Facet-dependent Bi_2MoO_6 for highly efficient photocatalytic selective oxidation of sp^3 C-H bonds using O_2 as the oxidant

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1. Experimental sections

1.1 Synthesis of Bi_2MoO_6 samples

A total of 5 mmol bismuth nitrate pentahydrate (Tianjin Kermel Chemical Reagent Co., Ltd.) and 0.36 mmol ammonium molybdate tetrahydrate (Alfa Aesar) were completely dissolved in 30 mL ethylene glycol (Shanghai Macklin Biochemical Technology Co., Ltd.) via an ultrasound treatment. Next, 1.8 mmol cetyltrimethylammonium bromide (CTAB, Tianjin Kermel Chemical Reagent Co., Ltd.) was dissolved in 30 mL deionized water via the ultrasound treatment, and was mixed in the abovementioned solution under vigorous stirring. The pH of the mixture was adjusted between 9 and 6 using an ammonia solution (Luoyang Haohua Chemical Reagent Co., Ltd.). The mixed solution was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 48 h. The as-prepared catalyst was centrifuged and washed with water and ethanol three times and dried at 70 °C in an oven. The as-prepared samples synthesized at 9 and 6 were denoted Bi_2MoO_6-(010) and Bi_2MoO_6-(001), respectively.

1.2 Characterization of Bi_2MoO_6 samples

The morphology of the Bi_2MoO_6 samples was analyzed through transmission electron microscopy (TEM; FEI Talos F200S) and scanning electron microscopy (SEM, Hitachi Regulus 8100). The bulk structure of the Bi_2MoO_6 samples was investigated by X-ray diffraction (XRD; Rigaku Ultima IV). The optical absorption of the Bi_2MoO_6 samples was analyzed by UV-visible diffuse reflectance spectroscopy (Shimadzu UV-3600i Plus). The oxygen vacancies on the surface of the Bi_2MoO_6 samples were determined via the electron spin resonance (ESR) technique (CIQTEK EPR200 Plus). The reactive oxygen species in the photocatalytic oxidation of toluene was detected via the electron spin resonance technique (Bruker EMXplus-6/1). The surface chemical composition of bismuth molybdate samples was determined by X-ray photoelectron spectroscopy (XPS, Shimadzu/Krayos AXIS Ultra DLD). The electrochemical properties of the Bi_2MoO_6 samples were analyzed at normal temperature and pressure via a self-made three electrode system and CHEI660 electrochemical workstation. The reference electrode was Hg/Hg_2SO_4, and the counter electrode was Pt net. The working electrode was prepared using the as-prepared bismuth molybdate catalyst according to the following reaction process. One drop of Triton-100 was added to 50 mg of the bismuth molybdate catalyst, and three drops of water were ground to form a slurry-like mixed solution. Next, the photocatalyst was attached to the F-doped tin oxide (FTO) electrode by scraping and finally pyrolyzed for 1 h in a muffle furnace at 350 °C.

1.3 Performance of Bi_2MoO_6 samples

The experiment of selective oxidation of hydrocarbons over the photocatalyst was carried out in a home-made photocatalyst reactor. Considering the toluene (Luoyang Haohua Chemical Reagent Co., Ltd.) as an example, 1.5 ml of toluene containing 0.1 mmol of internal standard m-dichlorobenzene (Shanghai Macklin Biochemical

Technology Co., Ltd.) and 40 mg of bismuth molybdate photocatalyst were added to the reactor. The reactor was connected to a O_2 balloon with 1 bar pressure. The reaction temperature was precisely controlled at 25 °C through the connected circulating water. Under dark conditions, the mixed solution was magnetically stirred for 0.5 h. The light source of the reaction was a Xe lamp of 300 W (Beijing Perfect Light Company, China). The photocatalytic reaction was carried out under the radiation of the Xe lamp. When the reaction was completed, the solid catalyst in the reaction was removed by centrifugation. The remaining reaction solution was injected into a gas chromatography system (Agilent gas chromatography, column HP-5, argon, column temperature 120 °C). The amount of benzyl alcohol and benzaldehyde generated by the internal standard and the selectivity of benzaldehyde were calculated. Similar reaction conditions were used for recycling experiments, and reactions with different substrates.

The controlled experiments without light, a photocatalyst, or dioxygen were carried out. Other conditions were identical to those used in the aforementioned photocatalytic reaction.

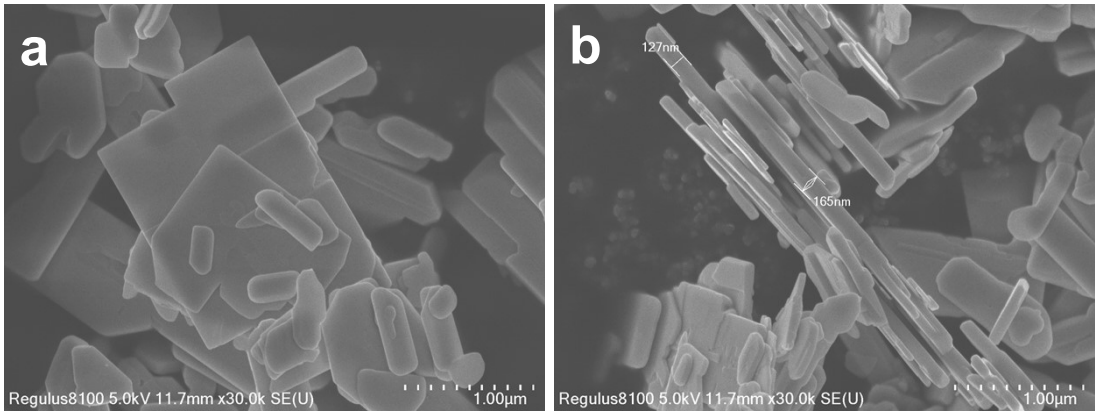

Fig. S1 SEM images of the Bi_2MoO_6-(010) sample. (a) Frontal view. (b) Side view.

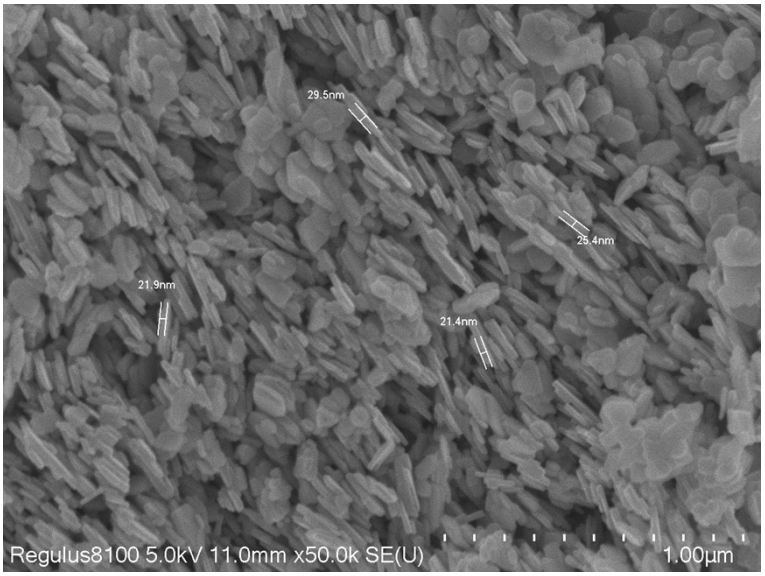

Fig. S2 SEM images of the Bi_2MoO_6-(001) sample

Table S1 Black experiments

Entry	Photocatalyst	Light	O_2	Photoactivity (μmol)	Selectivity (%)
1	+	+	+	75	98
2	-	+	+	-	-
3	+	-	+	-	-
4	+	+	-	-	-

Reaction conditions: Bi_2MoO_6-(010) catalyst, 40 mg; toluene, 1.5 mL; internal standard, m-dichlorobenzene; reaction time, 5 h; Xe lamp.

Table S2 Comparison with activity and selectivity of photocatalysts reported in the literature

References	Photocatalyst	Mass of photocatalyst (mg)	Substrate	Light	Production rate (μmol g^{-1} h^{-1})	Sel. (%)
[1]	$CdIn_2S_4$-CdS-140	10	47.2 μmol toluene	Visible light	631.7	98.8
[2]	BMOT-10	50	10 mmol toluene	Visible light	1036.8	97.2
[3]	$Cs_3Bi_2Br_9$/SBA-15	10	5 mL toluene	Visible light	12600	90
[4]	WO_3(10.3)/TiO_2	5	0.05 mmol toluene	λ>300 nm	169.4	50
[5]	CdS	8	0.1 mmol toluene	Visible light	412.5	100
[6]	CPB/Ti-180Cl	15	5 mL toluene	Visible light	1874	81.1
[7]	Pd/Bi_2WO_6-4	50	1 mL toluene	λ>400 nm	1140	90
[8]	CdS-150	10	50 μmol toluene	Visible light	1727.5	97.3
[9]	Fe(0.26)-BWO	20	10 mmol toluene	Visible light	1303.8	96.8
[10]	Pd/BiOBr	5	0.05 mmol toluene	Visible light	476.8	99
[11]	Pd/$BiVO_4$	10	1 mL toluene	Visible light	94.6	>90
[12]	3-1BiMO	50	1 mmol toluene	Visible light	778	96
[13]	$W_{18}O_{49}$	5	10 mL toluene	Visible light	410	92
[14]	$Cs_3Sb_2Br_9$/g-C_3N_4	2.5	5 mL toluene	Visible light	8346.8	81.1
[15]	Nb_2O_5	25	2 mL toluene	λ>390 nm	240	98
[16]	Bi_2MoO_6–$Bi_2Mo_3O_{12}$ composites	100	1 mmol toluene	Visible light	508	98.5
[17]	4CD/BiMO	20	350 μmol ethylbenzene	Visible light	415.6	-
[18]	CdS-ZnS	50	10 mmol toluene	Visible light	1078	98
[19]	BiOCl/$BiCl_3Br$−CTA	20	0.2 mmol	Visible	527	99

			toluene	light		
[20]	FLP−FLCN	10	0.25 mmol toluene	Visible light	82 600	96
[21]	$Cs_3Bi_{1.8}Sb_{0.2}Br_9$	10	5 mL toluene	Visible light	5830	70
[22]	Bi_2MoO_6/g-C_3N_4	50	1 mL toluene	Visible light	850.7	99
[23]	TiO_2	100	0.01 mL toluene	UV lamp	9.46	90
[24]	Ni-doped CdS	80	0.5 mmol toluene	Visible light	216.7	100
This study	Bi_2MoO_6-(010)	40	1.5 mL toluene	Visible light	375	96

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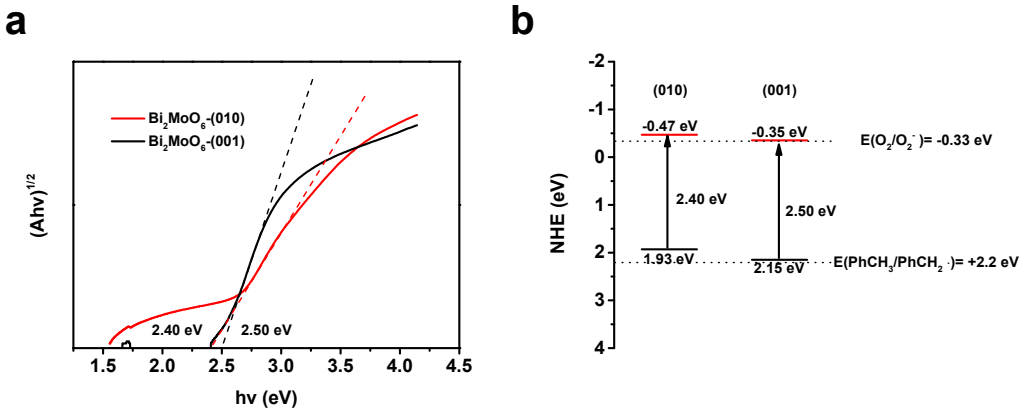

Fig. S3 (a) Tauc plots and (b) energy band structures of the Bi_2MoO_6 samples.

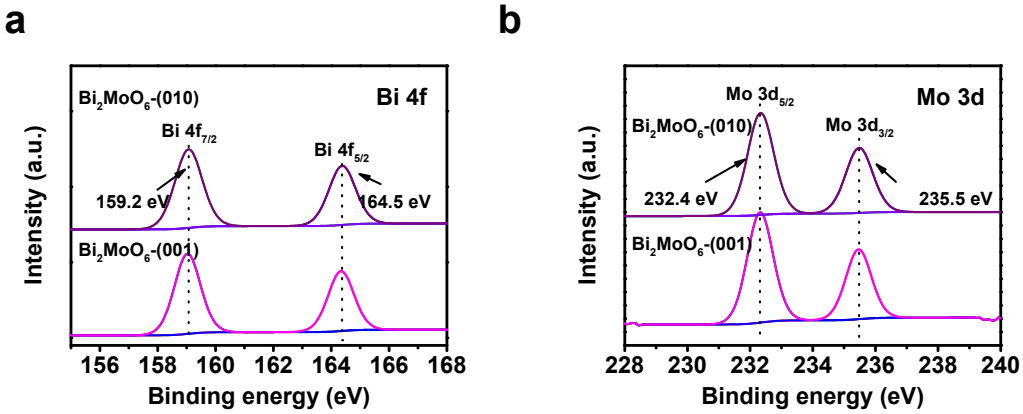

Fig. S4 Bi 4f, Mo 3d, and O1s of XPS profiles of Bi_2MoO_6-(010) and Bi_2MoO_6-(001) samples.

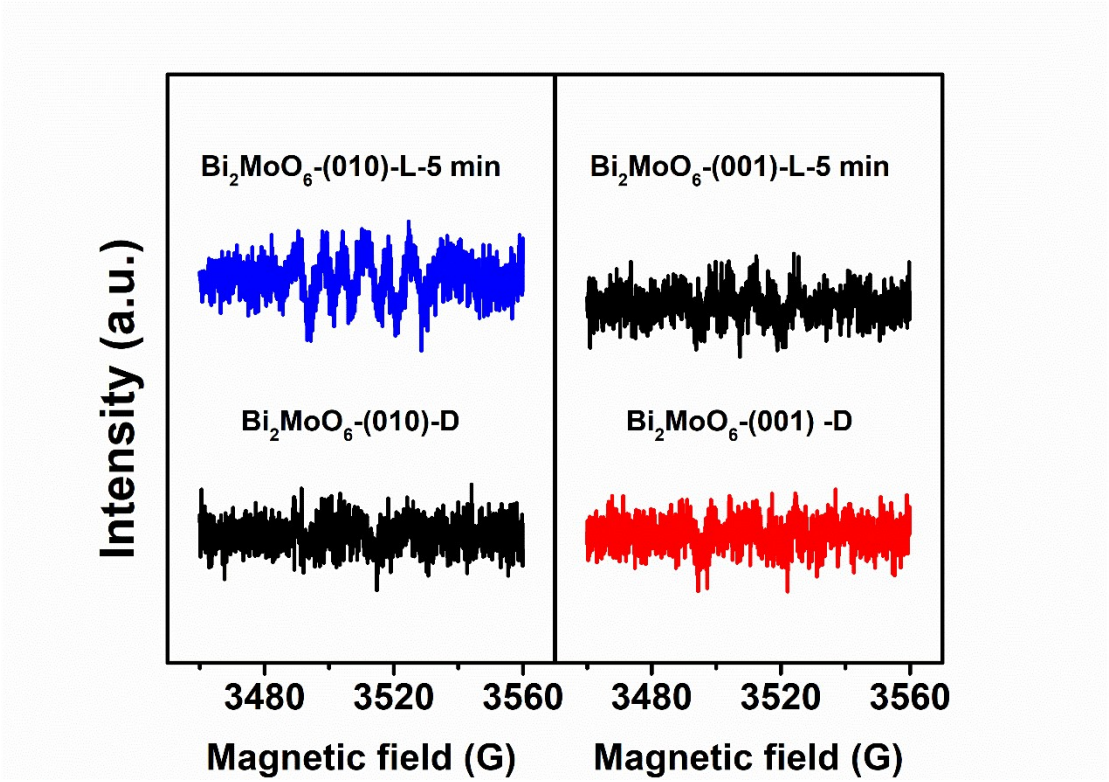

Fig. S5 ESR profile of the reactive oxygen species captured by DMPO over the Bi_2MoO_6 samples. The signals obtained under dark and visible light irradiation at 5 mins are denoted as D and L-5 min, respectively.

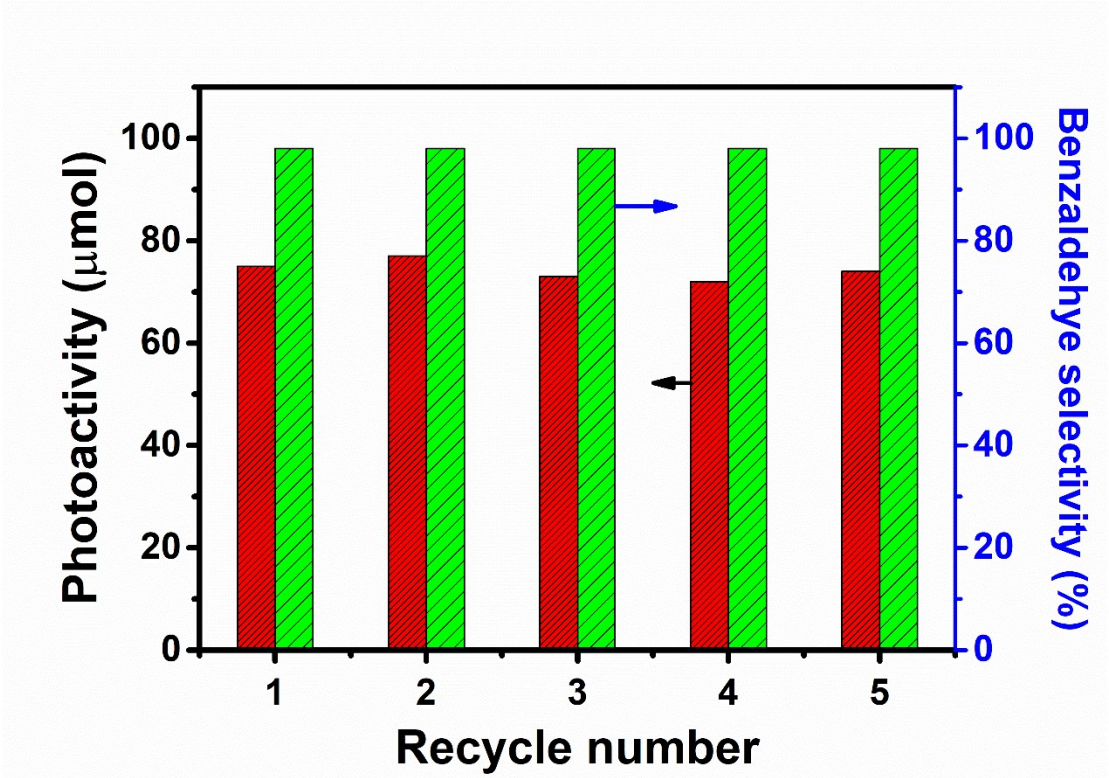

Fig. S6 Recycling experiment of the photocatalytic oxidation of toluene over the Bi_2MoO_6-(010) catalyst.

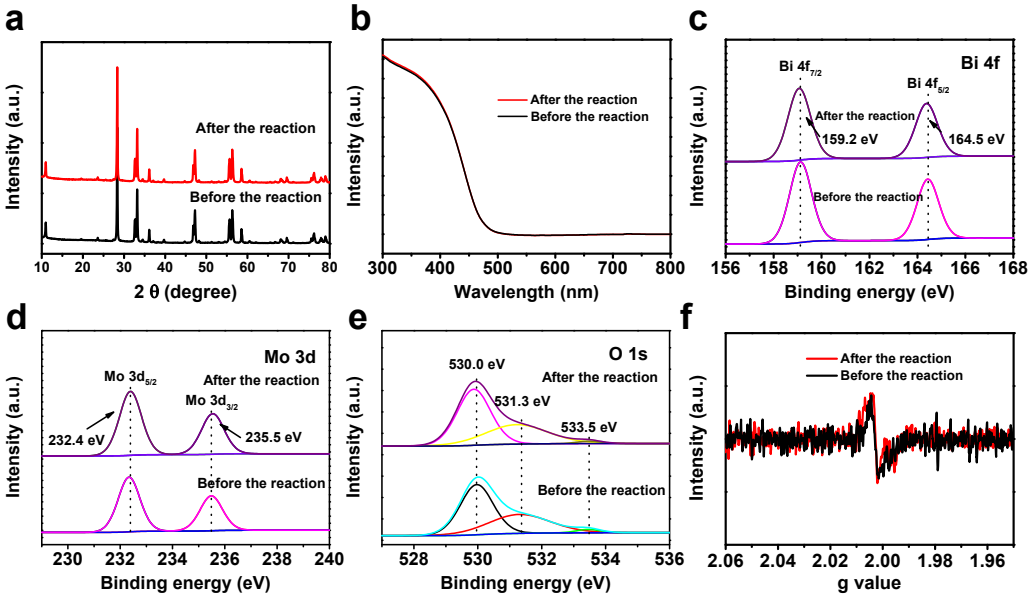

Fig. S7 Characterization of Bi_2MoO_6-(010) before and after the photocatalytic reaction. (a) XRD patterns of Bi_2MoO_6-(010) before and after the photocatalytic reaction. (b) UV-visible DRS profile of Bi_2MoO_6-(010) before and after the photocatalytic reaction. (c–e) Bi 4f, Mo 3d, and O1s XPS profiles of Bi_2MoO_6-(010) before and after the photocatalytic reaction. (f) ESR profile of Bi_2MoO_6-(010) before and after the photocatalytic reaction.

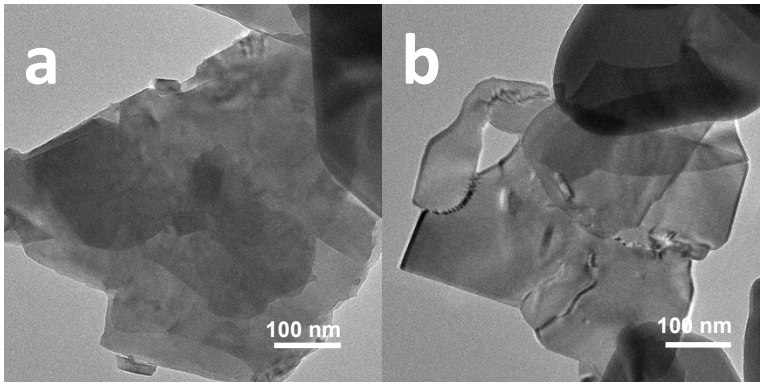

Fig. S8 TEM images of Bi_2MoO_6-(010) (a) before and (b) after the photocatalytic reaction.