## **Supporting Information**

## In situ construction of Bi<sub>5</sub>O<sub>7</sub>I/Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> heterostructure composite with plentiful phase interfaces for boosted selective oxidation of

## benzylic alcohols under visible light

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Fig. S1 SEM/EDS mapping of BOI/BTO-1.5.



**Fig. S2** (a) The survey XPS spectra of BOI, BTO and BOI/BTO-1.5; (b) the survey XPS spectra enlarged view of BOI, BTO and BOI/BTO-1.5.

Sample	Surface area $(m^2, g^{-1})$	Pore volume (cm <sup>3</sup> ·g <sup>-1</sup> )	Pore diameter (nm)
BOI	3.15	0.03	90.42
BTO	2.25	0.01	69.34
BOI/BTO-1	19.95	0.17	32.72
BOI/BTO-1.5	25.63	0.18	24.83
BOI/BTO-2	25.07	0.20	27.78
BOI/BTO-3	23.86	0.25	47.20

Table S1 Physicochemical parameters of different samples

Table S2 Photocatalytic activity for the oxidation of 4-MBA over BOI/BTO-1.5 with different amount of catalyst<sup>[a]</sup>

Entry	Catalyst amount	$4-MBA/H_2O_2$	Time	$h\nu^{[b]}$	Conversion	Selectivity
	(mg)	(molar ratio)	(h)		(%)	(%)
1	5	1:2	8	+	14.6	72.3
2	20	1:2	8	+	20.1	88.3
3	50	1:2	8	+	22.8	90.6
4	80	1:2	8	+	23.0	80.0
5	100	1:2	8	+	37.5	29.4

<sup>[a]</sup> Reaction conditions: catalyst (BOI/BTO-1.5), 4-MBA (0.2 mmol), DMF (5 mL),  $H_2O_2$  (0.4 mmol), in the air <sup>[b]</sup> Visible light ( $\lambda > 420$  nm)

Table S3 Photocatalytic activity for the oxidation of 4-MBA over BOI/BTO-1.5 with different molar ratios of 4-MBA/H<sub>2</sub>O<sub>2</sub><sup>[a]</sup>

Entry	Catalyst	4-MBA/H <sub>2</sub> O <sub>2</sub>	Time	$h\nu^{[b]}$	Conversion	Selectivity
		(molar ratio)	(h)		(%)	(%)
1	BOT/BTO-1.5	1:1	8	+	20.2	92.4
2	BOT/BTO-1.5	1:1.5	8	+	21.4	91.6
3	BOT/BTO-1.5	1:2	8	+	22.8	90.6
4	BOT/BTO-1.5	1:2.5	8	+	23.7	65.0
5	BOT/BTO-1.5	1:3	8	+	26.3	48.7
6	BOT/BTO-1.5	1:4	8	+	29.4	43.6

<sup>[a]</sup> Reaction conditions: catalyst (BOI/BTO-1.5, 50 mg), 4-MBA (0.2 mmol), DMF (5 mL), in the air <sup>[b]</sup> Visible light ( $\lambda$  > 420 nm)



Fig. S3 XRD patterns of the fresh and four cycles used BOI/BTO-1.5.

Table S4 BiOI-based photocatalysts for photocatalytic oxidation of benzylic alcohols

Catalyst	Operating condition	Conversion (%)	Selectivity (%)	Reference	
Bi <sub>2</sub> MoO <sub>6</sub> -Vo-poor	Visible-light irradiation	7.1	91.0		
Bi <sub>2</sub> MoO <sub>6</sub> -Vo-rich	4 h, O <sub>2</sub>	38.2	>99	//	
BiOCl/Bi2WO6	Visible-light irradiation	22.5	-		
BiOBr/Bi2WO6		30.9	-	62	
BiOI/Bi <sub>2</sub> WO <sub>6</sub>	4 II, O <sub>2</sub>	13.0	-		
0.3 wt% Pt/Bi <sub>2</sub> MoO <sub>6</sub>	Visible-light irradiation 1 h, O <sub>2</sub>	36.0	>99	63	
Bil <sub>2</sub> O <sub>17</sub> Cl <sub>2</sub>	Visible-light irradiation 8 h, O <sub>2</sub> , 50 °C	44.0	>99	64	
BOI/BTO	Visible-light irradiation 8 h, $H_2O_2$	20.2	92	Our work	