Facile one-step hydrothermal synthesis of noble-metal-free hetero-structural ternary composites and their photocatalytic water purification

Yuanyuan Zhang[a], Yongchao Ma[a], Lili Wang[a], Qinxing Sun[a], Xinzhi Sun[a], Yongsheng Shi[b], Dan Qu[a], Jinsheng Shi [a b*]

Affiliations:

[a] Qingdao Agricultural University, Department of Chemistry and Pharmaceutical Science

[b] Qingdao Bona Biomimetic Composite Reaserch Institute Co. Ltd.

Corresponding author:

Mailing address: Qingdao Agricultural University, Department of Chemistry and Pharmaceutical Science, Chengyang District, Qingdao, P.R. China

E-mail: jsshiqn@aliyun.com

Phone number: 86-0532-88030161

Fax: 86-0532-86080213

Experimental Section

1. Synthesis of BiOCl precursor microspheres

BiOCl precursor was synthesized by a facile hydrothermal method. Briefly, 3 mmol $Bi(NO_3)_3{\cdot}5H_2O$ was blended with 60 ml EG and stirred at room temperature for 30 min. After that, appropriate amount of KCl was introduced into the above solution with vigorous stirred for 30 min. Then the solution was transferred into 100-mL Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. After being cooled to room temperature, the obtained precipitate was washed several times with deionized water and then dried at 60 °C for 12 h.

2. Material characterization

Crystalline phases of samples were obtained by X-ray diffraction (XRD) using a Bruker D8 diffractometer. X-ray photoelectron spectra (XPS) was investigated on an ESCA-3 Mark II spectrometer (VG Scientific Ltd, England) using Al Ka (1486.6 eV) radiation. General morphologies of samples were measured by a scanning electron microscope (SEM, S4800, Hitachi). Adsorption-desorption isotherms and pore size distributions of catalysts were examined by volumetric adsorption equipment (NOVA Surface Area Analyzer Station A, USA). Ultraviolet visible (UV-vis) diffuse reflectance spectrum (DRS) was obtained by a UV-vis spectrophotometer (TU-1901, China). Photoluminescence (PL) spectra of samples were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Photoluminescence lifetimes of photocatalysts were calculated using a phosphorimeter attached to the main system with a Xe-flash lamp (25 W powers). Electron spin resonance (ESR) signals of adducts spin-trapped

by spin-trap reagent 5, 5-dimethyl-1-pirroline-N-oxide (DMPO) were detected on a Bruker model ESR JES-FA200 spectrometer. The degradation intermediate of RhB were detected by liquid chromatography-mass spectroscopy/ mass spectroscopy (LC-MS/MS) equipped with an electrospray ionization (ESI) source. Methanol/ammonium acetate solution (75:25, v/v) was used as mobile phase. Band structure and density of state (DOS) of BiOCl and Bi_2MoO_6 were examined via CASTEP code on the basis of density functional theory (DFT) within the plane wave pseudopotential method.

3. Photocatalytic experiments

3.1 Photocatalytic Disinfection Experiment

Photocatalytic inactivation of bacteria was investigated under a 300 W Xe lamp equipped with a cutoff filter (>420 nm). Staphylococcus aureus was selected as typical bacteria. Firstly, staphylococcus aureus was cultured in LB broth at 37 °C to realize a cell count of approximate 10^8 colony forming units (CFU)/mL. 100 mg obtained sample was introduced into 30 mL bacteria suspension solution. 1 mL solution was taken out at intervals of 0.5 h then immediately spread on nutrient agar plates and incubated at 37 °C for 24 h to confirm the number of viable cells.

3.2 Photocatalytic Degradation Experiment

Photodegradation performance of as-synthesized catalysts was examined by degrading of Rhodamine B (RhB) under visible light. Prior to irradiation, 30 mg of catalyst was dispersed in an aqueous solution of RhB (100 mL, 0.01 mM) under magnetic stirring for 30 min in darkness to realize adsorption-desorption equilibrium between photocatalysts and RhB. During irradiation, 5 mL of suspension was taken

and centrifugated at intervals of 15 min. Concentrations of dye were calculated by UV-vis absorption using a TU-1901 spectrophotometer.

4. Active species trapping experiments

In order to investigate main active species formed in photodegradation process, several scavengers including 1 mM p-benzoquinone (p-BQ), 1 mM ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) and 1 mM isopropanol (IPA) were introduced into solution to eliminate $\bullet O_2^-$, h^+ and •OH, respectively. The other process was consistent with the former photocatalytic experiments.

Photocatalyst species	$BiOCl/Bi_2MoO_6$	$BiOCl/Bi_2MoO_6/Bi$	BiOCl/Bi
Specific surface area (m^2/g)	62.80	126.5	77.04
Pore size (nm)	9.52	7.84	6.91
Pore volume (cm^3/g)	0.15	0.25	0.13

Table S1. BET specific surface area, average pore size and pore volume of catalysts.

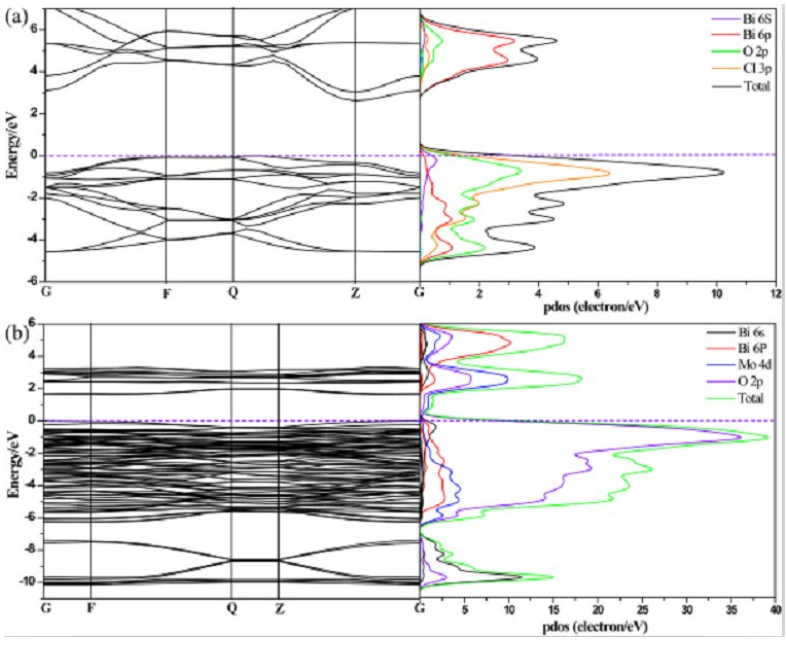

Fig. S1 Calculated band structures and total and partial density of states plots of (a)

BiOCl and (b) Bi_2MoO_6.

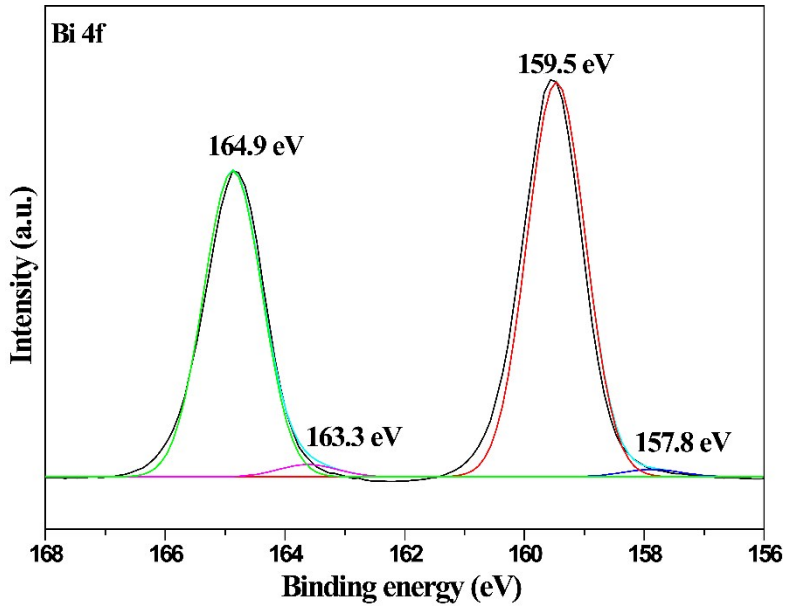

Fig. S2 Bi 4f XPS spectra of $BiOCl/Bi_2MoO_6/Bi$.

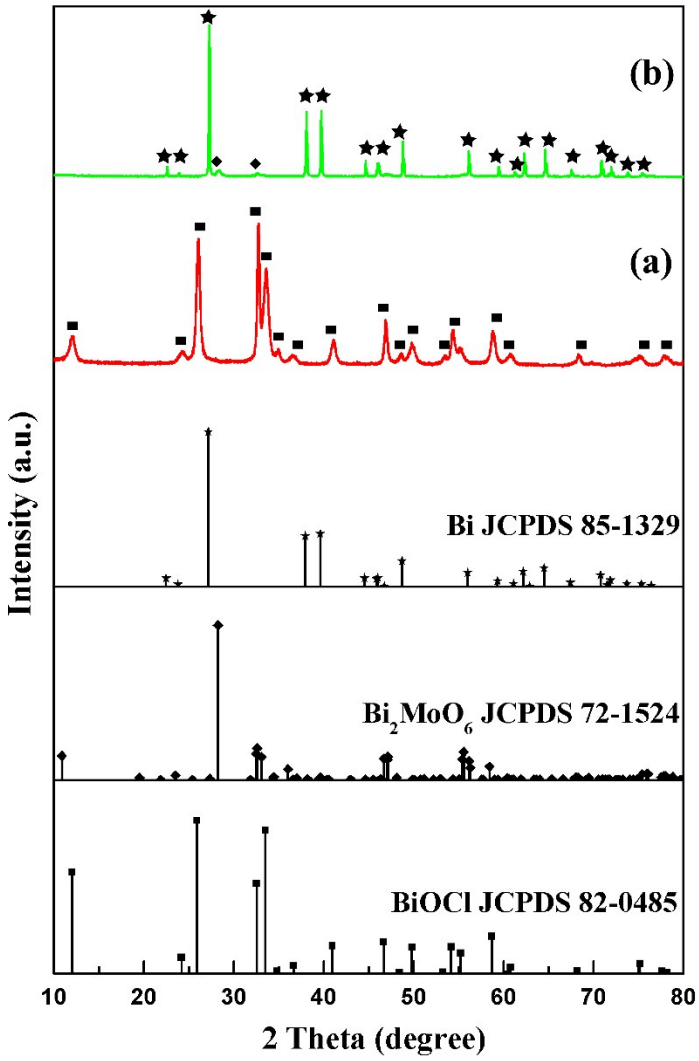

Fig. S3 XRD patterns of BiOCl and Bi_2MoO_6 samples after hydrothermal treatment.

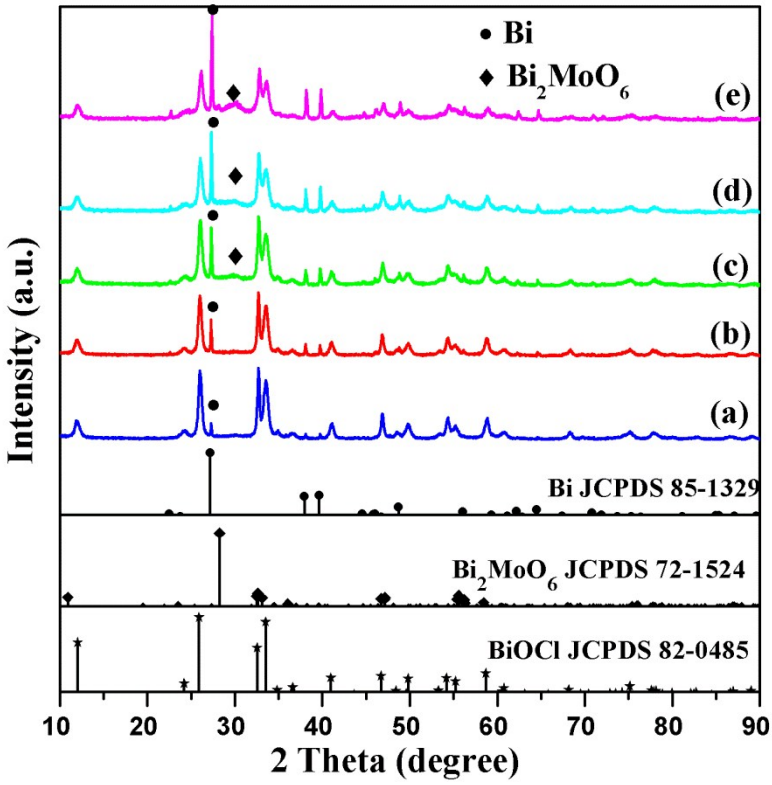

Fig. S4 XRD patterns of $BiOCl/Bi_2MoO_6/Bi$ composites with different $BiOCl/Na_2MoO_4$ molar ratios: (a) 30:1, (b) 10:1, (c) 6:1, (d) 4:1, (e) 3:1.

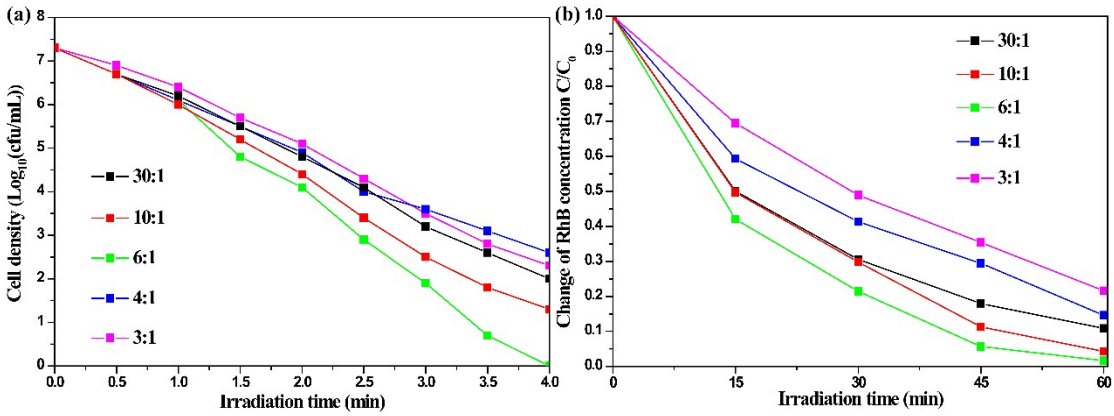

Fig. S5 (a) Photocatalytic disinfection and (b) RhB photodegradation of $BiOCl/Bi_2MoO_6/Bi$ composites with different $BiOCl/Na_2MoO_4$ molar ratios.

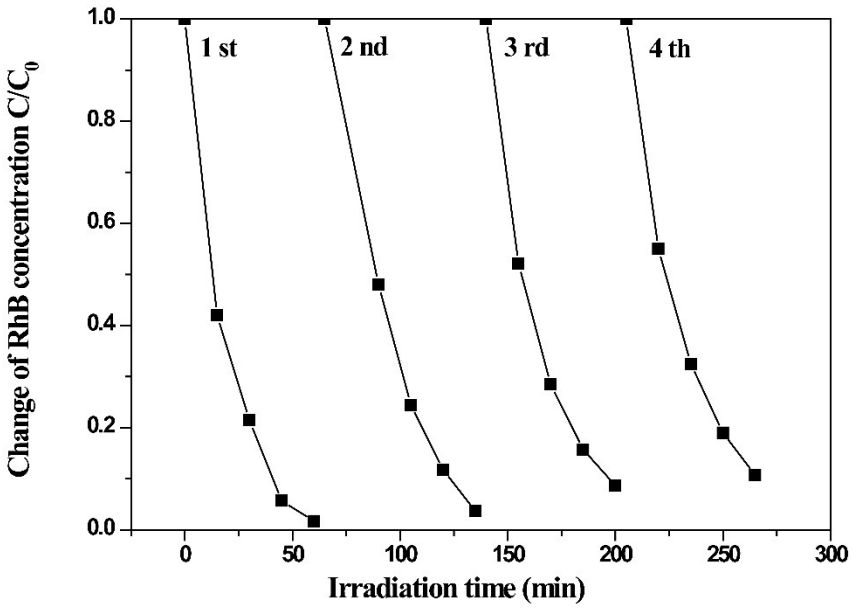

Fig. S6 Stability and recycle of $BiOCl/Bi_2MoO_6/Bi$.

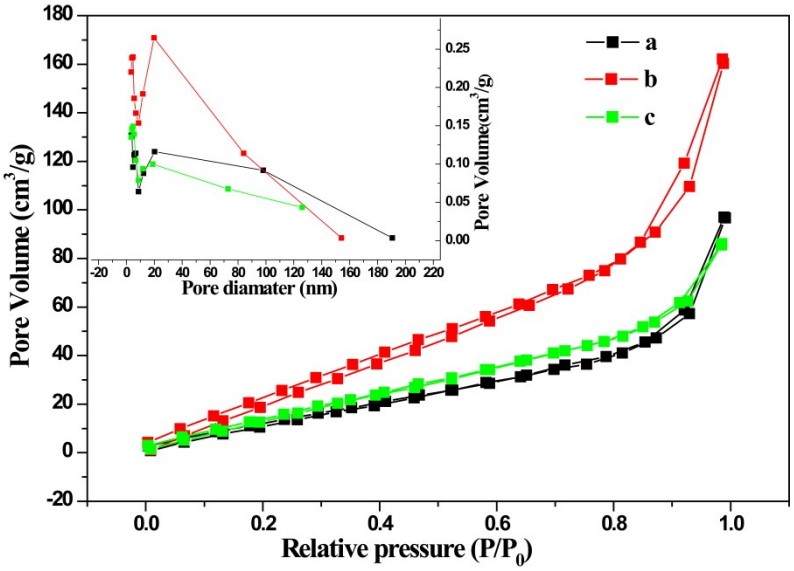

Fig. S7 Nitrogen adsorption-desorption isotherm plots and pore size distributions (inset) of samples formed in (a) H_2O, (b) EG and (c) GLY.

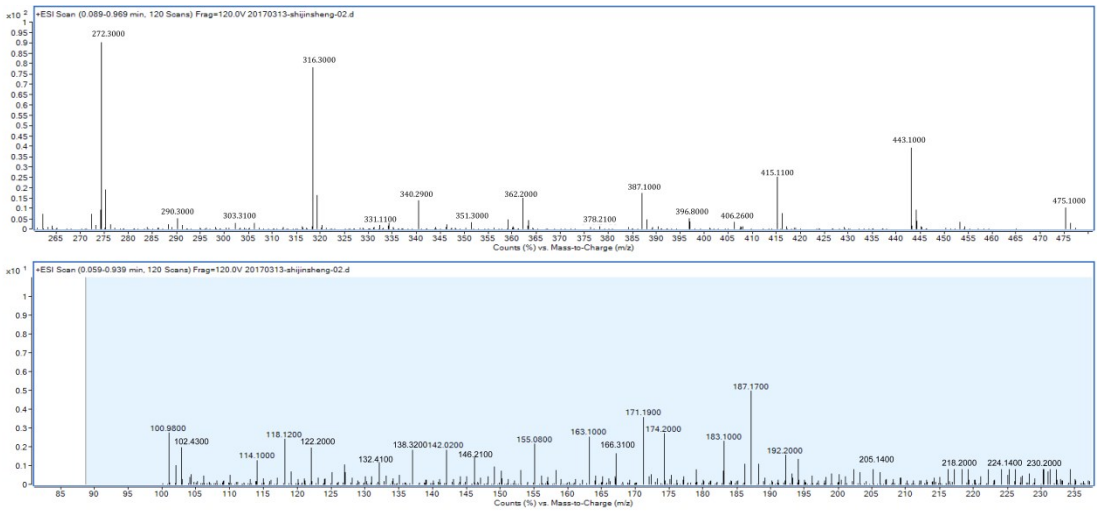

Fig. S8 Typical LC–MS/MS chromatogram of intermediates from RhB degradation.