Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Efficient liquid phase photothermal catalysis realized by the $Ag_2O/Bi_4O_5I_2$ heat-localization microreactor

Yukai Chen[a], Ruizhe Wang[a], Huimin Wei[b,c], Rulin Dong[a], Chunhua Lu[b,c]* and Jiahui Kou[b,c]**

[a]*Jiangsu 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.*

[b]*State Key Laboratory of Materials-Oriented Chemical Engineering, College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, P. R. China.*

[c]*Jiangsu 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 (C_2H_6O, 99.8%) was used in the whole experiment. Bismuth nitrate pentahydrate ($Bi(NO_3)_2{\cdot}5H_2O$, 99.0%), potassium iodide (KI, 99.0%) and sodium hydroxide (NaOH, 98.0%) were purchased from Macklin Chemical Reagent Co., Ltd. Silver nitrate ($AgNO_3$, 99.0%) was purchased from Aladdin Chemical Reagent Co., Ltd. Tetracycline ($C_{22}H_{24}N_2O_8$, TC, 97.0%) was purchased from Sinopharm Chemical Reagent Co., Ltd.

Preparation of $Bi_4O_5I_2$ nanosheets

In a typical preparation process, 1 mmol $Bi(NO_3)_2{\cdot}5H_2O$ 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 $Bi_4O_5I_2$ nanosheets.

Preparation of $Ag_2O/Bi_4O_5I_2$ composite

To prepare the $Ag_2O/Bi_4O_5I_2$ composite, 200 mg $Bi_4O_5I_2$ powder was ultrasonically dispersed in 50 mL distilled water. A certain amount of $AgNO_3$ 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. $Ag_2O/Bi_4O_5I_2$ 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%$Ag_2O/Bi_4O_5I_2$), 10%AO/BOI (10%$Ag_2O/Bi_4O_5I_2$), 20%AO/BOI (20%$Ag_2O/Bi_4O_5I_2$) and 50%AO/BOI (50%$Ag_2O/Bi_4O_5I_2$), respectively. For the pure Ag_2O, 200 mg $AgNO_3$ was used without adding $Bi_4O_5I_2$ powder.

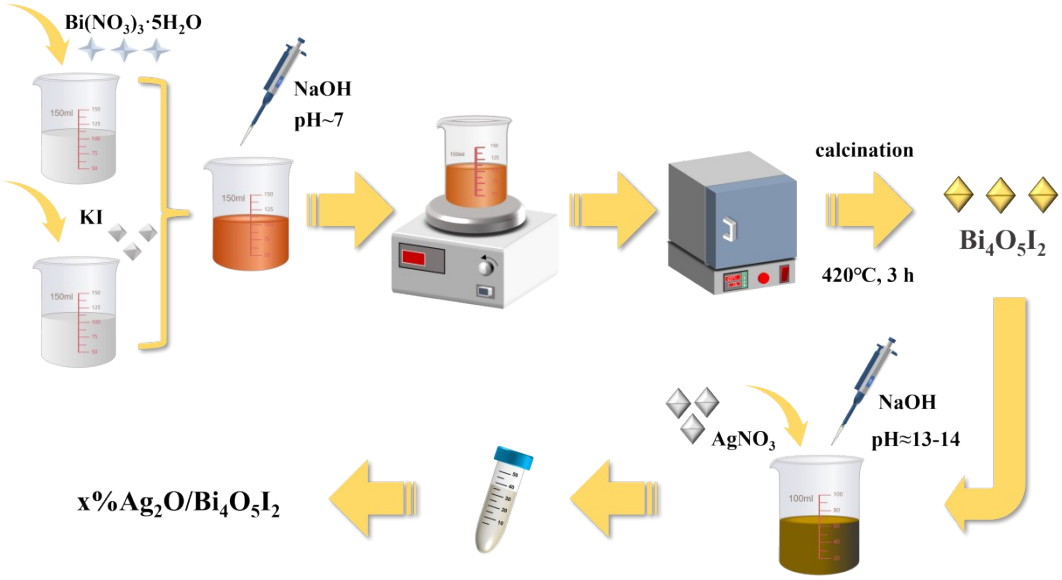
Characterizations

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).

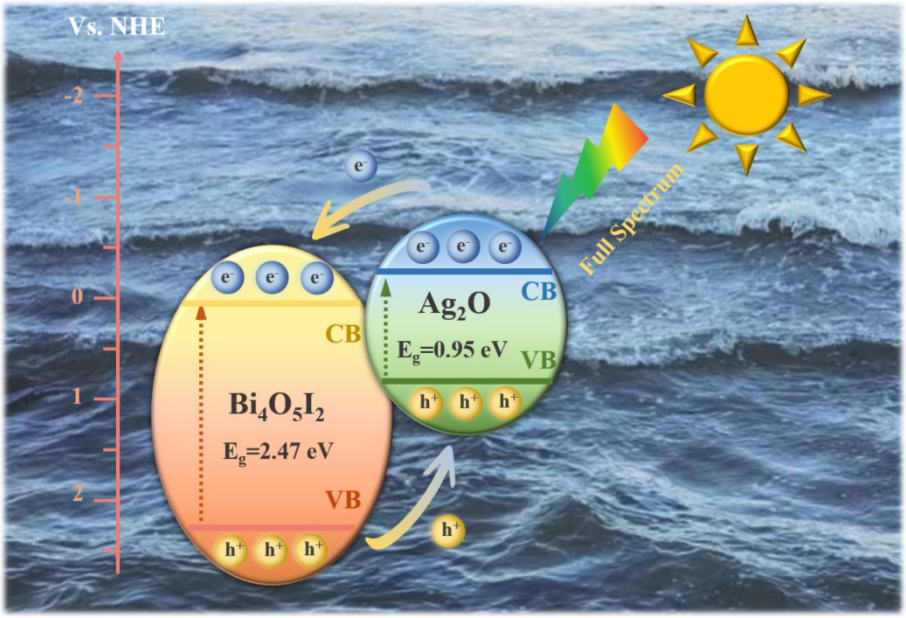
Photocatalytic performance evaluation

For the evaluation of $Ag_2O/Bi_4O_5I_2$ powders with different Ag_2O 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%$Ag_2O/Bi_4O_5I_2$ 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%$Ag_2O/Bi_4O_5I_2$ composite photocatalysts.



Scheme S2 The possible photocatalytic mechanism of the $Ag_2O/Bi_4O_5I_2$ heterojunction.

Table S1 Elements contents measured by EDS in 20%$Ag_2O/Bi_4O_5I_2$.

Element	Wt%	Wt % Sigma	At%
O	8.93	0.24	50.13

Ag	17.96	0.26	14.96
I	12.44	0.21	8.81
Bi	60.67	0.32	26.09

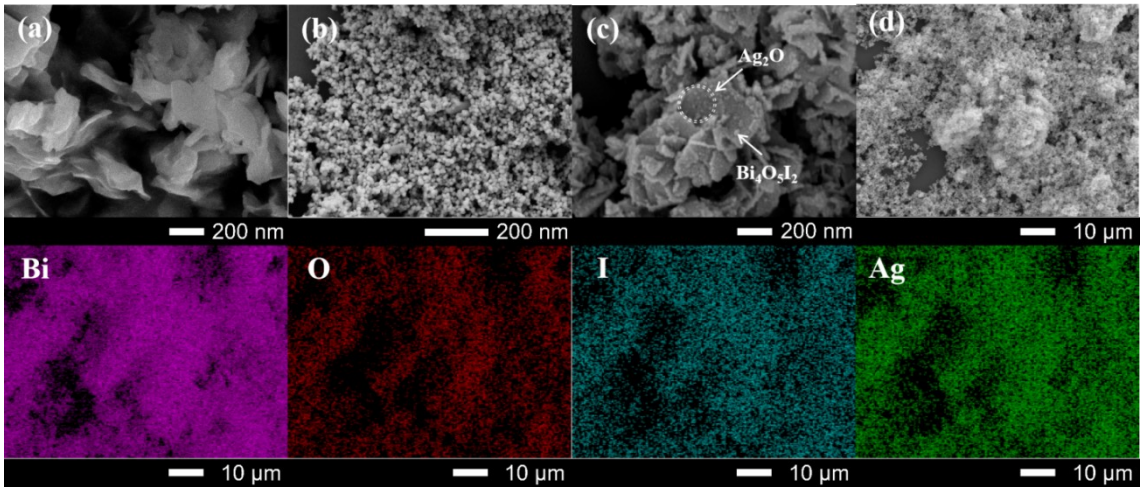


Fig. S1 FESEM images of (a) $Bi_4O_5I_2$, (b) Ag_2O and (c) 20%Ag_2O/$Bi_4O_5I_2$. (d) EDS mapping images of 20%Ag_2O/$Bi_4O_5I_2$.

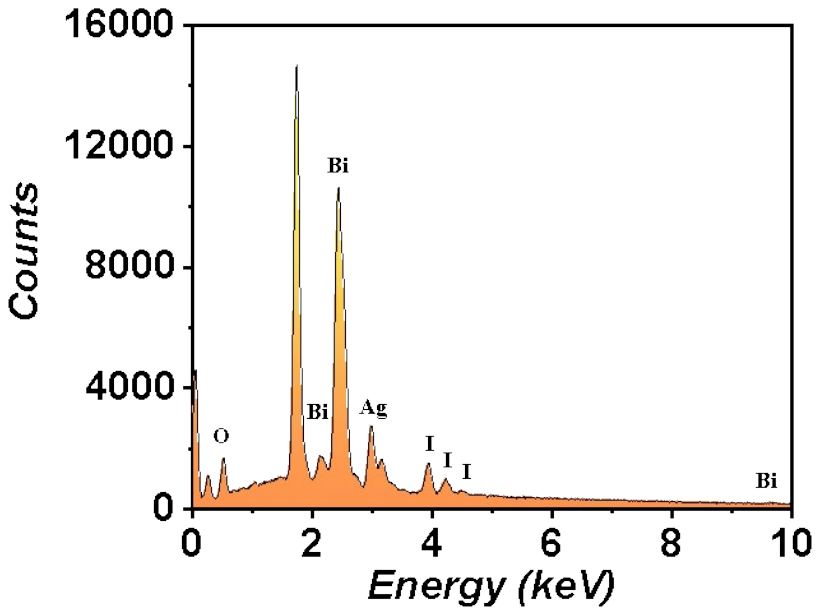


Fig. S2 Energy dispersive spectrum of 20%$Ag_2O/Bi_4O_5I_2$.

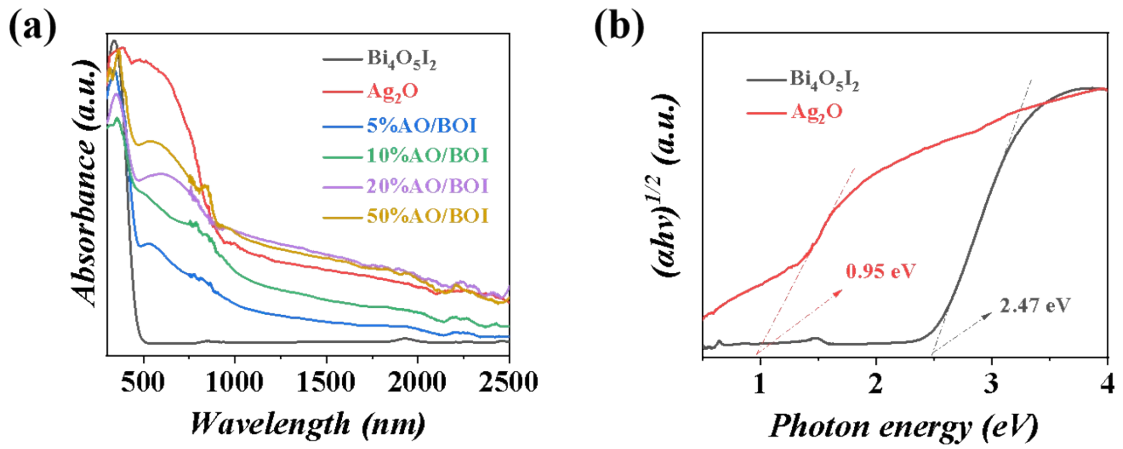


Fig. S3 (a) UV-visible-NIR spectra of $Ag_2O/Bi_4O_5I_2$ samples. (b) Tauc plots and bandgaps of $Bi_4O_5I_2$ and Ag_2O samples.

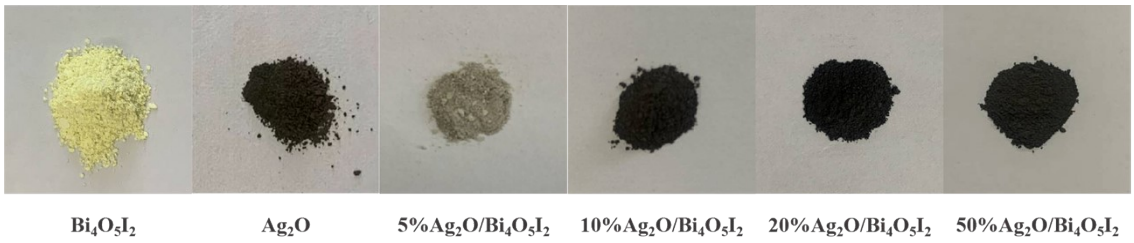


Fig. S4 Digital photos of $Ag_2O/Bi_4O_5I_2$ powders.

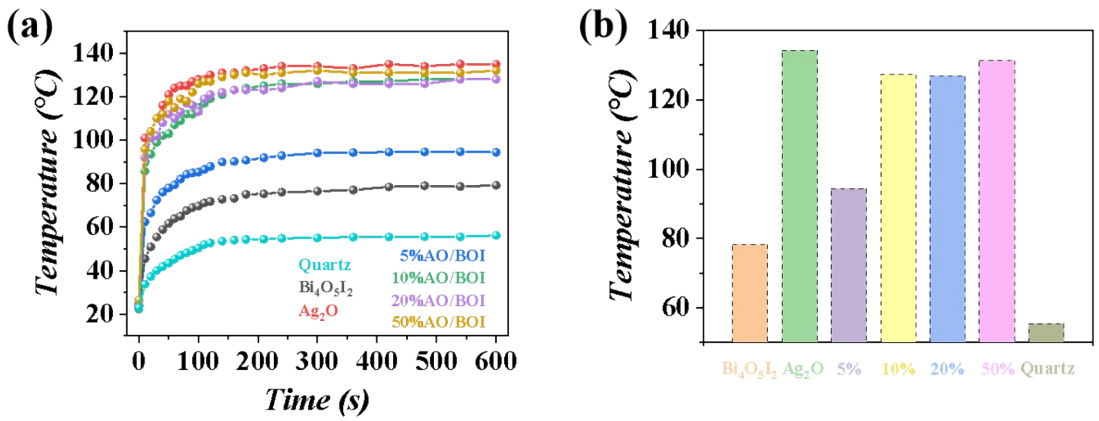


Fig. S5 (a) Temperature curves and (b) average temperature during 5-10 min of $Ag_2O/Bi_4O_5I_2$ samples irradiated in air.

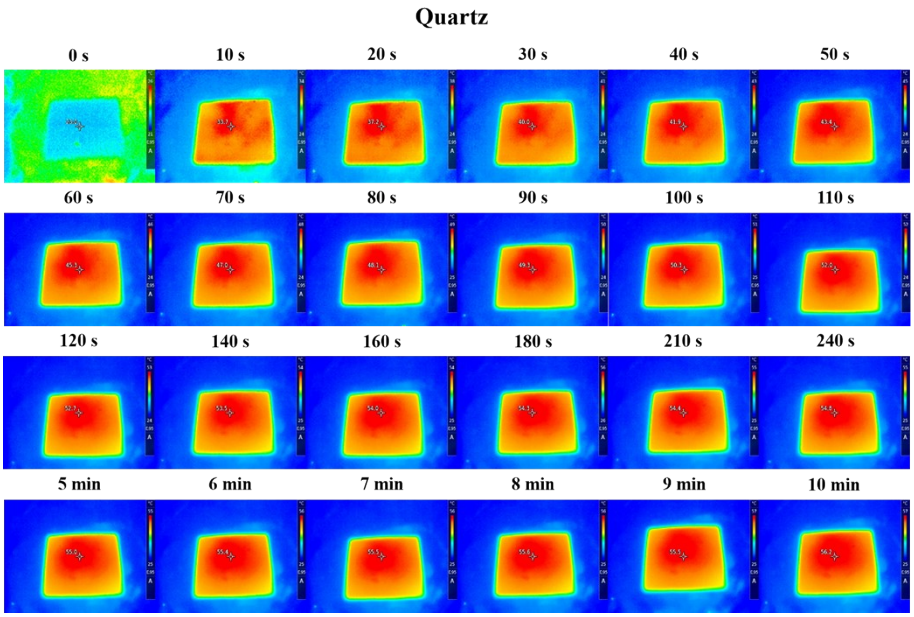


Fig. S6 Thermal images of the quartz glass irradiated in air for 10 min.

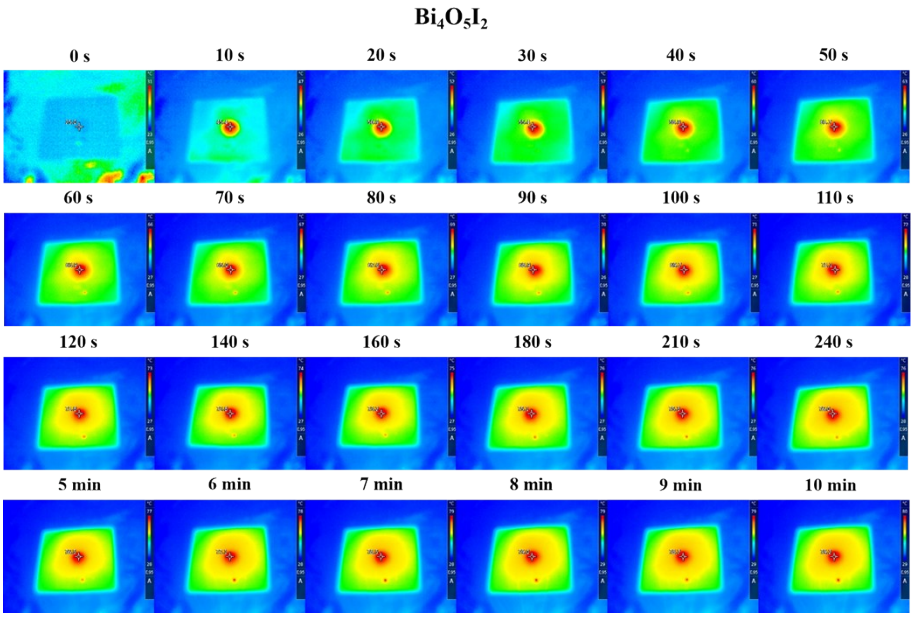


Fig. S7 Thermal images of the $Bi_4O_5I_2$ powder irradiated in air for 10 min.

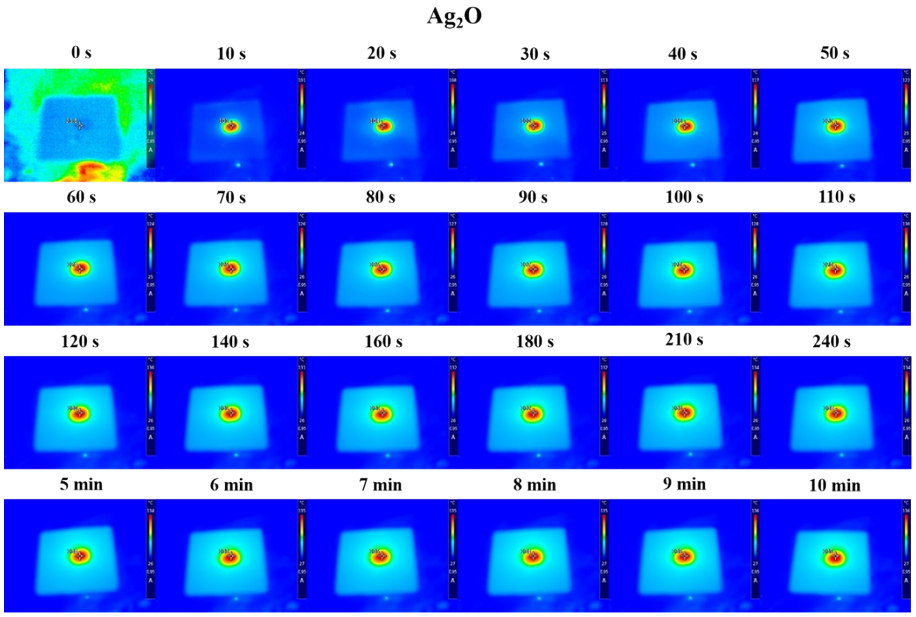


Fig. S8 Thermal images of the Ag_2O powder irradiated in air for 10 min.

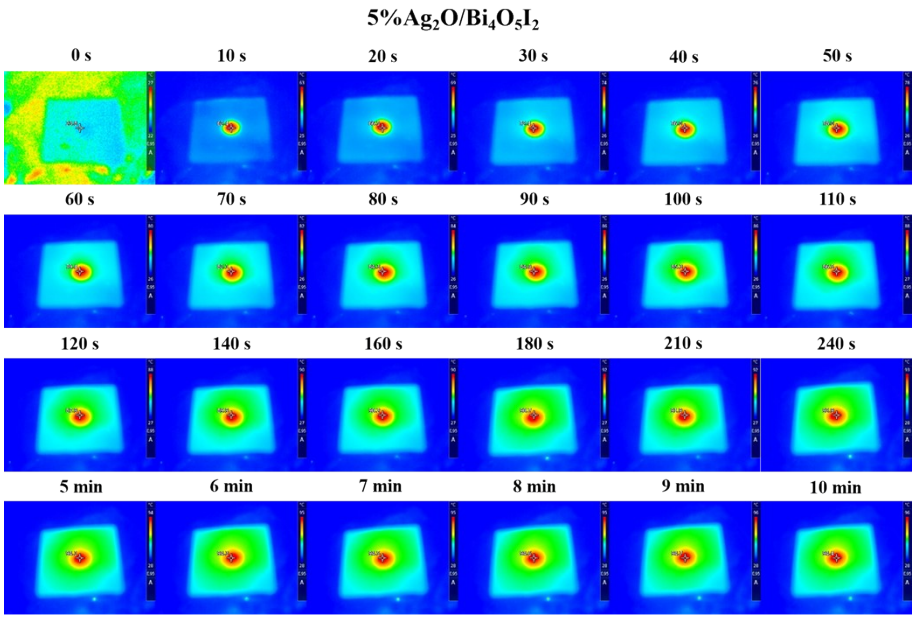


Fig. S9 Thermal images of the $5\%Ag_2O/Bi_4O_5I_2$ powder irradiated in air for 10 min.

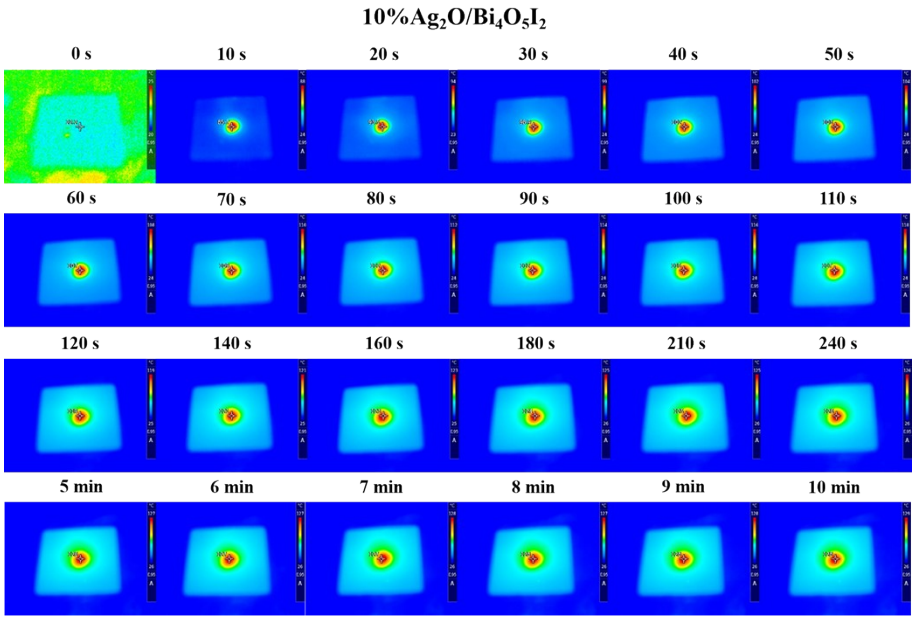


Fig. S10 Thermal images of the 10%$Ag_2O/Bi_4O_5I_2$ powder irradiated in air for 10 min.

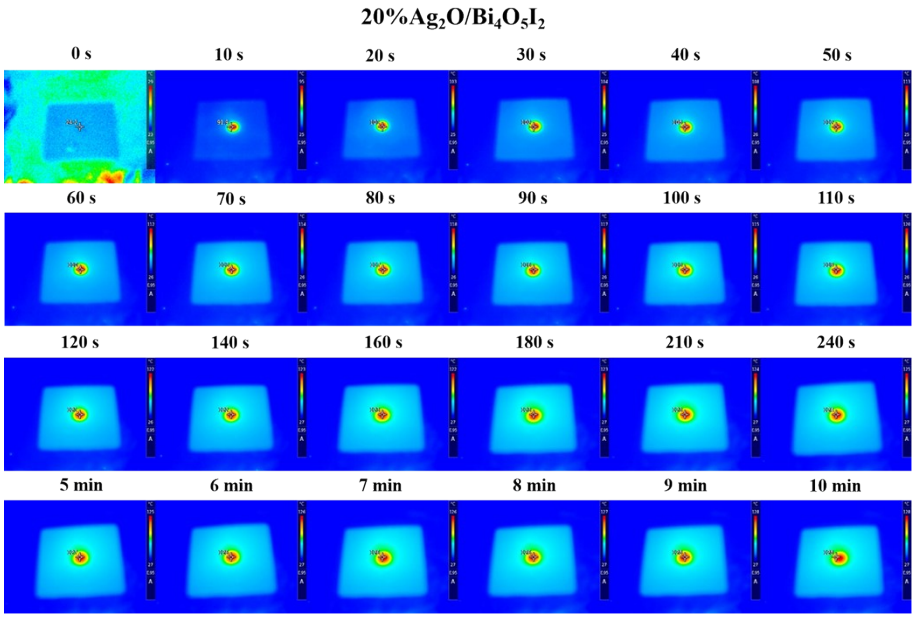


Fig. S11 Thermal images of the 20%$Ag_2O/Bi_4O_5I_2$ powder irradiated in air for 10 min.

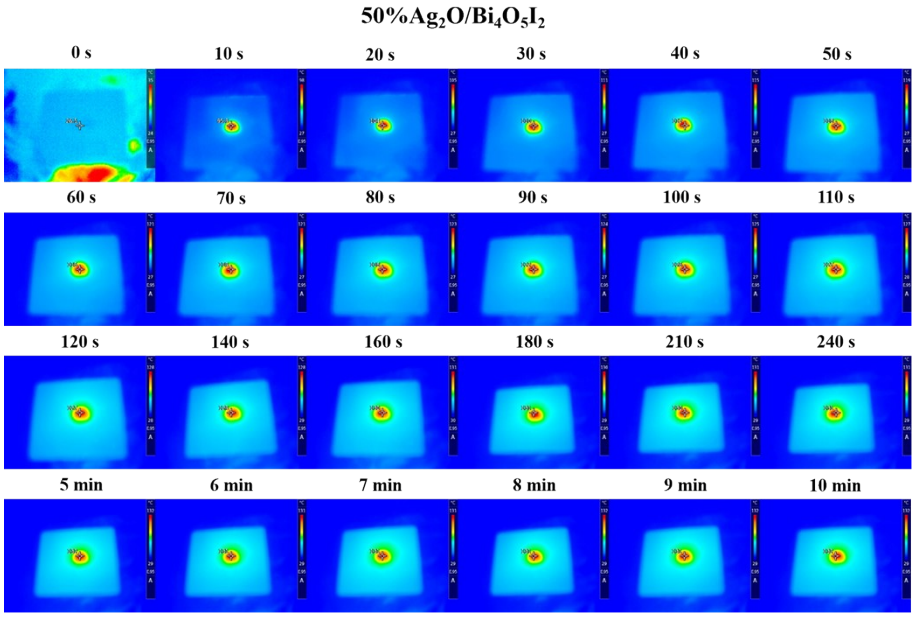


Fig. S12 Thermal images of the 50%$Ag_2O/Bi_4O_5I_2$ powder irradiated in air for 10 min.

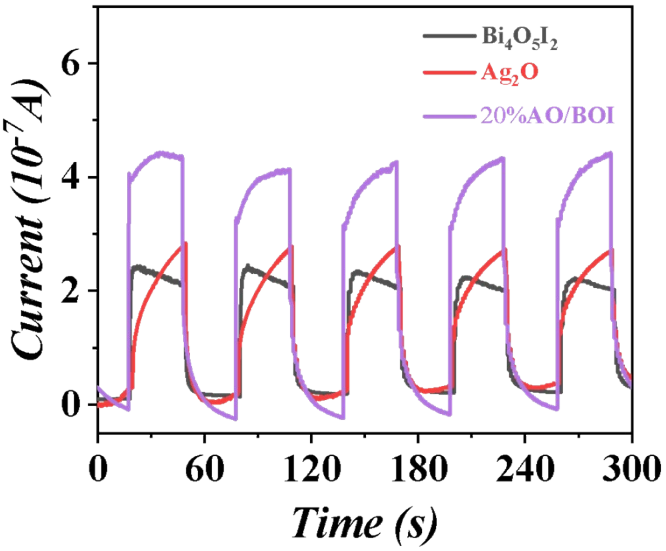


Fig. S13 Transient photocurrent response plots of $Ag_2O/Bi_4O_5I_2$ samples under irradiation.

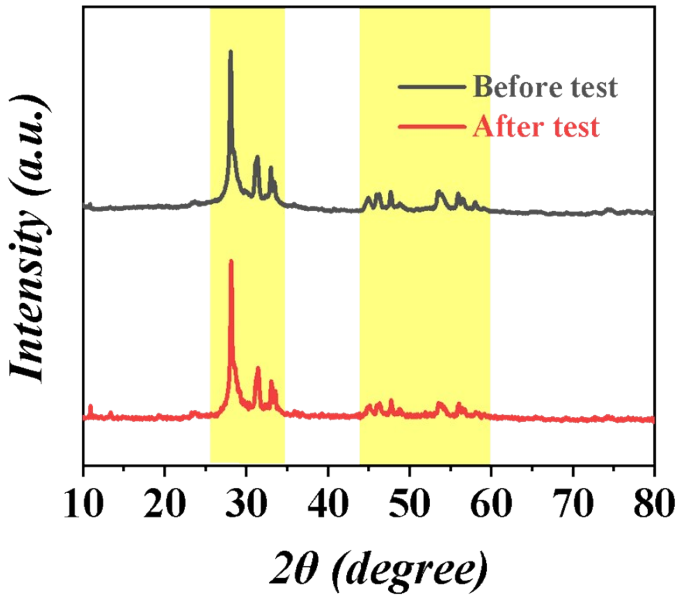


Fig. S14 XRD patterns of 20%$Ag_2O/Bi_4O_5I_2$ powder before and after the photocatalysis.

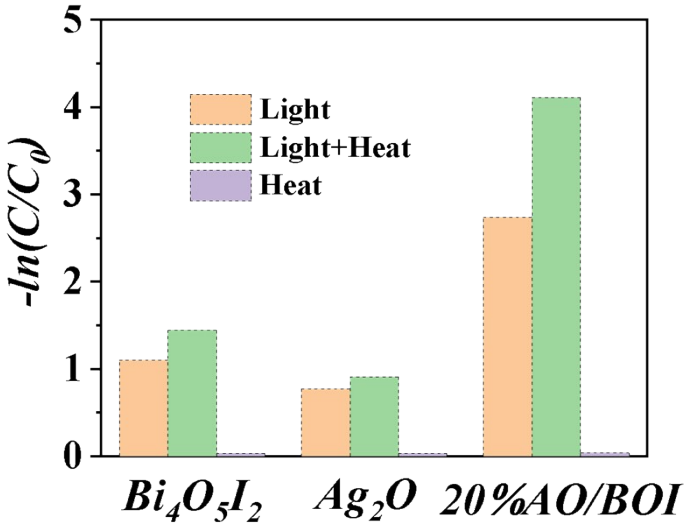


Fig. S15 Degradation performance of $Ag_2O/Bi_4O_5I_2$ samples under photocatalytic, thermal catalytic and photothermal catalytic conditions.

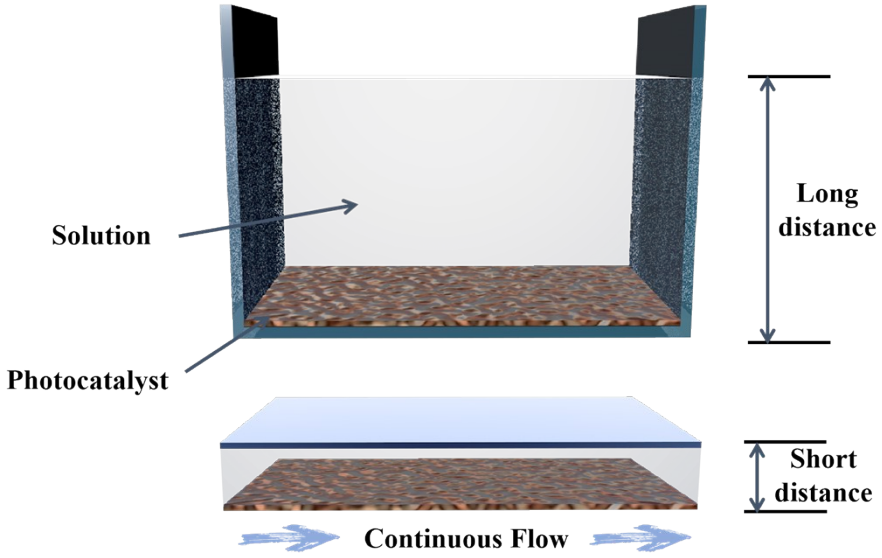


Fig. S16 Schematic diagram of comparison between the bulk reactor and the microreactor.

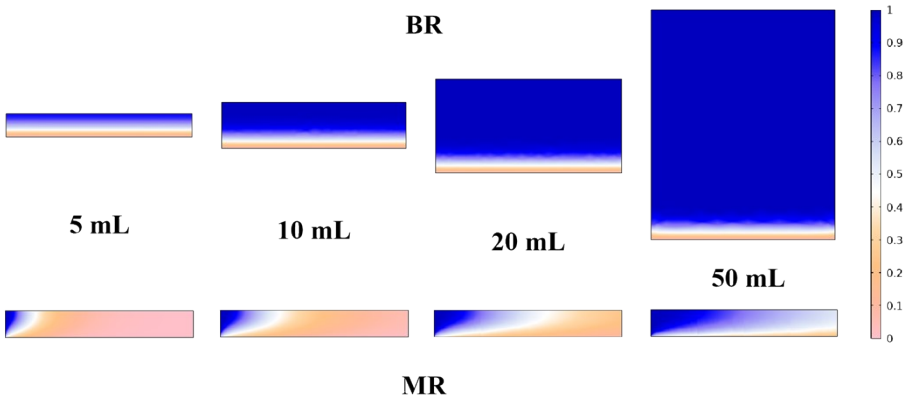


Fig. S17 Concentration distribution of target molecules during photocatalysis in the bulk reactor and the microreactor.

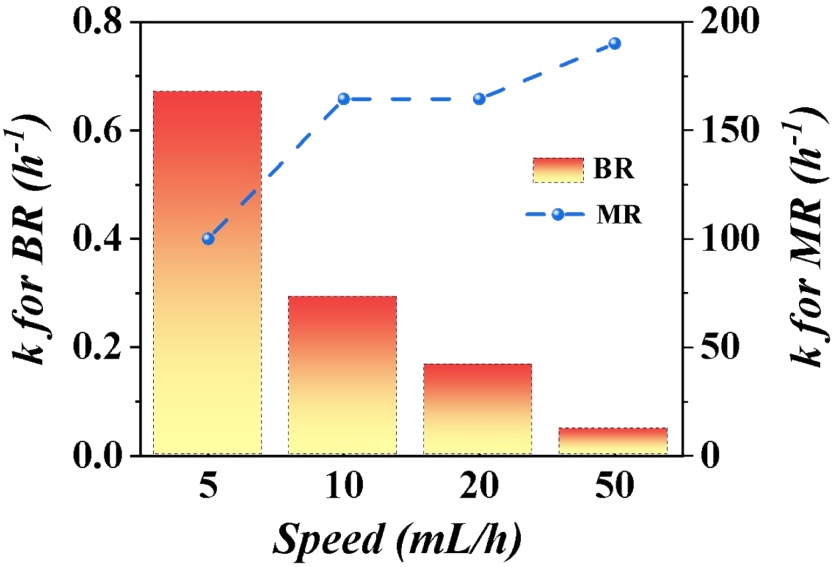


Fig. S18 Reaction rate *k* of the bulk reactor and the microreactor under irradiation.

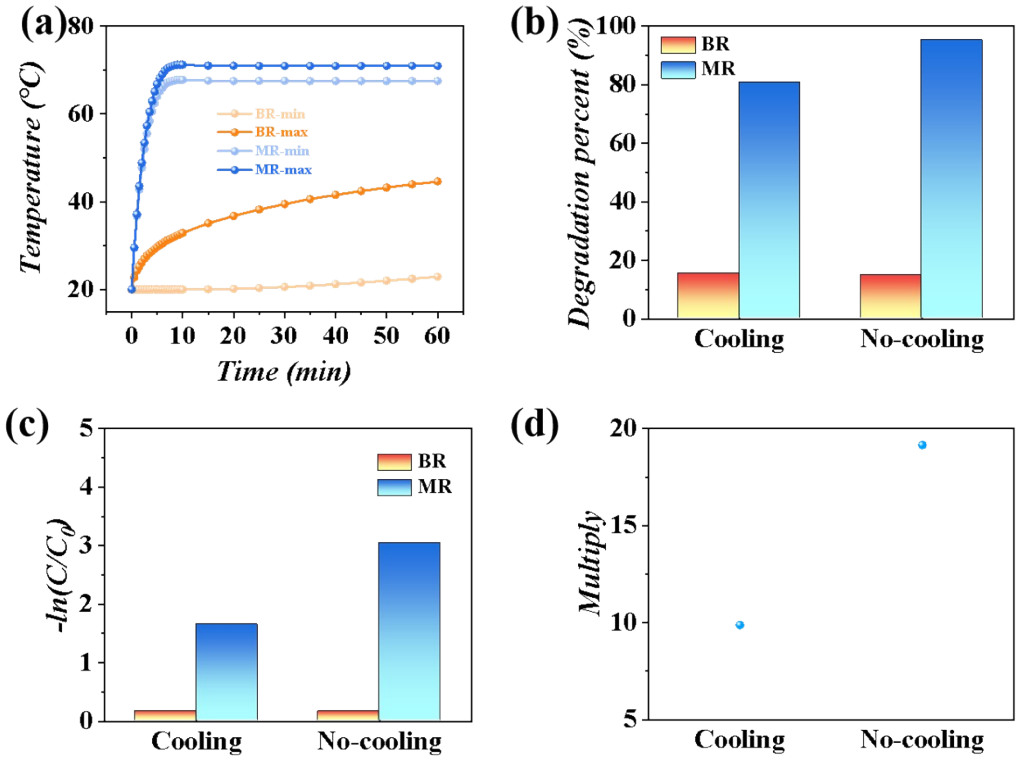


Fig. S19 (a) Temperature curves of the 20%$Ag_2O/Bi_4O_5I_2$ BR and MR. (b) Photocatalytic degradation percent, (c) fitted reaction rate, (d) performance multiplies of the 20%$Ag_2O/Bi_4O_5I_2$ BR and MR with

or without cooling.

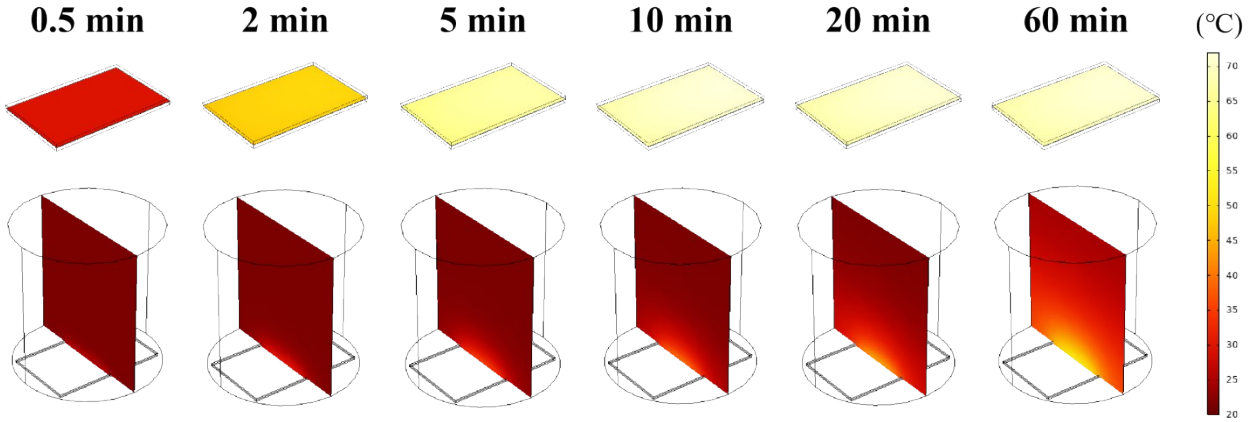


Fig. S20 Temperature changing and distribution of the bulk reactor and the microreactor under irradiation.

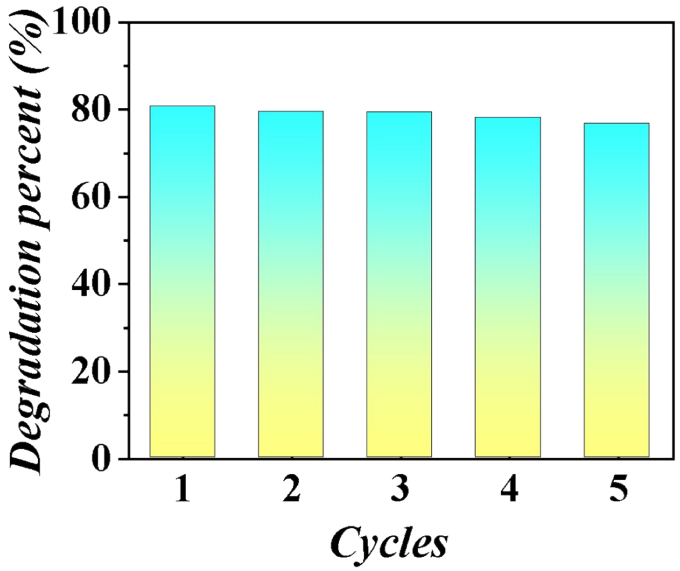


Fig. S21 Cycling test of the 20%Ag_2O/Bi4O_5I_2 microreactor for 20 mL TC degradation.