Supporting Information

Efficient liquid phase photothermal catalysis realized by the Ag₂O/Bi₄O₅I₂ heat-localization microreactor

Yukai Chen, Ruizhe Wang, Huimin Wei, Rulin Dong, Chunhua Lu and Jiahui Kou

aJiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Advanced Catalysis and Green Manufacturing Collaborative Innovation Center, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, P. R. China.
bState Key Laboratory of Materials-Oriented Chemical Engineering, College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, P. R. China.
cJiangsu Collaborative Innovation Center for Advanced Inorganic Function Composites, Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University, Nanjing 210009, P. R. China.
Experimental

Materials

All the reagents were of analytical grade and were used without future purification. Distilled water and ethanol (C₂H₆O, 99.8%) was used in the whole experiment. Bismuth nitrate pentahydrate (Bi(NO₃)₂·5H₂O, 99.0%), potassium iodide (KI, 99.0%) and sodium hydroxide (NaOH, 98.0%) were purchased from Macklin Chemical Reagent Co., Ltd. Silver nitrate (AgNO₃, 99.0%) was purchased from Aladdin Chemical Reagent Co., Ltd. Tetracycline (C₂₂H₂₄N₂O₈, TC, 97.0%) was purchased from Sinopharm Chemical Reagent Co., Ltd.

Preparation of Bi₄O₃I₂ nanosheets

In a typical preparation process, 1 mmol Bi(NO₃)₂·5H₂O was dissolved in 60 mL ethanol under 1 h of continuous stirring, followed by adding 1 mmol KI and stirring for another 30 min. 2.2 mL NaOH (1 M) was dropped in aforementioned solution by the speed of 50 µL/s. This solution was kept in a water bath of 80 °C for 5 h. Washing by water and ethanol was repeated for six times before drying at 60 °C for 12 h to get the BiOI precursor. Finally, the BiOI precursor was treated under 420 °C for 3 h in air to acquire Bi₄O₃I₂ nanosheets.

Preparation of Ag₂O/Bi₄O₃I₂ composite

To prepare the Ag₂O/Bi₄O₃I₂ composite, 200 mg Bi₄O₃I₂ powder was ultrasonically dispersed in 50 mL distilled water. A certain amount of AgNO₃ was added to the solution under continuous stirring. 2.3 mL NaOH (1 M) was dropped in to the solution and 4 h stirring was applied subsequently. Ag₂O/Bi₄O₃I₂ composite powder was obtained by washing, centrifuging and finally drying at 60 °C for 12 h. The obtained powders were abbreviated as 5%AO/BOI (5%Ag₂O/Bi₄O₃I₂), 10%AO/BOI (10%Ag₂O/Bi₄O₃I₂), 20%AO/BOI (20%Ag₂O/Bi₄O₃I₂) and 50%AO/BOI (50%Ag₂O/Bi₄O₃I₂), respectively. For the pure Ag₂O, 200 mg AgNO₃ was used without adding Bi₄O₃I₂ powder.

Characterizations
The crystal structures were identified using an X-ray diffractometer (XRD, Rigaku SmartLab, Japan) with Cu Kα radiation (λ = 0.15406 nm). The elemental statuses were examined by an X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi, America). The morphological features of the prepared samples were characterized using a field-emission scanning electron microscope (FESEM, HITACHI SU-8010, Japan) with an accelerating voltage of 3 kV. Optical spectra were obtained by an ultraviolet-visible spectrophotometer (UV-vis, Agilent Cary 5000, America). Thermal images were taken by a thermal imager (Gaozhi Testo 869, China). Photocatalytic performance evaluations were carried out with a 300 W Xe arc lamp (CEAU, CEL-HXF300E, China).

**Photocatalytic performance evaluation**

For the evaluation of Ag₂O/Bi₄O₅I₂ powders with different Ag₂O contents, 10 mg photocatalyst was scattered in 50 mL TC solution (20 mg/L) followed by stirring under darkness for 30 min to reach an absorption-desorption equilibrium. Continuous stirring was applied during photocatalysis to scatter the photocatalysts. The suspension solution was withdrawn every 10 min before centrifuged to measure absorbance data.

For the comparison of photocatalytic performance between the microreactors and bulk reactors, a piece of glass with 20%Ag₂O/Bi₄O₅I₂ coated on was assembled into a planar microreactor while another piece was put on the bottom inside a bulk reactor. In a typical experiment, 20 mL TC (20 mg/L) were stored a syringe before being injected into the microreactor by an injection pump within 1 h. Same volume of TC was added into the bulk reactor for comparison. They were irradiated under the same xenon lamp for 1 h. The solution after reaction was collected and tested by the UVPC.
Scheme S1 Preparation procedure diagram of $x\%$Ag$_2$O/Bi$_4$O$_5$I$_2$ composite photocatalysts.

Scheme S2 The possible photocatalytic mechanism of the Ag$_2$O/Bi$_4$O$_5$I$_2$ heterojunction.

Table S1 Elements contents measured by EDS in 20%Ag$_2$O/Bi$_4$O$_5$I$_2$.

<table>
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<th>Element</th>
<th>Wt%</th>
<th>Wt% Sigma</th>
<th>At%</th>
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<tr>
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<tr>
<td>Bi</td>
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<td>0.32</td>
<td>26.09</td>
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Fig. S1 FESEM images of (a) Bi$_4$O$_2$I$_2$, (b) Ag$_2$O and (c) 20%Ag$_2$O/Bi$_4$O$_2$I$_2$. (d) EDS mapping images of 20%Ag$_2$O/Bi$_4$O$_2$I$_2$. 
Fig. S2 Energy dispersive spectrum of 20%Ag₂O/Bi₄O₅I₂.

Fig. S3 (a) UV-visible-NIR spectra of Ag₂O/Bi₄O₅I₂ samples. (b) Tauc plots and bandgaps of Bi₄O₅I₂ and Ag₂O samples.
**Fig. S4** Digital photos of Ag$_2$O/Bi$_4$O$_5$I$_2$ powders.

**Fig. S5** (a) Temperature curves and (b) average temperature during 5-10 min of Ag$_2$O/Bi$_4$O$_5$I$_2$ samples irradiated in air.
Fig. S6 Thermal images of the quartz glass irradiated in air for 10 min.

Fig. S7 Thermal images of the Bi$_4$O$_2$I$_2$ powder irradiated in air for 10 min.
Fig. S8 Thermal images of the Ag$_2$O powder irradiated in air for 10 min.

Fig. S9 Thermal images of the 5%Ag$_2$O/Bi$_4$O$_3$I$_2$ powder irradiated in air for 10 min.
**Fig. S10** Thermal images of the 10%Ag₂O/Bi₄O₅I₂ powder irradiated in air for 10 min.

**Fig. S11** Thermal images of the 20%Ag₂O/Bi₄O₅I₂ powder irradiated in air for 10 min.
**Fig. S12** Thermal images of the 50%Ag$_2$O/Bi$_4$O$_5$I$_2$ powder irradiated in air for 10 min.

**Fig. S13** Transient photocurrent response plots of Ag$_2$O/Bi$_4$O$_5$I$_2$ samples under irradiation.
Fig. S14 XRD patterns of 20%Ag$_2$O/Bi$_4$O$_3$I$_2$ powder before and after the photocatalysis.

Fig. S15 Degradation performance of Ag$_2$O/Bi$_4$O$_3$I$_2$ samples under photocatalytic, thermal catalytic and photothermal catalytic conditions.
**Fig. S16** Schematic diagram of comparison between the bulk reactor and the microreactor.

**Fig. S17** Concentration distribution of target molecules during photocatalysis in the bulk reactor and the microreactor.
Fig. S18 Reaction rate $k$ of the bulk reactor and the microreactor under irradiation.

Fig. S19 (a) Temperature curves of the 20\%Ag$_2$O/Bi$_4$O$_5$I$_2$ BR and MR. (b) Photocatalytic degradation percent, (c) fitted reaction rate, (d) performance multiplies of the 20\%Ag$_2$O/Bi$_4$O$_5$I$_2$ BR and MR with
or without cooling.

Fig. S20 Temperature changing and distribution of the bulk reactor and the microreactor under irradiation.

Fig. S21 Cycling test of the 20%Ag₂O/Bi₄O₃I₂ microreactor for 20 mL TC degradation.