Supplementary information for

Innovative $BiOI@AgBiS_2@NaYF_4$:Yb,Tm Ternary Heterostructure for Efficient Solar Energy Harvesting towards Tetracycline Hydrochloride Degradation

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1 Chemicals

Yttrium(III) nitrate hexahydrate ($Y(NO_3)_3·6H_2O$, 99.99%), ytterbium(III) nitrate pentahydrate ($Yb(NO_3)_3·5H_2O$, 99.9%), thulium(III) nitrate pentahydrate ($Tm(NO_3)_3·5H_2O$, 99.9%), citric acid monohydrate ($C_6H_8O_7·H_2O$, 99.8%), sodium fluoride (NaF, 98%), bismuth nitrate pentahydrate ($Bi(NO_3)_3·5H_2O$, 99.99%), Thiourea (CH_4N_2S, 99%), potassium iodide (KI, 99%), ethanol (99.7%), Tetracycline hydrochloride (TC, 96%) were purchased from Aladdin Reagents Co., Ltd. Silver nitrate ($AgNO_3$, 99.5%), Ethylene glycol (EG) ($C_2H_6O_2$, 99%) and Polyethylene glycol 400 ($H(OCH_2CH_2)nOH$, PEG**)** were purchased from Guangzhou Chemical Reagent Factory. All of the chemicals were used as received without further purification.

2 Experimental

2.1 Synthesis of BiOI

2.43 g $Bi(NO_3)_3·5H_2O$ were added to 30 mL of 1 M mannitol solution under vigorous stirring for 30 min. Then 5 mL of saturated KI solution was slowly dropped into the solution. After another 30 min stirring, the solution was transferred to a 50 mL autoclave, kept at 160°C for 3 h, and then cooled naturally to room temperature. After centrifugal precipitation, the powder was washed with ethanol and deionized water several times. Finally, obtained powder was dried at 60°C for 12 h.

2.2 Synthesis of $AgBiS_2$

0.17g $AgNO_3$, 0.486 g $Bi(NO_3)_3·5H_2O$ and 0.01 g PEG were added to 30 mL of EG under vigorous stirring for 1 h. Then 0.3 g thiourea was added to above solution. After another 30 min stirring, the solution was transferred to a 50 mL autoclave, kept at 180°C for 3 h, and then cooled naturally to room temperature. After centrifugal precipitation, the powder was washed with ethanol and deionized water several times. Finally, obtained powder was dried at 60°C for 12 h.

2.3 Synthesis of BiOI@$AgBiS_2$ (BABS)

100 mg BiOI and different weight $AgBiS_2$ were mixed and ground evenly. The ground solid was added to 15 mL anhydrous ethanol and sonicated for 15 min. Subsequently, the ultrasonic solution was placed in a drying oven at 60°C, till all ethanol was evaporated to obtain dry solid, the solid was ground to obtain a uniform BiOI@$AgBiS_2$. When the weight of $AgBiS_2$ was 2 mg, 4 mg, 6 mg, 8 mg, 10 mg, 15 mg, BiOI@$AgBiS_2$ was denoted as BABS-2%, BABS-4%, BABS-2%, BABS-8%, BABS-10%, BABS-15%, respectively. The mass percentage and the corresponding mol percentage of $AgBiS_2$ to BiOI are shown in the following table.

	The ratio of $AgBiS_2$ to BiOI					
mass percentage (%)	2	4	6	8	10	15
mol percentage (mol%)	1.85	3.7	5.55	7.4	9.25	13.875

2.4 Synthesis of $NaYF_4$:Yb,Tm

$NaYF_4$:Yb,Tm microparticles were prepared by a hydrothermal method. A total of 2 mmol $Ln(NO_3)_3$ and 5 mmol citric acid were added to 20 mL deionized water and stirred for half an hour. Subsequently, 1 g NaF was added and stirred for 30 min. Then, the solution was transferred to a 50 mL polytetrafluoroethylene-lined autoclave and placed in a high-temperature oven at 180 °C for 24 h. The resulting products were collected and washed with a mixed solution of deionized water and absolute ethanol at a ratio of 2:1. Finally, the samples were dried at 60 °C for 12 h.

2.5 Synthesis of the BiOI@$AgBiS_2$@$NaYF_4$:Yb,Tm composites (BABS-Tm)

0.21 g (1 mmol) $NaYF_4$:Yb,Tm and 0.07 g (0.2 mmol) BiOI@$AgBiS_2$-2% were mixed and ground evenly. The ground solid was added to 15 mL of anhydrous ethanol and sonicated for 15 min. Subsequently, the ultrasonic solution was placed in a drying oven at 60°C until all ethanol evaporated to obtain a dry solid; the solid was ground to obtain a uniform BiOI@$AgBiS_2$.

2 Characterization

The crystal structure was conducted utilizing X-ray diffraction (XRD, D-Max 2200, Rigaku). The microstructure were examined using Scanning Electron Microscope (SEM, Gemini 500, Zeiss). The microstructure of the samples was characterized by transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) using a Jeol JEM-ARM200P. X-ray Photoelectron Spectroscopy (XPS) analyses were conducted using an ESCALAB Xi+ system (Thermo Fisher Scientific, UK) to elucidate the chemical states of the elements present. The optical properties were explored through Diffuse Reflectance Spectrum (DRS) using a Shimadzu UV-3600 spectrophotometer. The upconversion photoluminescence (PL) spectra were characterized by Fluorescence Spectrometer (FLS 980, Edinburgh) coupled

with a 980 nm laser (MDL-III-980-2W). The excitation power and slit widths of upconversion luminescence measurements are 0.03 W and 0.02. Electrochemical tests were measured by CHI760E (Chenhua) electrochemical workstation.

3 Photocatalytic tests

The photocatalytic activity was conducted by a CEL-LB70 photocatalytic reaction apparatus (China Education Au-Light). The sample's photocatalyst efficiency was evaluated by testing TC photodegradation under different light sources. A 200 W xenon lamp is used as a simulated solar light source, and an optical filter (> 780 nm) is used to obtain a NIR light source. In the typical photocatalytic experiments under simulated solar, the concentration of TC is 10 mg/L. 7.5 mg sample was accurately weighed and placed in a tube filled with 40 mL pollutants solvent. The solvent was set in the dark under stirring to achieve adsorption/desorption equilibrium. Then, the solution was exposed to different light irradiation. The tube was kept at room temperature through a circulating water system throughout the photocatalytic process. The solution was sampled at various photocatalytic time intervals, and 3.5 mL of solution was taken and centrifuged.

A Shimadzu UV-1800 spectrometer measured the TC solution's absorbance at 360 nm. The removal rate of TC is calculated using the following formula: C_0 and C_t are the solution's initial absorbance and the absorbance after different time irradiation, respectively.

$$\text{Removal rate} = (1 - C_t/C_0) * 100\%$$

In the NIR photocatalytic experiments, the weight of sample is 20 mg. When discussing the influence of experimental parameters on photocatalytic performance, the $AgBiS_2$/BiOI ratios is from 2% to 15%, the dosages of BiOI@$AgBiS_2$ is from 2.5 mg to 25 mg, and the TC solution concentration is from 5 mg/L to 80 mg/L

To investigate the reactive oxygen species generated during photocatalytic tests, the capture experiments of reactive oxygen species were carried out. T-Butanol (T-BuOH, 0.01 M), disodium edetate (EDTA, 0.01 M), and p-Benzoquinone (BQ, 0.01 M) were utilized as scavengers for hydroxyl radicals (·OH), holes (h^+), and superoxide radicals ($\cdot O_2^-$), respectively. The photocatalytic capture experiment is the same as the photodegradation experiment, but 0.4 mL scavenger solution is added to 40 mL pollutants solvent before the photocatalytic experiment.

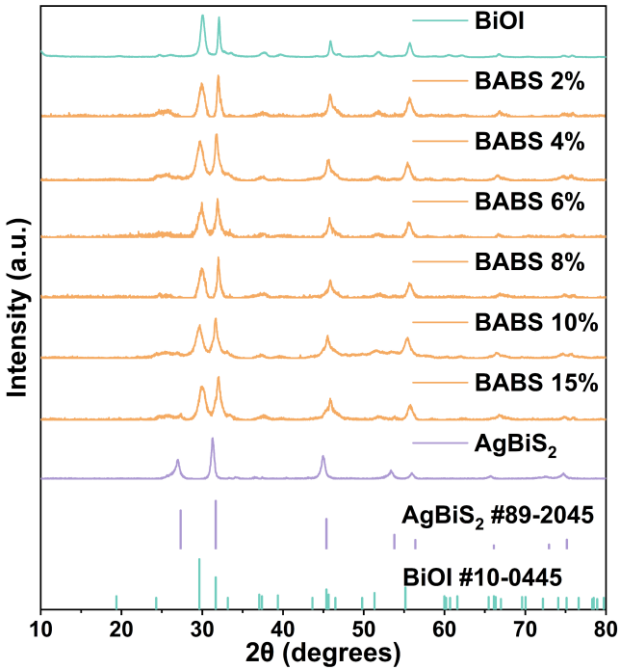

Fig. S1 XRD patterns of BiOI, $AgBiS_2$ and BABS.

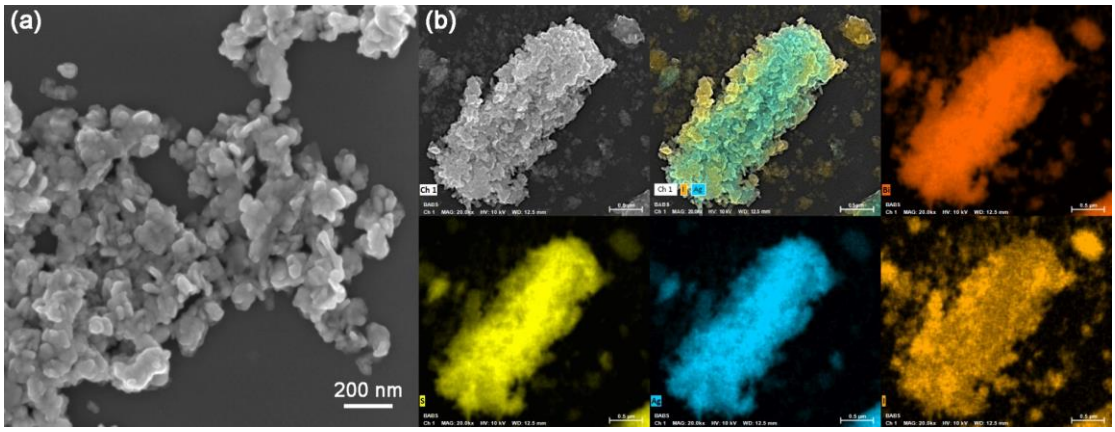

Fig. S2 (a) SEM image of BABS. (b) EDS element mappings of BABS, including element Bi, S, Ag and I.

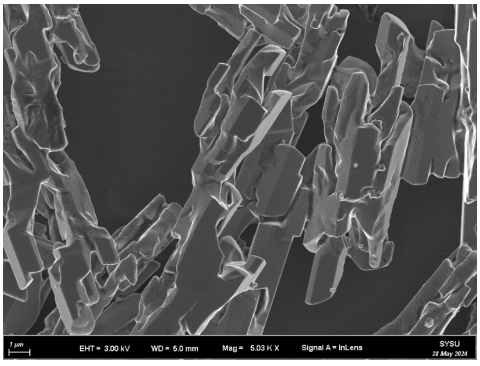

Fig. S3 SEM image of $NaYF_4$:Yb,Tm.

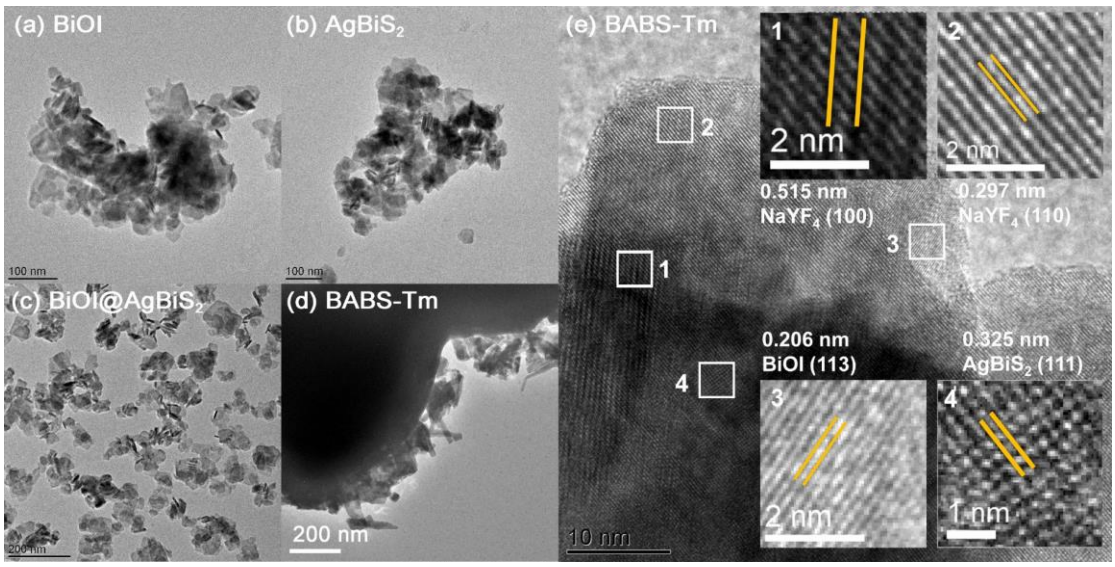

Fig. S4 TEM image of BiOI (a), $AgBiS_2$ (b), BABS (c) and BABS-Tm (d). (e) HRTEM image of BABS-Tm.

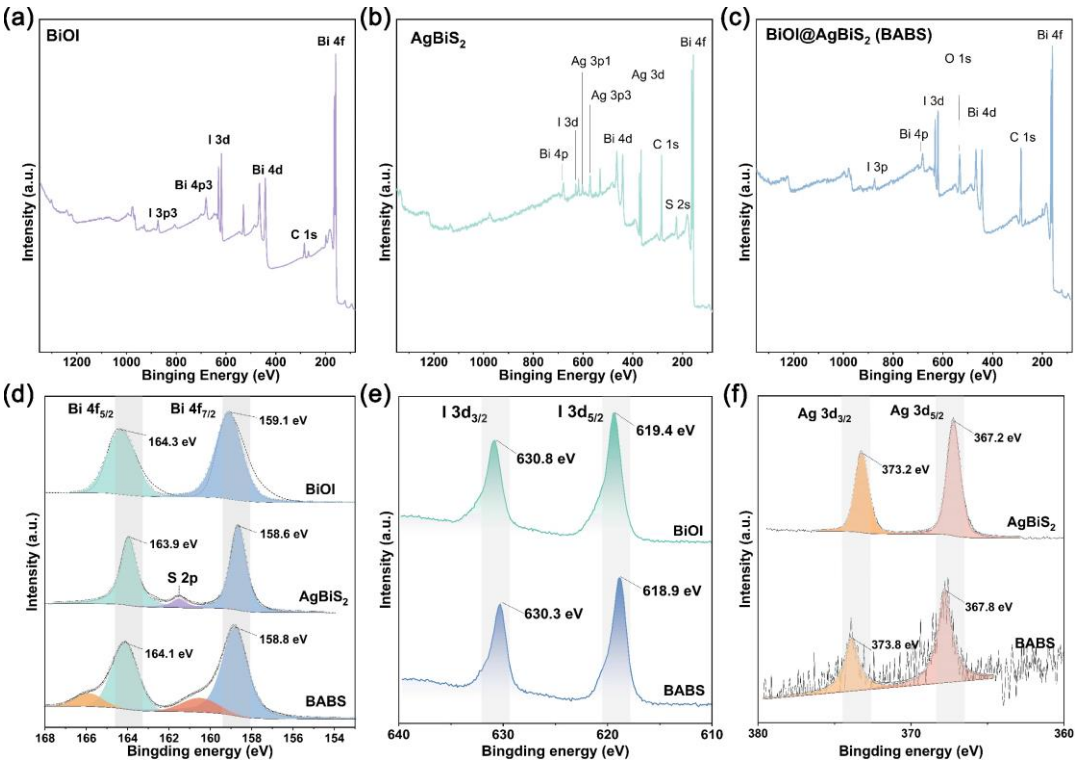

Fig. S5 XPS survey spectra of BiOI (a), $AgBiS_2$ (b) and BABS (c). High-resolution XPS spectra Bi 4f (d), I 3d (e) and Ag 3d (f).

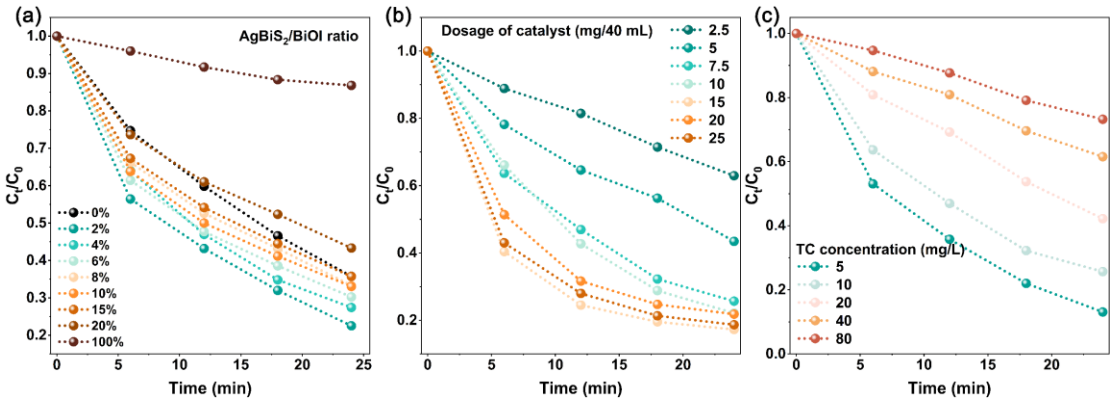

Fig. S6 The effects of experimental parameters such as $AgBiS_2$/BiOI ratios (a), dosages of BiOI@$AgBiS_2$ (b) and TC solution concentration (c) on photocatalytic performance.

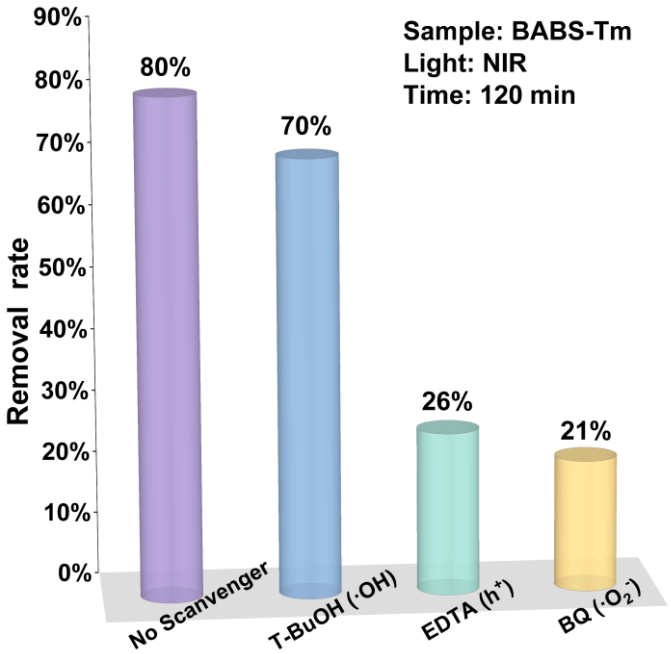

Fig. S7 Removal rate of TC with different scavengers.

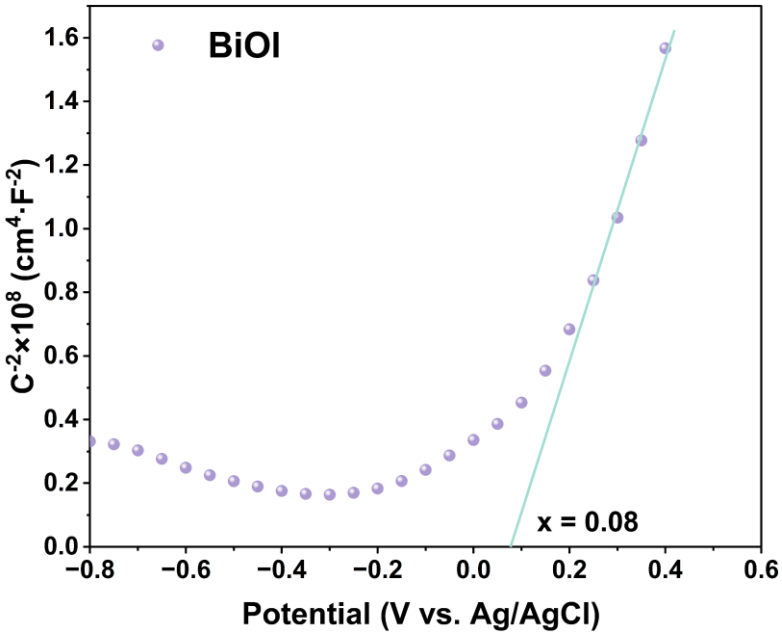

Fig. S8 M-S curves of BiOI.