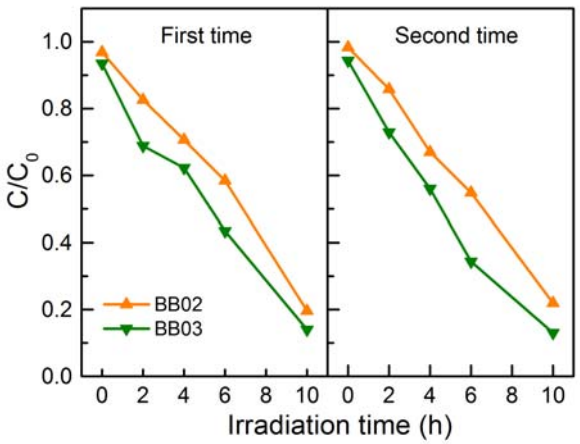
SI Figure 4 (a) TEM image and (b) its corresponding SAED pattern of a pure *m*-$BiVO_4$ octahedral single crystal.



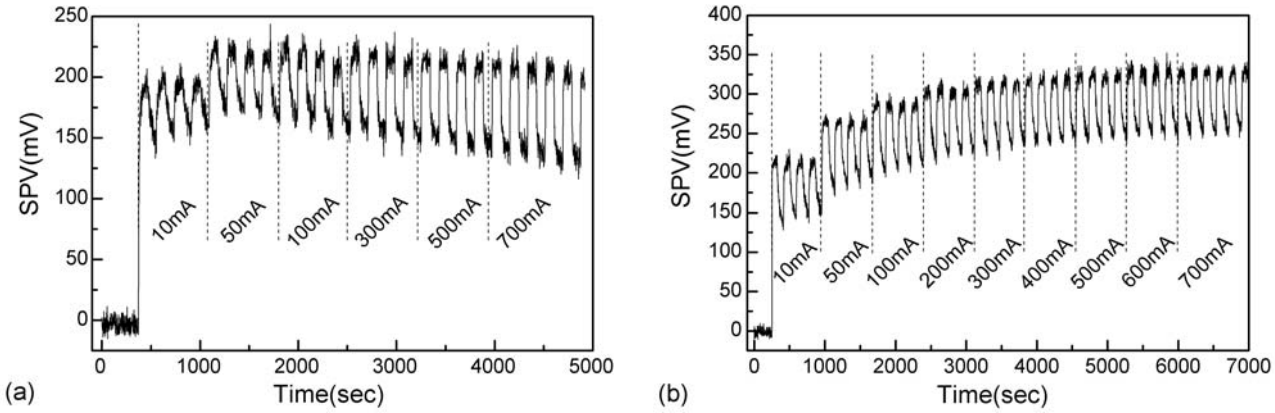
SI Figure 5 Crystal structure comparison between (a) cubic γ-Bi_2O_3 and (b) monoclinic scheelite $BiVO_4$.



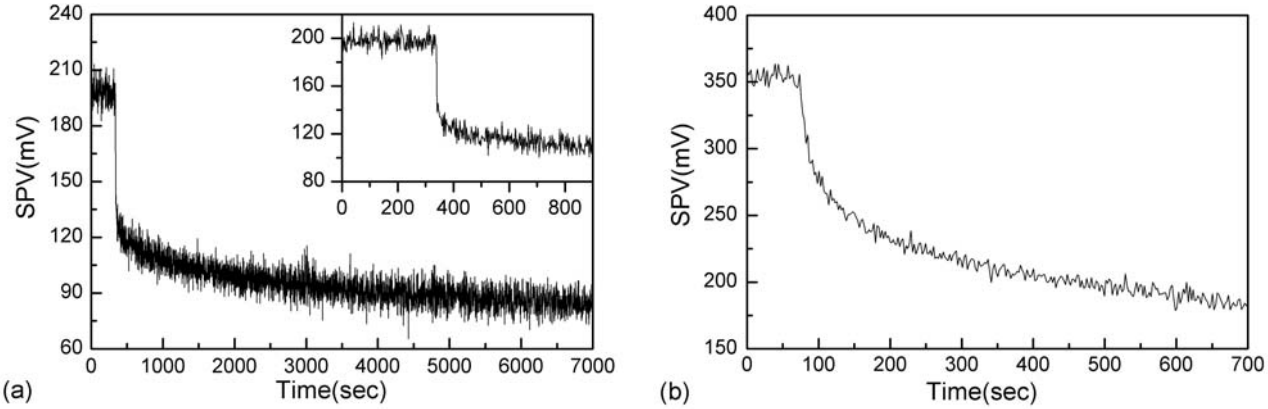
SI Figure 6 XRD patterns of the samples (a) BB02 and (b) BB03 before (lower black) and after (upper red) photocatalytic test in the degradation of RhB.



SI Figure 7 the repeated photocatalytic test of the samples BB02 and BB03 in the degradation of RhB.



SI Figure 8 Transient SPV spectra of (a) pure *m*-$BiVO_4$ and (b) BB03.



SI Figure 9 Transient SPV spectra of (a) pure *m*-$BiVO_4$ and (b) BB03 after irradiation turned off.

References

[1] Wu Li, Hsueh Pao, *Acta Physica Sinica.* 32 (1983) 1053-1060.
[2] Harwig H, *Z. Anorg. Allg. Chem.* 444 (1978) 151-166.