

Electronic Supplementary Information (ESI)

First synthesis of Bi self-doped Bi_2MoO_6 - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ composite and its photocatalytic performance for selective oxidation of aromatic alkanes under visible light irradiation

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Experimental Details

Preparation of catalysts

Preparation of $\text{Bi}_{3.64}\text{Mo}_{0.36}\text{O}_{6.55}$ nanospheres. $\text{Bi}_{3.64}\text{Mo}_{0.36}\text{O}_{6.55}$ nanospheres were synthesized following method previously reported in the literature [S1]. Typically, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (5 mmol) was dissolved in 25 mL of distilled water under magnetic stirring until it was completely dissolved. Meanwhile, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (0.36 mmol) was dissolved in 25 mL of distilled water, and the solution was added dropwise into the $\text{Bi}(\text{NO}_3)_3$ solution, then 5 mL of ethanol was added for proper mixing. The pH of the mixed solution was adjusted to 13 through the use of a NaOH solution (0.8 mol NaOH in 25 mL of distilled water). After being stirred for 30 min at room temperature, the mixture was subject to ultrasonic treatment for 30 min and then

to hydrothermal treatment in a 100 mL Teflon-lined stainless steel autoclave at 160 °C for 24 h. Finally, the products were collected by centrifugation, washed with deionized water and ethanol for three times, and dried in air at 60 °C for several hours.

Preparation of BMO-x nanosheets. The nanosheets of self-doped $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ - Bi_2MoO_6 composites were also synthesized hydrothermally. Briefly, $\text{Bi}(\text{NO}_3)_3$ solutions of different concentrations were prepared by dissolving independently 0.5, 1.0, 1.5, 2.0, and 2.5 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 10 mL of 1.5 M HNO_3 . Then 1 mmol $\text{Bi}_{3.64}\text{Mo}_{0.36}\text{O}_{6.55}$ was dissolved in 70 mL of distilled water under magnetic stirring, and the solution was added dropwise into the solutions of different $\text{Bi}(\text{NO}_3)_3$ concentrations. Each mixture was stirred for 10 min at room temperature in air and then kept in a 100 mL Teflon-lined autoclave at 160 °C for 24 h. Finally, the products were collected by filtration, washed thoroughly with ethanol and deionized water, and dried in air at 60 °C for several hours. The five as-obtained samples are denoted herein as BMO-x ($x = 0.5, 1.0, 1.5, 2.0,$ and 2.5).

Preparation of γ - Bi_2MoO_6 , α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and mechanically mixed α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 of different ratios. The α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 catalysts were prepared by a hydrothermal method [S2, 3]. 5 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in distilled water then the solution was then added dropwise into aqueous solution containing 1.07 and 0.36mmol $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ respectively under vigorous stirring. The pH of the two mixed solution was precisely controlled using known amounts of ammonia solution. The pH values were maintained at 1.0 and 7.0 in the preparation of α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 , respectively. After the resulting solution was vigorously stirred at room temperature for 1 h, it was kept in an autoclave at 160 °C for 24 h. Finally, the precipitate was collected, washed thoroughly with ethanol and deionized water, and dried at 50 °C for several hours. A series of catalysts composed of a mixture of α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 were also prepared by simple mixing and grinding. Mixtures of α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 in different ratios (molar fraction of $\text{Bi}_2\text{MoO}_6 = 40\%, 50\%, 60\%, 70\%,$ and 80%) were properly ground. The five as-obtained mixtures are denoted as Bi_2MoO_6 -x% ($x = 40, 50, 60, 70,$ and 80).

Preparation of $\text{Bi}_{2.1}\text{MoO}_6$ and $\text{Bi}_{2.1}\text{Mo}_3\text{O}_{12}$. $\text{Bi}_{2.1}\text{MoO}_6$ was synthesized following the procedure previously reported in literature [S4]. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in Bi/Mo molar ratio of 2.1 were mixed in 80 mL of distilled water in a 100 mL Teflon-lined autoclave. The mixture was stirred for 0.5 h at room temperature in air and then kept in the autoclave at 160 °C for 24 h. Finally, the

precipitate was collected, washed thoroughly with ethanol and deionized water, and dried at 50 °C for several hours. Bi_{2.1}Mo₃O₁₂ was synthesized in a similar manner, except that the Bi/Mo molar ratio was 0.7, and the pH value was 1.

Catalyst characterization

The Bi-to-Mo ratios were calculated based on the data of elemental analysis collected by means of inductively coupled plasma-optical emission spectroscopy (ICP-OES). The morphology and microscopic structure were analyzed using a scanning electron microscope (FE-SEM, Hitachi S-4800) and a high-resolution transmission electron microscope (HR-TEM, JEM-2100F). The crystal phase of samples was determined over a Bruker D8 Advance X-ray diffractometer with monochromatized Cu-K α radiation ($\lambda = 0.154\ 06\ \text{nm}$). The X-ray photoelectron spectroscopic (XPS) results (Bi 4f, Mo 3d and O 1s) of surface bismuth, molybdenum and oxygen species were collected over a VG Multilab 2000 equipment using Mg-K α ($h\nu = 1253.6\ \text{eV}$) as excitation source (XPS, SSX-100, Mg-K α). The UV-vis diffuse reflectance spectra (UV-vis DRS) were obtained over a Cary-100 spectrophotometer, using BaSO₄ background as reference. Brunauer–Emmett–Teller (BET) surface areas of samples were determined by nitrogen adsorption–desorption isotherm measurements at 77 K over a Micromeritics Tristar-3000 nitrogen adsorption apparatus. Photoluminescence (PL) spectra were acquired over a Shimadzu RF-5301PC fluorescence spectrophotometer.

Photoelectrochemical experiments

The photocurrent measurement was performed on a CHI660E electrochemistry workstation and electrochemical impedance spectroscopic (EIS) measurement was performed on an Autolab electrochemistry workstation at room temperature. All the experiments were carried out in a standard three-electrode cells containing 0.5 mol/L Na₂SO₄ aqueous solution with a platinum foil and a saturated calomel electrode as counter electrode and reference electrode, respectively. To prepare the working electrodes, FTO glass was ultrasonically cleaned in soap-suds, deionized water, and acetone successively. The electrodes were prepared by mixing a slurry containing 40 mg of as-prepared photocatalyst, 10% dimethylformamide (DMF) and 10% nafion on FTO glass and then dried in air at 60 °C for 6 h. The area of electrodes was roughly 2×2 cm². A 500 W Xe lamp with a 400 nm cut off filter was used as light source.

Photocatalytic activity

The photocatalytic performance of the catalysts was evaluated in the photocatalytic oxidation of toluene under ambient conditions (i.e., room temperature and atmospheric pressure) [S5–7]. Typically, toluene (1 mmol) and 100 mg of catalyst were mechanically mixed with 3 mL of benzotrifluoride (BTF, supplied from Aladin with a purity of 99%) in a round bottom flask. A condenser pipe was installed to trap toluene and products. To blend the catalyst evenly in the solution, the suspension was stirred for half an hour under a flow of O₂ (rate = 3 mL·min⁻¹). The reaction was carried out by exposing the suspension to visible-light irradiation from a 300 W Xe lamp (PLS-SXE 300C, Perfectlight) with a 400 nm cut off filter ($\lambda \geq 400$ nm). After the reaction, the catalyst particles were thoroughly removed by centrifugation, and the products were analyzed using a SHIMADZU Gas Chromatograph (GC-2010, with a capillary SHRtx-1701 analysis column). Controlled experiments using different scavengers (ammonium oxalate for photogenerated holes, K₂S₂O₈ for photogenerated electrons, tert-butyl alcohol for hydroxyl radicals, and benzoquinone for superoxide radicals) were performed with the addition of 0.1 mmol of scavenger to the reaction system [S4–5]. We completed the mass balance according to the gross mass before and after reaction, the gross mass should have increased slightly after the reaction because the major end product is aldehyde. Instead, we found the mass keep unchanged which is nearly unavoidable because of saturated vapor pressure of the system. Conversion of aromatics and selectivity to the corresponding aldehydes is defined as follows:

$$\text{Conversion (\%)} = \frac{\text{moles of toluene reacted}}{\text{moles of toluene supplied}} \times 100\%$$

$$\text{Conversion (\%)} = \frac{\text{moles of corresponding aldehyde formed}}{\text{moles of toluene reacted}} \times 100\%$$

Figures

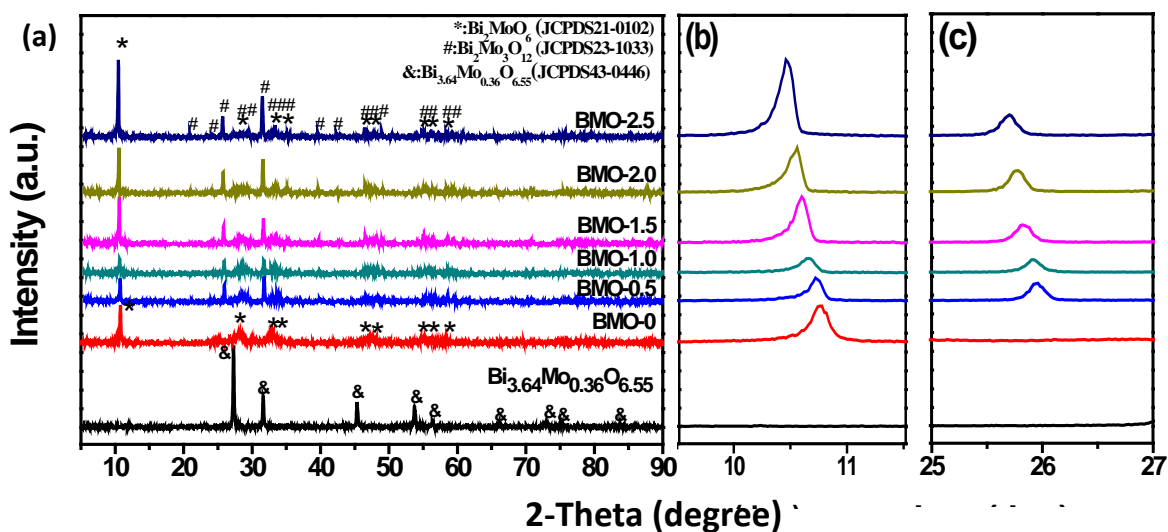


Fig. S1 XRD patterns of $\text{Bi}_{3.64}\text{Mo}_{0.36}\text{O}_{6.55}$ and BMO-x samples with different Bi^{3+} contents

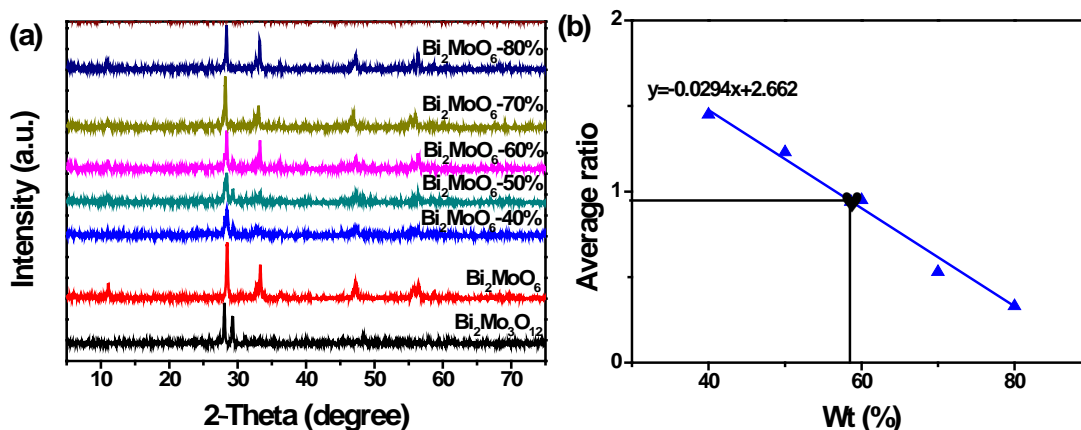


Fig. S2 (a) XRD patterns of $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, Bi_2MoO_6 and mixtures of $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and Bi_2MoO_6 in different molar fractions, and (b) average ratio of characteristic peaks intensity of $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and Bi_2MoO_6 versus molar fraction of Bi_2MoO_6 in mixtures of $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and Bi_2MoO_6 plotted according to the data in Table S2.

According to the data in Table S2, the average ratio of characteristic peak intensity of $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and Bi_2MoO_6 in BMO-1.0 is 0.94, Fig. S2b shows that the abscissa value corresponding to 0.94 is 58.6. In other words, before the self-doping action there is 58.6% of Bi_2MoO_6 in BMO-1.0.

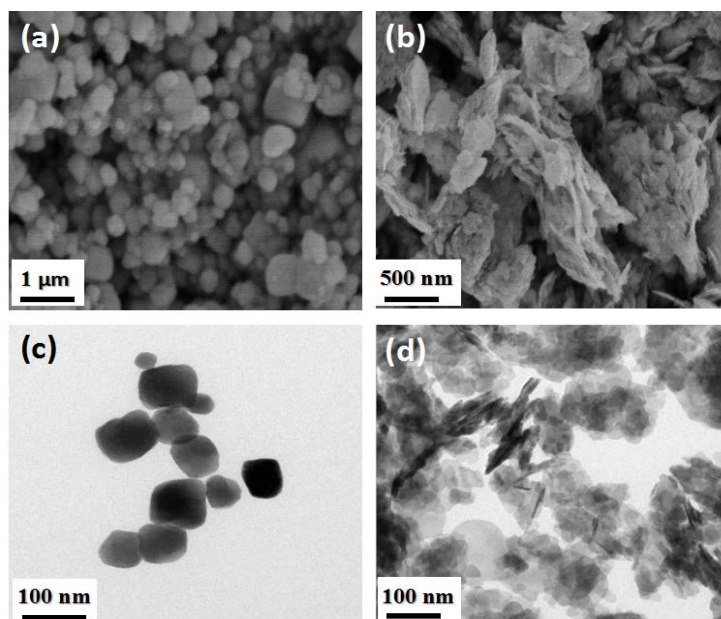


Fig. S3 SEM images of (a) $\text{Bi}_{3.64}\text{O}_{0.36}\text{O}_{6.55}$ and (b) BMO-1.0 samples, TEM images of (c) $\text{Bi}_{3.64}\text{O}_{0.36}\text{O}_{6.55}$ and (d) BMO-1.0 samples.

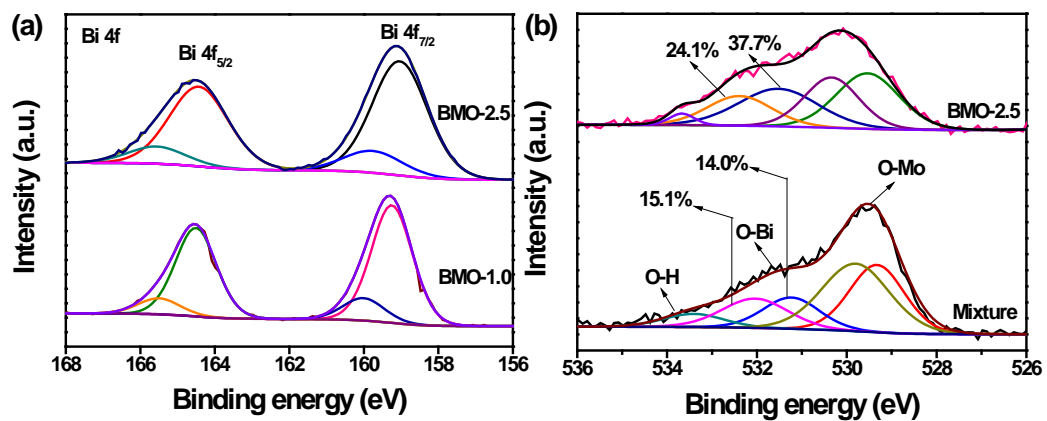


Fig. S4 High-resolution (a) Bi 4f and (b) O 1s spectra of BMO-1.0 and BMO-2.5

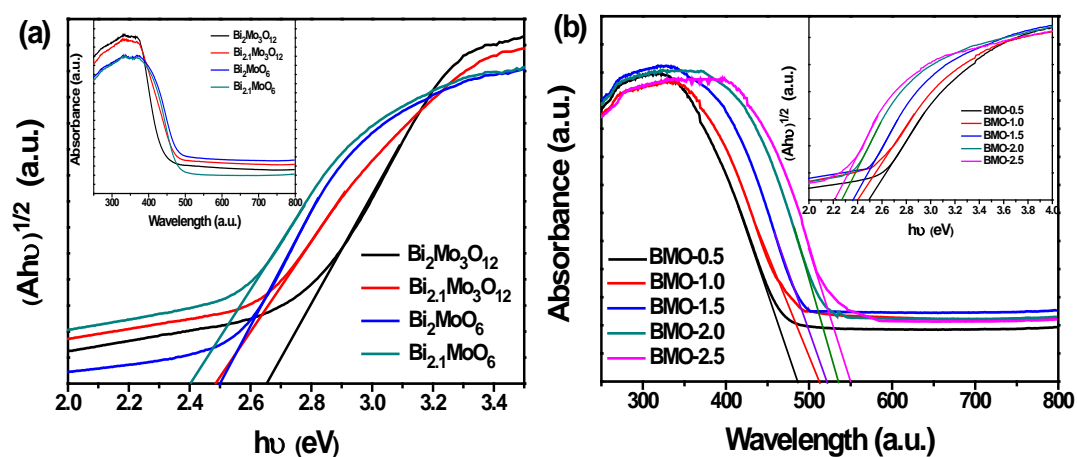


Fig. S5 (a) The plots of transformed Kubelka–Munk function versus light energy and DRS (inset) of BMO samples, (b) UV-vis diffuse reflectance spectra (DRS) and the corresponding $(Ah\nu)^{1/2}$ versus photon energy plot of BMO-x.

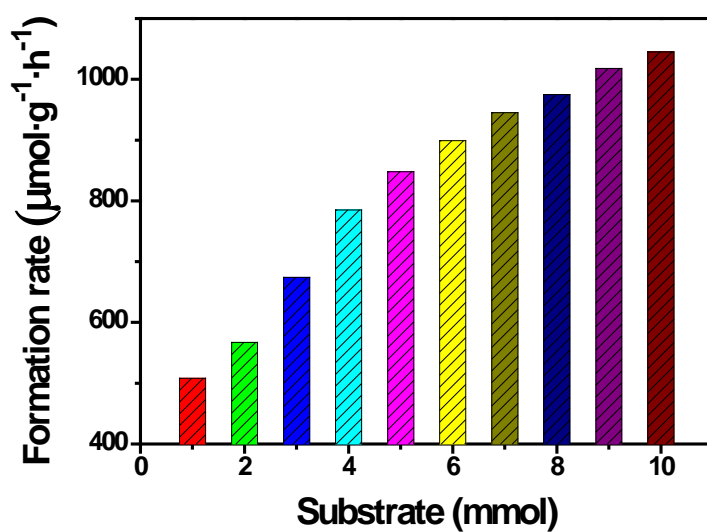


Fig. S6 Photocatalytic performance toward selective oxidation of toluene over BMO-1.0 under visible-light irradiation using different amounts of toluene adopted in experiments performed under the standard reaction condition.

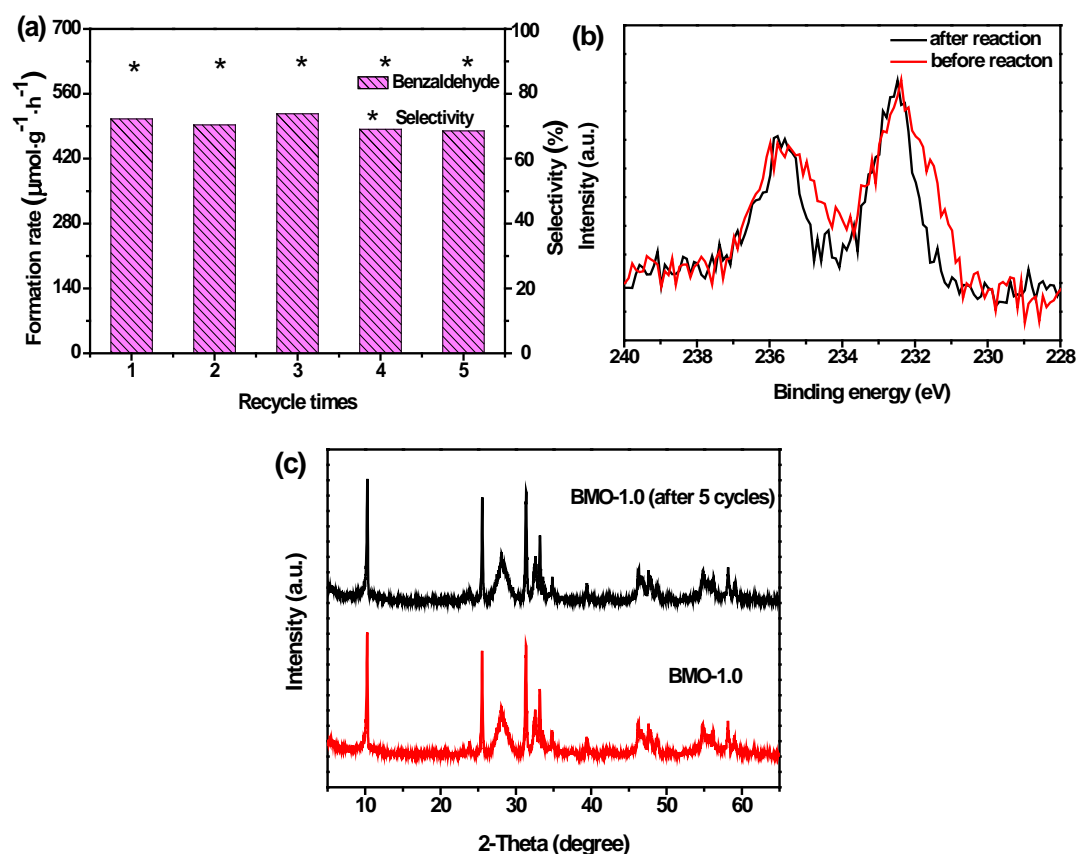


Fig. S7 (a) Recycle experiments of BMO-1 for the selective oxidation of toluene to benzaldehyde under visible light for 3 h. (b) Comparison of the XPS Mo 3d peaks of BMO-1.0 sample before and after 5 cycles of reaction and (c) XRD patterns of BMO-1 before and after 5 cycles of toluene oxidation.

As shown in Fig. S7b, there is no significant change of the Mo 3d shoulder peak even after 5 cycles of reaction, confirming that the population of defects does not change during the reaction. We also recorded and compared the XRD patterns of BMO-1.0 before and after the photocatalytic reaction (Fig. S7c), and found that there is no significant change of crystal structure after 5 cycles of visible light irradiation, thus excluding the possibility of photo-corrosion.

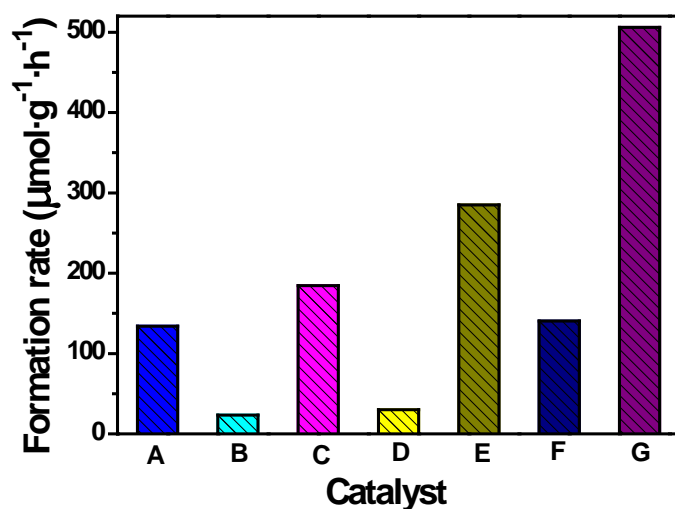


Fig. S8 Formation rate of benzaldehyde in selective oxidation of toluene over various bismuth molybdates under visible-light irradiation: A is Bi_2MoO_6 , B is $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, C is $\text{Bi}_{2.1}\text{MoO}_6$, D is $\text{Bi}_{2.1}\text{Mo}_3\text{O}_{12}$, E is a mixture of 58.6% $\text{Bi}_{2.1}\text{MoO}_6$ and 41.4% $\text{Bi}_{2.1}\text{Mo}_3\text{O}_{12}$, F is the sum of benzaldehyde yields over $\text{Bi}_{2.1}\text{MoO}_6$ and $\text{Bi}_{2.1}\text{Mo}_3\text{O}_{12}$ having a ratio the same as that of E, and finally G is BMO-1. (irradiation time 3 h, $\lambda \geq 400$ nm)

It was observed that $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and $\text{Bi}_{2.1}\text{Mo}_3\text{O}_{12}$ are poor in visible-light-induced activity while over Bi_2MoO_6 and $\text{Bi}_{2.1}\text{MoO}_6$ under identical reaction conditions the reaction rate of benzaldehyde is 134.2 and $185.4 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, respectively. In order to establish the concept of charge transfer among the components of BMO-1.0, the photocatalytic activity of a mixture of 58.6% $\text{Bi}_{2.1}\text{MoO}_6$ and 41.4% $\text{Bi}_{2.1}\text{Mo}_3\text{O}_{12}$ was measured. And a benzaldehyde formation rate of $285.0 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ much higher than the sum of benzaldehyde formation rate measured over individual $\text{Bi}_{2.1}\text{MoO}_6$ and $\text{Bi}_{2.1}\text{Mo}_3\text{O}_{12}$ of similar ratio was recorded under the same reaction conditions. The substantial performance of the former can be ascribed to the synergistic effect between the two bismuth molybdates, because oxygen species formed on the Bi_2MoO_6 migrate onto the surface of the $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ to create active sites.

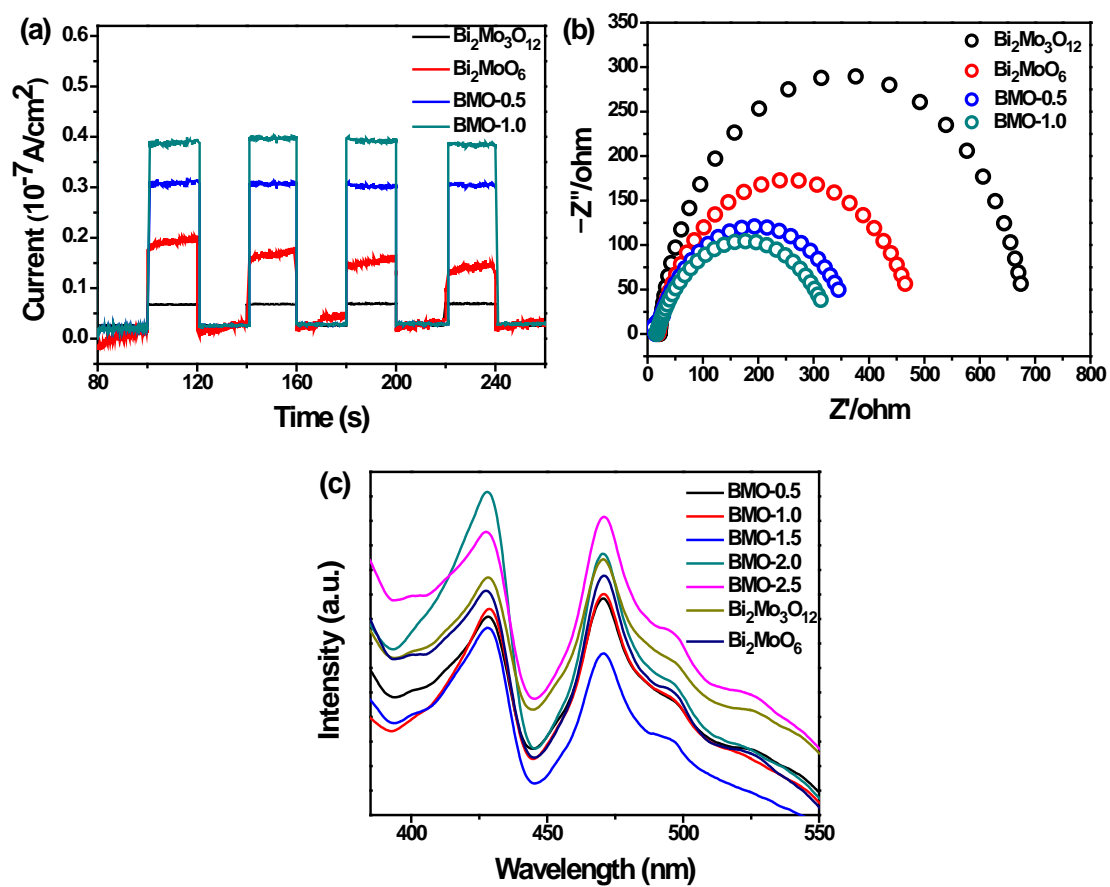


Fig. S9 (a) Photocurrent response under visible-light irradiation, (b) electrochemical impedance spectroscopy, and (c) photoluminescence spectra of BMO samples.

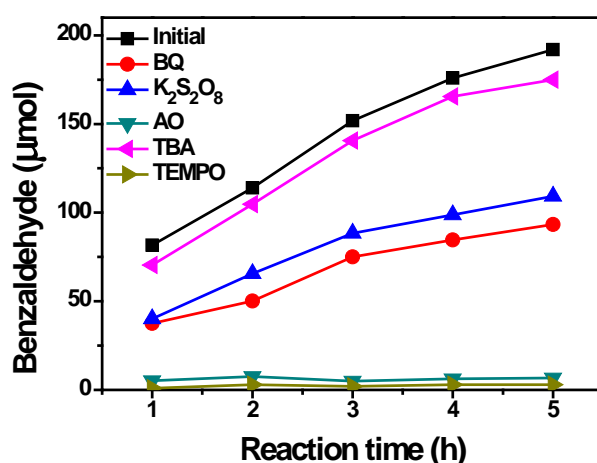
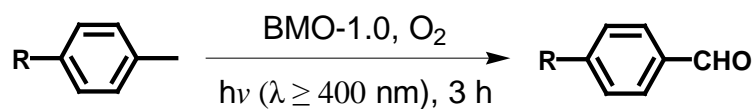

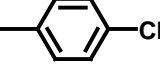
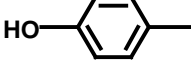







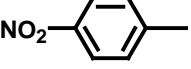
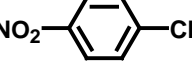


Fig. S10 Kinetic experiments for the selective oxidation of toluene with or without the addition of scavengers in the presence of dioxygen: tetra-methylpiperidine N-oxide (TEMPO for quenching all radicals), benzoquinone (BQ for quenching superoxide radicals), tert-butyl alcohol (TBA for quenching hydroxyl radicals), ammonium oxalate (AO for quenching holes) and $K_2S_2O_8$ (for quenching electrons) over BMO-1 under visible-light irradiation for 5 h.

As shown in Fig. S10, control experiment performed using tetra-methylpiperidine N-oxide (TEMPO) shows only minute conversion of toluene. When ammonium oxalate (AO) is added as holes scavenger, the conversion of toluene is almost terminated and there is no increase of conversion with time. The results indicate that the presence of holes is vital for the activation of toluene. When benzoquinone (BQ) is added to quench superoxide radicals, the conversion of toluene is significantly inhibited. Such a phenomenon is also observed when $K_2S_2O_8$ is added as electron scavenger. It is known that the quenching of electrons results in poor formation of superoxide radicals which are produced through the activation of molecular oxygen by photogenerated electrons. Thus, it is understandable that the conversion of toluene can be significantly inhibited by both BQ and $K_2S_2O_8$. Furthermore, the addition of tert-butyl alcohol (TBA) as scavenger for hydroxyl radicals has little effect on toluene conversion. The results of the control experiments clearly suggest that the photogenerated holes play a predominant role in the photocatalytic oxidation of toluene over BMO-1.0.



R = CH₃, OH, OCH₃, Cl, F, NO₂

Substrate	Product	Formation rate ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	Conv. (%)	Sel. (%)
		576.7	17.3	96.3
		546.7	16.4	98.6
		563.3	16.9	98.7
		376.7	11.3	> 99
		356.7	10.7	> 99
		333.3	10.0	> 99

Scheme S1 Substrate scope of the photocatalytic oxidation of aromatic alkanes into aldehydes. Substrate (1 mmol), catalyst (100 mg), O₂ flow rate (3 mL·min⁻¹), benzotrifluoride (3 mL), visible-light irradiation ($\lambda \geq 400$ nm, 3 h).

Table S1 Bismuth and molybdenum molar ratios of various bismuth molybdates according to the results of ICP measurements.

Samples	Bi/Mo molar ratio
Bi _{3.64} Mo _{0.36} O _{6.55}	9.81
BMO-0.5	1.44
BMO-1.0	1.63
BMO-1.5	1.79
BMO-2.0	2.01
BMO-2.5	2.19

Table S2 Peak intensity of mechanically mixed α -Bi₂Mo₃O₁₂ and γ -Bi₂MoO₆ in different ratios.^a

Catalyst	Intensity ratio			Average value
	25.802°:32.530°	28.036°:32.630°	29.159°:47.175°	
Bi ₂ MoO ₆ -40%	1.01	2.08	1.26	1.45
Bi ₂ MoO ₆ -50%	0.58	1.80	1.33	1.23
Bi ₂ MoO ₆ -60%	0.57	1.49	0.78	0.95
Bi ₂ MoO ₆ -70%	0.26	0.81	0.52	0.53
Bi ₂ MoO ₆ -80%	0.29	0.36	0.34	0.33
BMO-0.5	0.52	1.19	1.04	0.92
BMO-1.0	0.77	1.13	0.94	0.94
BMO-1.5	0.69	1.36	1.23	1.09
BMO-2.0	0.72	1.23	1.16	1.03
BMO-2.5	0.78	1.04	1.30	1.04

^a Peaks at $2\theta = 25.802, 28.036, 29.159$ degree and $2\theta = 32.530, 32.630, 47.175^\circ$ are characteristic peaks of α -Bi₂Mo₃O₁₂ and γ -Bi₂MoO₆, respectively.

Table S3 Summary of BMO physicochemical properties.

Catalyst	S _{BET} (m ² ·g ⁻¹)	Pore volum (cm ³ ·g ⁻¹)	Average pore size (nm)
Bi ₂ MoO ₆	7.52	0.02	16.83
Bi ₂ Mo ₃ O ₁₂	6.63	0.04	14.64
BMO-0.5	14.36	0.06	16.58
BMO-1.0	12.91	0.06	18.03
BMO-1.5	14.51	0.06	15.32
BMO-2.0	8.55	0.06	28.96
BMO-2.5	5.08	0.04	31.25

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