

Supporting information for

**Synthesis of NiTiO<sub>3</sub>-Bi<sub>2</sub>MoO<sub>6</sub> core-shell fiber-shaped heterojunctions  
as efficient and easily recyclable photocatalysts**

Yuming Jin,<sup>‡a</sup> Xiaofeng Shen,<sup>‡a</sup> Zixiao Liu,<sup>b</sup> Zhaojie Wang,<sup>b</sup> Bo Zhu,<sup>b</sup> Pengfei Xu,<sup>a</sup>

Li Luo,<sup>a</sup> Lisha Zhang<sup>\*a</sup>

## 1 Experimental section

### 1.1 Materials and chemicals

Nickel acetate tetrahydrate (C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>Ni·4H<sub>2</sub>O), Bismuth nitrate pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O), sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O), absolute ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) and Tetrabutyl titanate (C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Ti) were purchased from Sinopharm Chemical Reagent Co., Ltd (P. R. China). *N, N*-Dimethylformamide (DMF) and ethylene glycol (EG) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd (P. R. China). Polyvinylpyrrolidone (PVP) and Rhodamine B were purchased from Sigma (America). 4-chlorophenol (4-CP) was purchased from J&K Chemical Ltd (P.R. China). All chemicals were of analytical grade and were used without further purification.

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<sup>a</sup> State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, State Environmental Protection Engineering Center for Pollution Treatment and Control in Textile Industry, College of Environmental Science and Engineering, Donghua University, Shanghai, 201620, China. E-mail: [lszhang@dhu.edu.cn](mailto:lszhang@dhu.edu.cn); Tel.: +86-21-67792548; Fax: +86-21-67792522

<sup>b</sup> College of Materials Science and Engineering, Donghua University, Shanghai 201620, China.

<sup>‡</sup> These authors contributed equally to this work.

## 1.2 Characterization of photocatalysts

X-Ray diffraction (XRD) measurement was performed on a D/max 2550 PC X-ray diffractometer which uses Cu-K $\alpha$  radiation at wavelength at 0.15418 nm. The scanning electron microscope (SEM) and transmission electron microscope (TEM) were also applied to characterize the sizes and morphologies of samples on a Hitachi S-4800 emission field scanning electron microscope and a JEOL JEM-2100 high-resolution transmission electron microscope respectively. UV-vis-NIR spectrophotometer was used to measure optical diffuse reflectance spectra on a Shimadzu UV-3101PC. The Brunauer-Emmett-Teller (BET) surface area was determined by a multipoint BET method using the adsorption data in the relative (P/P<sub>0</sub>) range of 0.05-0.3. Adsorption isotherm was used to determine the pore size desorption via the Barrett-Joyner-Halenda (BJH) method, assuming a cylinder pore model.

## 1.3 Measurements of photocatalytic activity

Total organic carbon (TOC) tests were also applied to test the mineralization degree of photocatalyst. In TOC test, 250 mg NiTiO<sub>3</sub>-Bi<sub>2</sub>MoO<sub>6</sub> heterojunctions were added into 250 mL rhodamine B (50 mg L<sup>-1</sup>) and the solution was magnetically stirred in the darkness for 30 min in order to ensure that organic contaminants and photocatalysts reach an adsorption-desorption equilibrium. Under visible light irradiation, 20 mL of solution was collected each 1 h and then filtered with a 0.45  $\mu$ m filter to remove photocatalysts for future analysis. TOC was measured by Shimadzu

TOC-VCPH total organic carbon analyzer.

The degradation intermediates and products were analyzed by a GCMS-QP2010Ultra. Before injection, the sample was pre-treated as follow: 100 mL sample was treated by extraction, steaming, blowing off, silanization. Finally, the prepared organic phase was filtered with the 0.22  $\mu\text{m}$  polytetrafluoroethylene membranes and stocked in brown sample bottles. For GC/MS detection, 200  $\mu\text{L}$  sample was injected in splitless mode for analysis. The temperature was maintained at 80  $^{\circ}\text{C}$  for 5 min, and then increased to 310  $^{\circ}\text{C}$  at a rate of 15  $^{\circ}\text{C}/\text{min}$  and held 310  $^{\circ}\text{C}$  for 7 min.

Radical trapping experiments were conducted by adding 1.0 mL isopropanol (IPA, a quencher of  $\cdot\text{OH}$ ), 1 mM benzoquinone (BQ, a quencher of  $\cdot\text{O}_2^-$ ), 1 mM ammonium oxalate (AO, a quencher of  $\text{h}^+$ ) or 6 mM silver nitrate ( $\text{AgNO}_3$ , a quencher of  $\text{e}^-$ ) into rhodamine B solution (50 mL, 10  $\text{mg L}^{-1}$ ) before the standard photocatalytic tests.

In the stability and reusability test of  $\text{NiTiO}_3\text{-Bi}_2\text{MoO}_6$  heterojunctions, four consecutive cycles of photocatalysis were tested under the simulated visible light illumination. After each cycle,  $\text{NiTiO}_3\text{-Bi}_2\text{MoO}_6$  heterojunctions was sedimentated and then dried at 60  $^{\circ}\text{C}$  for 2 h. Then  $\text{NiTiO}_3\text{-Bi}_2\text{MoO}_6$  heterojunctions was immersed in the same volume (50 mL, 10  $\text{mg L}^{-1}$ ) of fresh rhodamine B solution again, under the other identical conditions.

## 2 Figures and tables

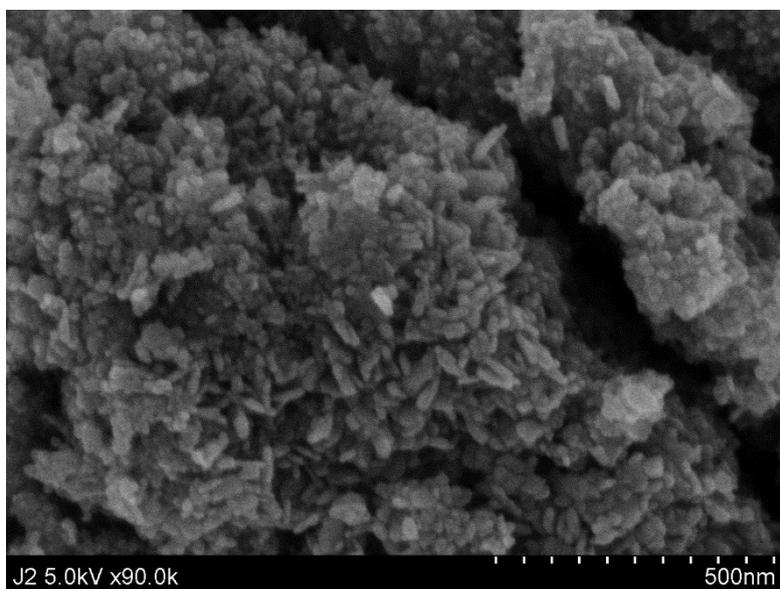
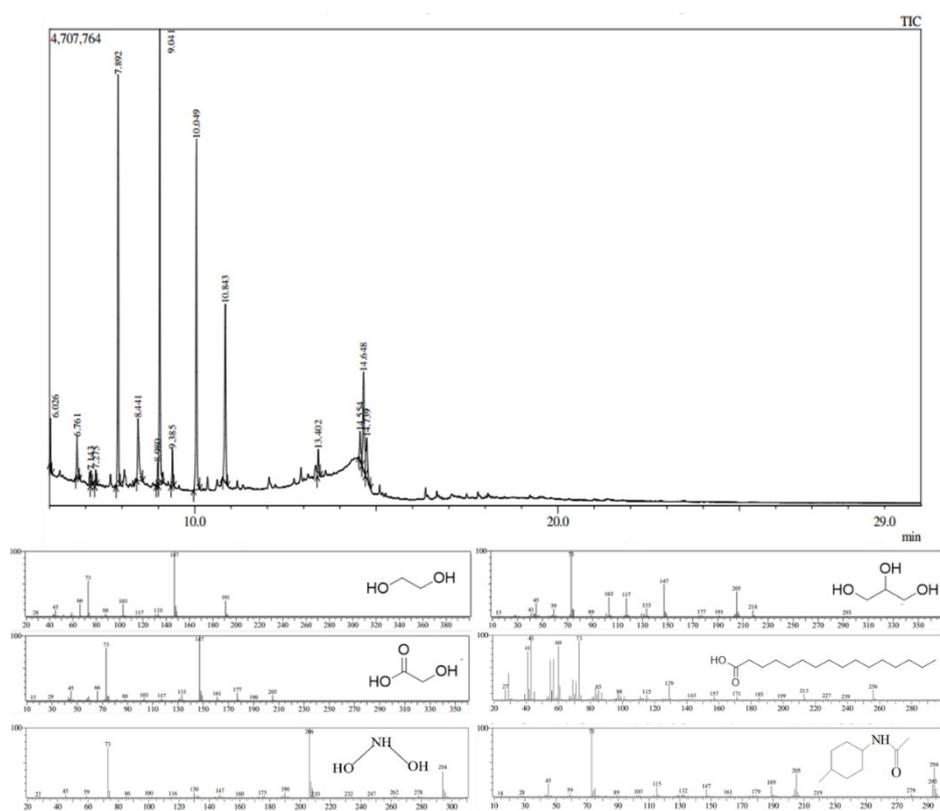
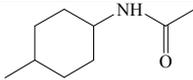
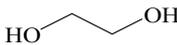
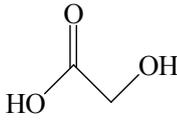
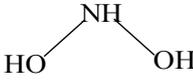
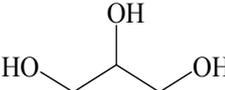
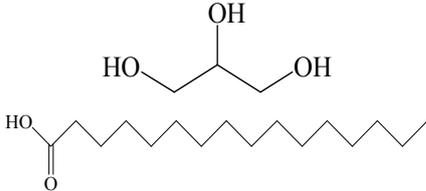


Fig. S1 SEM image of Bi<sub>2</sub>MoO<sub>6</sub> nanoparticles



**Fig. S2** Mass spectra obtained for the degradation products of 4-CP.

**Table. S1** Reaction intermediates for the degradation of 4-CP identified by GC-MS

| Number | Retention (min) | Intermediate  |
|--------|-----------------|---|
| 1      | 7.140           |   |
| 2      | 7.635           |   |
| 3      | 8.855           |   |
| 4      | 9.040           |   |
| 5      | 11.035          |   |
| 6      | 17.005          |  |

During the photodegradation of 4-CP (Fig. S2), there are six predominant intermediate products, as shown in Table S1. The main degradation process is proposed as follow. The free radical attacks in the different positions of the benzene ring producing two phenols, and two phenols are further attracted by the free radicals, being converted into small molecules. These oxidized products can ultimately be mineralized to H<sub>2</sub>O and CO<sub>2</sub>.

**Table. S2** Concentration of Ni, Ti, Bi and Mo atoms in the solution

| Atom | Concentration ( $\mu\text{g mL}^{-1}$ ) |
|------|---|
| Ni   | $\leq 0.01$                             |
| Ti   | $\leq 0.01$                             |
| Bi   | $\leq 0.01$                             |

Mo

$\leq 0.01$

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