Electronic Supplementary Information

Development and photocatalytic mechanism of monolayer Bi_2MoO_6 nanosheets for the selective oxidation of benzylic alcohols

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Experimental Details

1. Material Synthesis.

1.1 Chemicals: All chemicals are analytical grade and used as received without further purification .

1.2 Preparation of monolayer Bi_2MoO_6 nanosheets

In the preparation of Bi_2MoO_6 monolayers, the start materials 0.242 g $Na_2MoO_4.2H_2O$, and 0.970 g $Bi(NO_3)_3$ $.5H_2O$ and 0.3 g CTAB were added in 80 ml deionized water. After 30 min stirring, the mixed solution was poured into a 100 ml Teflon-lined autoclave. Then the autoclave was sealed into a stainless steel tank and treated at 180 °C for 16 h. Finally, the final product was collected by centrifuging the mixture, washed with deionized water and absolute ethanol for many times, and then dried at 60 °C in air for 10 h. The bulk Bi_2MoO_6 was prepared without CTAB assistance, while keeping other parameters unchanged.

2. Characterizations

The as-prepared samples were characterized by powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer operated at 40 kV and 40 mA. Ultraviolet–visible diffuse reflectance (ultraviolet–visible diffuse reflectance spectrum) spectra were obtained with a self-supporting sample disk on a ultraviolet–visible spectrophotometer (Cary 500), where $BaSO_4$ was used as a reflectance standard. X-ray photoelectron spectra (XPS) were acquired on an ESCALAB MKII with Mg Kα (hυ = 1253.6 eV) as the excitation source. The binding energies obtained in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.6 eV. The morphologies of the products were examined by fieldemission scanning electron microscopy at an accelerating voltage of 5 kV (Hitachi New Generation SU8010). Transmission electron microscopy (TEM) images, higher-resolution transmission electron microscopy (HRTEM) images, selected area electron diffraction (SAED) was recorded using a JEOL model JEM2010 EX microscope at an accelerating voltage of 200 kV. AFM images were recorded using Agilent 5,500 AFM (Agilent Technologies, USA). All the images were acquired using tapping mode under ambient conditions (ca. 40-50 % relative humidity, 25 °C temperature). The used Si cantilevers/tips (Bruker) have a spring constant of 40 N m^{-1} and a resonance frequency of 300 kHz. During an AFM experiment, sample was dispersed in ethanol using an ultrasonic bath for 20 min and then the dispersion was diluted in ethanol. A drop of the above diluted dispersion was deposited on a new cleaved mica surface and dried in air used to evaluate the morphology of the obtained nanosheets on the mica substrate. The electrochemical analysis was carried out in a conventional threeelectrode cell using a Pt plate and an Ag/AgCl electrode as the counter electrode and reference electrode, respectively. The electrolyte was 0.2 M Na_2SO_4 aqueous solution without additive (pH 6.8). The working electrode was prepared on indium-tin oxide (ITO) glass that was cleaned by sonication in ethanol for 2 h and dried at 353 K. The boundary of ITO glass was protected using Scotch tape. The 8 mg sample was dispersed in 0.5 mL of DMF by sonication to get slurry. The slurry was spread onto the pretreated ITO glass. After air drying, the working electrode was further dried at

393 K for 2 h to improve adhesion. Electron spin resonance (ESR) signals were recorded with a Brucker A300 spectrometer. A 300 W Xe lamp (Beijing Trustech, PLS-SXE300c) with a 400 nm cut-off filter was used as a light source. Thermogravimetric (TG) analyses were carried out on a SDT Q600 thermal analyzer (TA Instruments, USA). Steady-state PL measurements were carried out on an FLS980 spectrophotometer, 397 nm laser as the excitation wavelength, (Edinburgh Analytical Instrument, UK). The Brunauer–Emmett–Teller (BET) surface area was measured with an ASAP2020M apparatus (Micromeritics Instrument Corp.) Surface basic property of the samples was estimated by temperature programmed desorption of CO_2 (CO_2-TPD) on an Autochem II 2920-QIC20. Firstly, Bi_2MoO_6 samples (50 mg) was purged with dry Ar (50 $mL\cdot min^{-1}$, purity > 99.999%) at 300 ^oC for 3 h, followed by reducing the furnace temperature to 50 ^oC, and switching to a flow of 10% (volume fraction) CO_2/Ar for 1 h to execute CO_2 adsorption. Then, the samples adsorbed CO_2 were desorbed in the range of 50—400 ^oC at a heating at a rate of 5 ^oC min^{-1}

2.1 In-situ FTIR measurement

The in-situ infrared spectra of benzyl alcohol and pyridine adsorbed on the catalysts were obtained on a Nicolet Nexus 670 Fourier transform infrared (FT-IR) spectrometer at a resolution of 4 cm^{-1}. A total of 64 scans were performed to obtain each spectrum. Firstly, the powder samples were first pressed into a self-supporting IR disk (18 mm diameter, 20 mg), then the disk was placed into the sample holder which could be moved vertically along the cell's tube. Before initiating the FTIR measurements, the disk was treated under dynamic vacuum (6×10^{-4} Torr) at 250 °C for 2.5 h to remove surface contaminants. After the disk cooling to RT, 10 μL of benzyl alcohol or pyridine was spiked into the cell with a syringe via the septum. 30 min later, after adsorption equilibrium was reached, the FTIR spectra of the samples were collected. The physisorbed benzyl alcohol and pyridine were removed by a further evacuation at 150 °C for 3 min under 6×10^{-4} Torr, and then, another FTIR spectrum of the sample was then taken.

3. Evaluation of photocatalytic activity

The details of photocatalytic selective oxidation of various benzylic alcohols was performed as follow. A mixture of alcohol (0.1 mmol) and 16 mg of catalyst was dissolved in the solvent of benzotrifluoride (BTF) (1.5 mL), which was saturated with pure molecular oxygen. The choice of solvent BTF is because of its inertness to oxidation and high solubility for molecular oxygen. Then the mixture was transferred into a 10 mL Pyrex glass bottle filled with molecular oxygen at a pressure of 1 bar and stirred to make the catalyst blend evenly in the solution. The suspensions were irradiated by a 300 W Xe arc lamp (PLS-SXE 300, Beijing Perfectlight Co. Ltd.) with a 400 nm-CUT filter to cut off UV light. After the reaction, the mixture was centrifuged to completely remove the catalyst particles. The remaining solution was analyzed with an Aglient Gas Chromatograph (GC-6890N). Conversion of alcohol and selectivity for aldehyde were defined as follows:

Conversion (%) = [(C0-Calcohol)/C0]*100

Selectivity (%) = [Caldehyde /(C0-Calcohol)]*100

Where C0 is the initial concentration of alcohol, and Calcohol and Caldehyde are the concentrations of the substrate alcohol and the corresponding aldehyde, respectively.

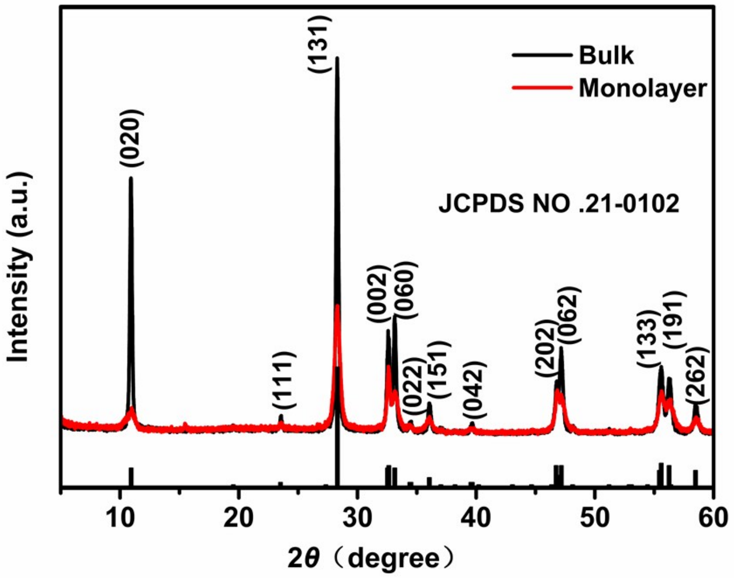


Fig. S1 XRD patterns of prepared Bi_2MoO_6 samples prepared with and without CTAB assistance.

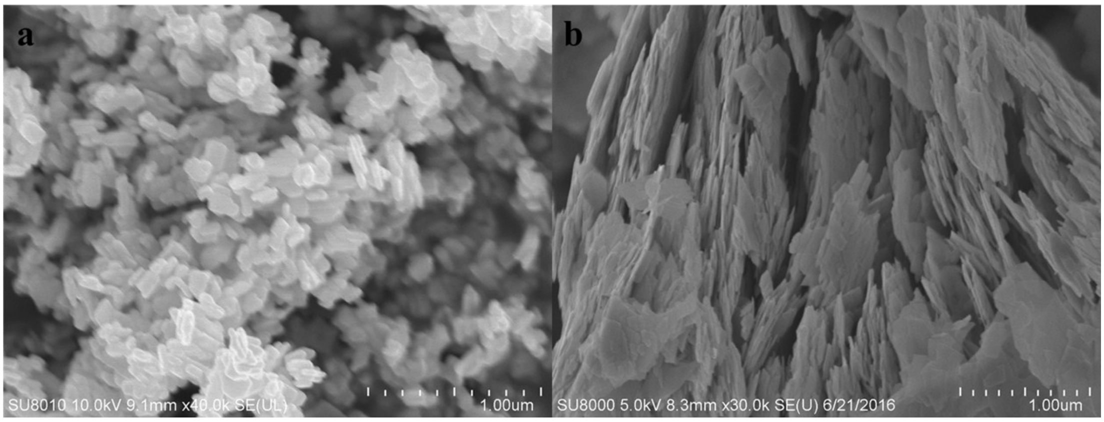


Fig. S2 The SEM images of Bi_2MoO_6 samples prepared (a) without and (b) with CTAB assistance.

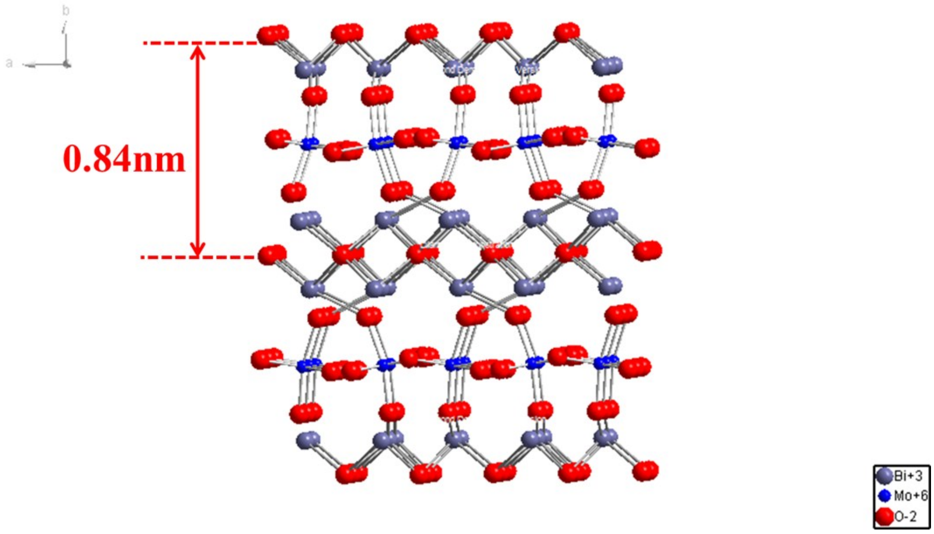


Fig. S3 Single unit cell structure in b-axis direction about Bi_2MoO_6.

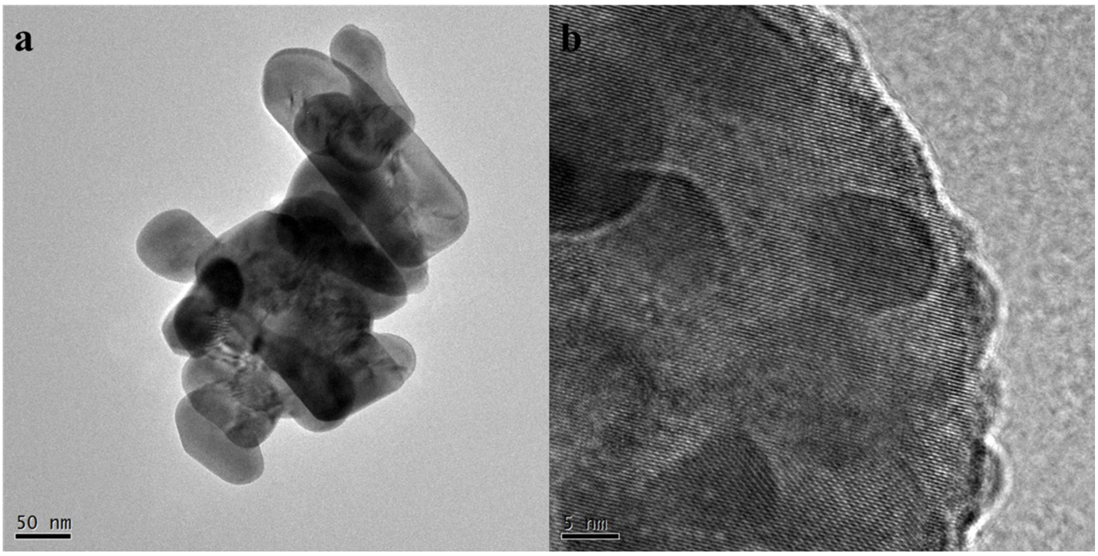


Fig. S4 TEM and HRTEM images of bulk Bi_2MoO_6.

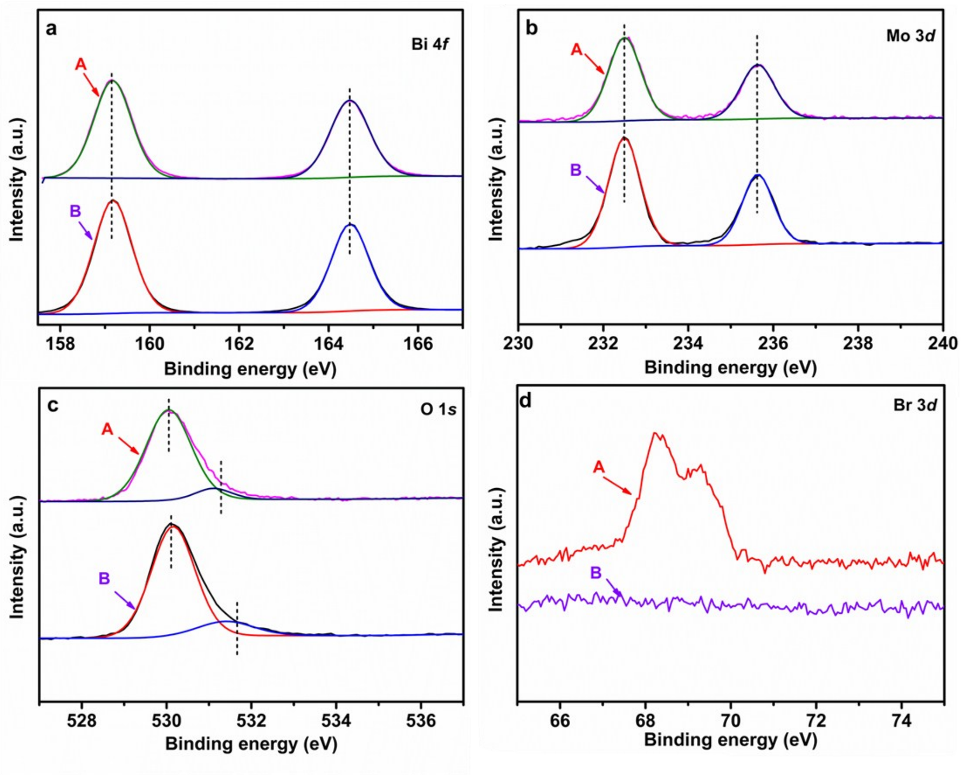


Fig. S5 High-resolution XPS spectra of Monolayer Bi_2MoO_6 nanosheets (A) and bulk Bi_2MoO_6 (B): (a) Bi 4*f*, (b) Mo 3*d*, (c) O 1*s*, (d) Br 3*d*.

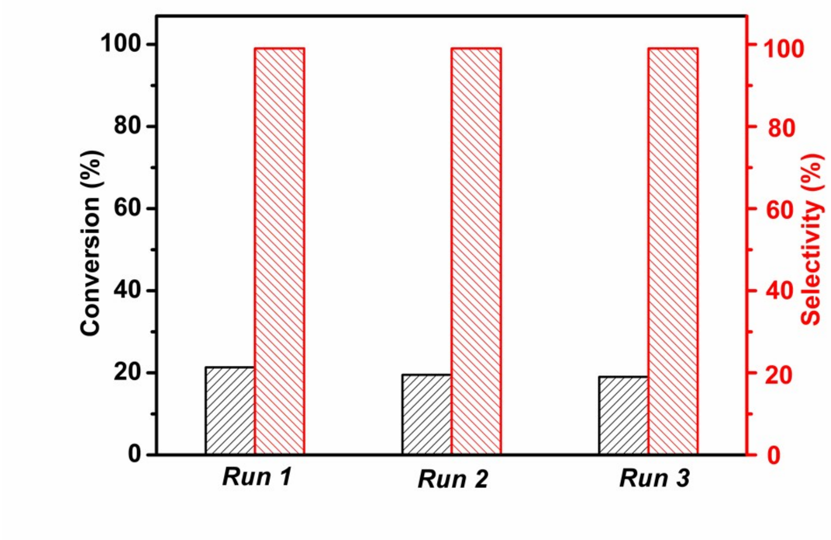


Fig. S6 Cyclic test of the photocatalytic oxidation of benzyl alcohol over monolayer Bi_2MoO_6 nanosheets under light irradiation. Reaction condition: catalyst: 16 mg; λ ≥400 nm at 298 K. Reaction time for each run: 4 h.

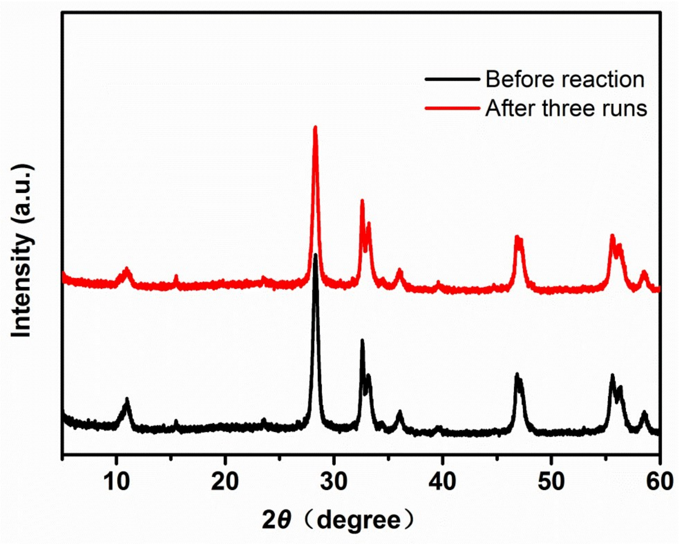


Fig. S7 XRD patterns of monolayer Bi_2MoO_6 nanosheets before the reaction and after three runs.

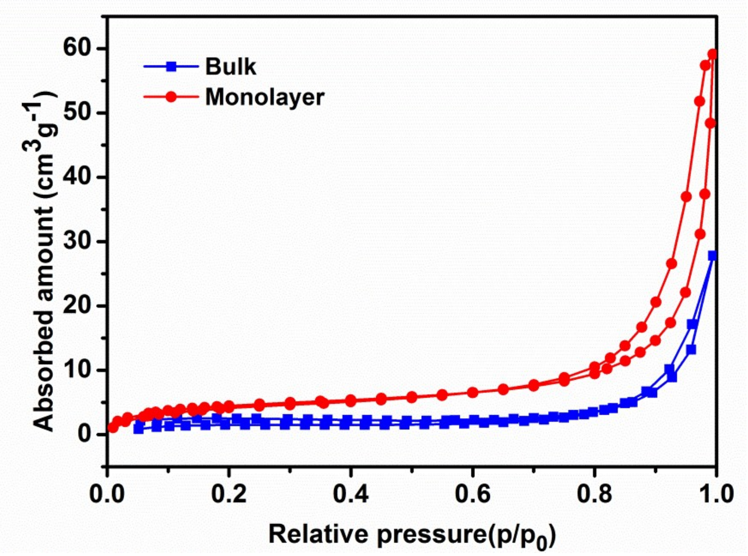


Fig. S8 N_2 adsorption-desorption isotherms on Bi_2MoO_6 samples

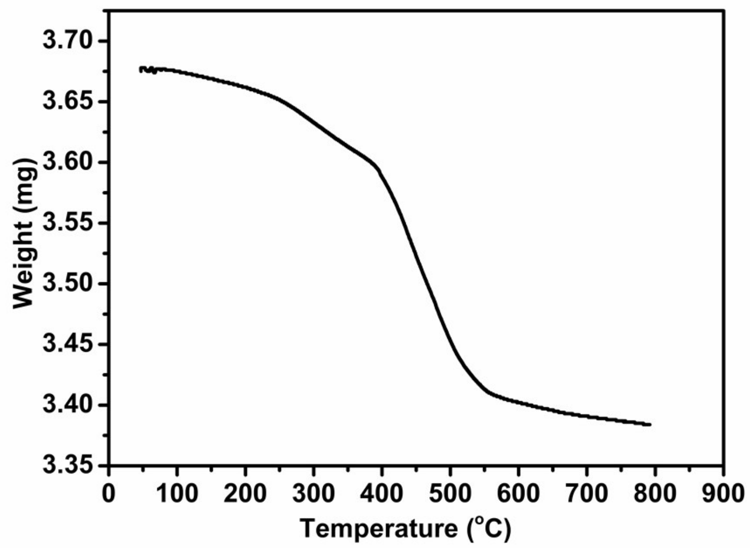


Fig. S9 TG curve of Bi_2MoO_6 samples.

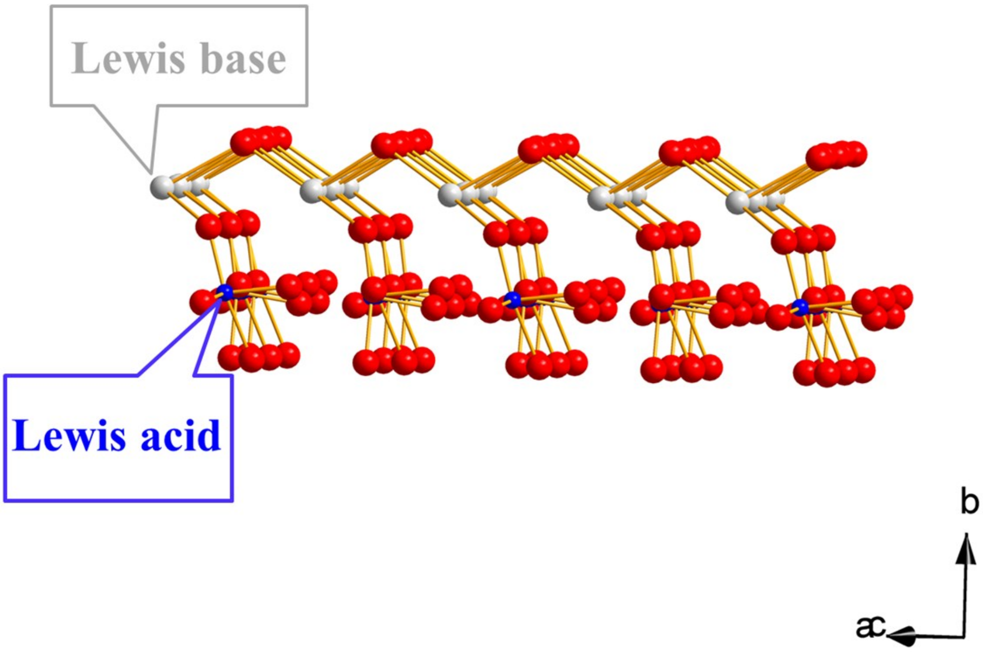


Fig. S10 Schematic structure of the monolayer Bi_2MoO_6 nanosheets. Atoms are color labeled: Bi (white), Mo (blue), and O (red)

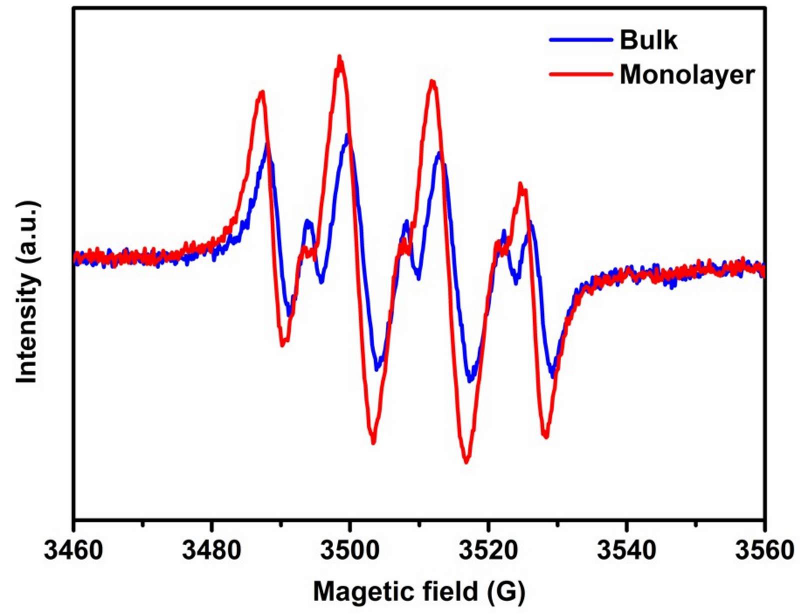


Fig. S11 ESR spectra of superoxide radical species trapped by DMPO in Bi_2MoO_6 samples dispersion in the solvent of BTF under visible-light irradiation**.**

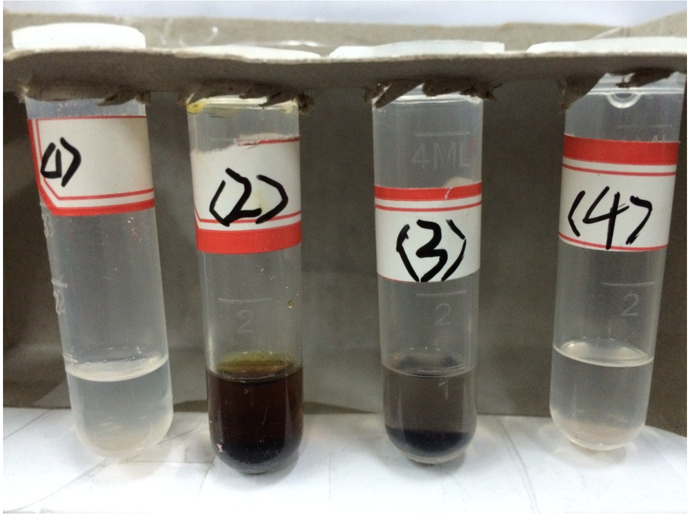


Fig. S12 Photographs of (1) a solution containing starch (5 mg), KI (0.1 M) and acetic acid (0.1 M); (2) a solution of starch (5 mg), KI (0.1 M), acetic acid (0.1 M) and H_2O_2 (30 %, 3 μL); solution of starch (5 mg), KI (0.1 M), acetic acid (0.1 M), benzyl alcohol (0.1 mmol) with (3) monolayer Bi_2MoO_6 nanosheets (16 mg), (4) without catalyst after irradiation for 4 h using 300 W Xe arc lamp ($\lambda \geq$ 400 nm) at O_2 atmosphere.

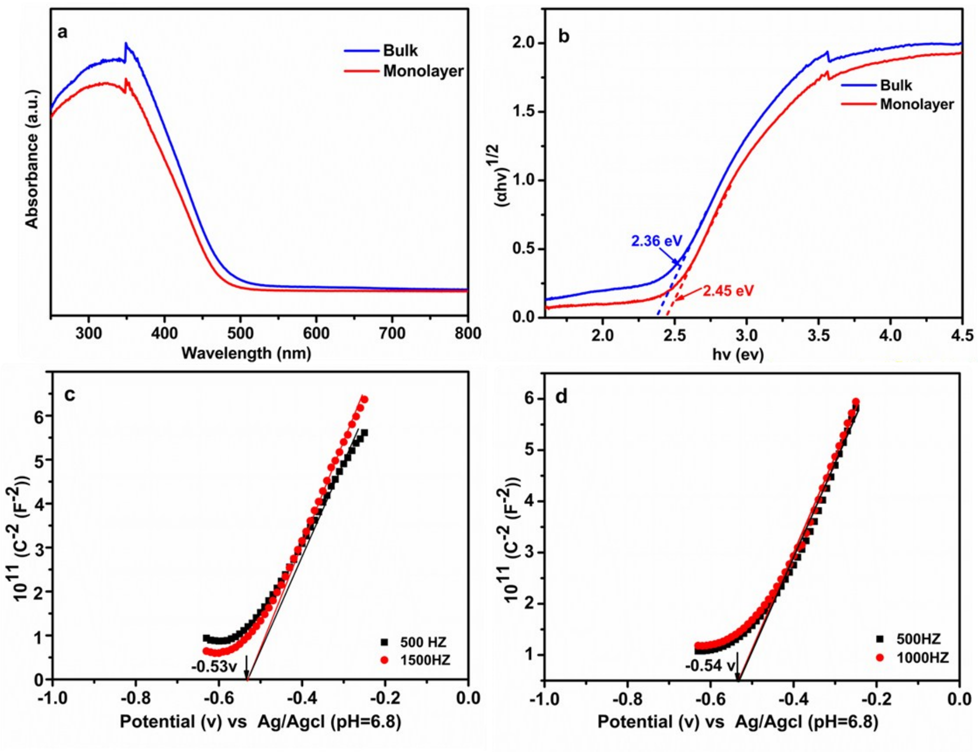
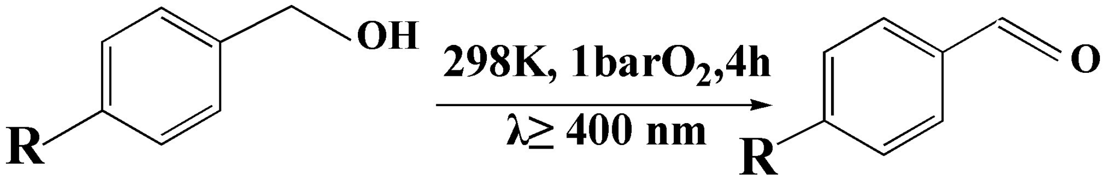


Fig. S13 (a) UV-vis DRS spectroscopy of bulk Bi_2MoO_6 and monolayer Bi_2MoO_6 nanosheets. (b) The bandgap value, estimated by a related curve of $(\alpha h\nu)^{1/2}$ versus photon energy plotted. Typical Mott-Schottky plots of Bi_2MoO_6 samples (c) bulk (d)monolayer nanosheets in 0.2 M Na_2SO_4 aqueous solution (pH= 6.8).

Table S1. Photocatalytic activities for selective oxidation of benzylic alcohols over bulk Bi_2MoO_6 samples with (+) visible light.



Entry	Sample	R	T[a](K)	H_{υ}[b]	Atm.	Conv. (%)	Sel. (%)
1	Bulk[c]	H	298	+	O_2	3.2	>99
2	Bulk	OCH_3	298	+	O_2	13.8	>85
3	Bulk	CH_3	298	+	O_2	6.9	>99
4	Bulk	F	298	+	O_2	3.9	>99
5	Bulk	Cl	298	+	O_2	9.5	>99

[a] Reaction temperature; [b] λ ≥ 400 nm; [c] Bulk Bi_2MoO_6 ;

Table S2. Photocatalytic activities for selective oxidation of benzyl alcohols over Bi_2MoO_6 samples with (+) visible light. The thermocatalysis of Bi_2MoO_6 samples without (-) visible light.

Entry	Sample	R	T[a](K)	H_{υ}[b]	Atm.	Conv. (%)	Sel. (%)
1	M[c]	H	298	-	O_2	0	-
2	M	H	298	+	N_2	2.0	>99
3	-	H	298	+	O_2	0	-
4	M	H	298	+	Air	17.4	>99
5	-	H	298	-	0.5eqv.H_2O_2[d]	0.0068	>93
6	-	H	298	-	1eqv.H_2O_2[d]	0.0060	>99
7	-	H	298	-	1.5eqv.H_2O_2[d]	0.0059	>98
8	Bi_2MoO_6 –water[1]	H	298	+	O_2	2.5	>99
9	Bi_2MoO_6 -glycol[1]	H	298	+	O_2	10.4	>99

[a] Reaction temperature; [b] λ ≥ 400 nm [c] Monolayer Bi_2MoO_6 nanosheets ; [d] The amount of H_2O_2 added is relative to that of benzyl alcohol.

[1] B. Zhang, J. Li, Y. Gao, R. Chong, Z. Wang, L. Guo, X. Zhang and C. Li, *J. Catal.,* 2017, **345**, 96-103.