Supporting Information

Highly Porous BiOBr@NU-1000 Z-scheme Heterojunction Synergistic Efficient Adsorption and Photocatalytic Degradation of Tetracycline

All the chemicals were commercially available and used without further purification. NU-1000 was synthesized according to a previously reported procedure. Powder X-ray diffraction (PXRD) patterns were taken on a Bruker Advance D8 Powder X-ray Diffractometer with Ni-filtered Cu Kα radiation operating at 40 kV and 40 mA. The microstructural morphologies of the materials were characterized by a Zeiss Sigma 500 scanning electron microscopy (SEM) and a JEM-2100 transmission electron microscopy (TEM). Inductively coupled plasma emission spectroscopy (ICP-OES) was recorded on an PerkinElmer 8300 spectrometer. The N_2 adsorption and desorption isotherms dates were collected at a Microtrac BEL Corp at 77 K and the Pore-size distributions were obtained using DFT calculations using a carbon slit-pore model with a N_2 kernel. UV-vis Diffuse Reflectance Spectra (UV-vis DRS) was measured at the JASCO V-750 UV-vis spectrophotometer. Luminescence spectra was carried out on the Instrument JASCO FP-8300 fluorescence spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi-type instrument with the excitation source of monochrome aluminum Kα ray source. Electron Spin Resonance (ESR) measurements were detected by a Bruker A300E spectrometer and the signals of the spin-trapped radicals were examined using the 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) under xenon lamp irradiation. Photoelectrochemical measurements were performed on a CHI660E electrochemical workstation using a standard three-electrode system.

Synthesis of NU-1000.

NU-1000 was synthesized in compliance with a reported process. In brief, benzoic acid (54 g) and $ZrOCl_2 \cdot 8H_2O$(6.02 mmol, 1.94 g) were combined in DMF (40 mL) and then dissolved using an ultrasonic treatment. In the next stage, the obtained transparent solution was incubated in an oven at 80 ℃ for 1 h and cooled down to room

temperature. At the same time, 800 mg H_4TBAPy was weighed and dissolved in 40 mL DMF solvent and heated at 100 ℃ for 1 h. A solution containing zirconium precursors and H_4TBAPy was mixed and heated in a drying oven at 120 ℃ for 16 h to obtain a yellowish precipitate. Then cooled down to room temperature. The resulting suspension is filtered out, producing a yellow polycrystalline solid. Then, it was washed with DMF, and then dried at 80 ℃ under vacuum.

Synthesis of BiOBr.

$Bi(NO_3)_3.5H_2O$ (1.94 g) and KBr (0.72 g) in the 60 mL ethylene glycol through stirring until it is completely dissolved, and then transfer it to a stainless steel autoclave lined with 100 mL Teflon-lined autoclave and heated at 120℃ for 6 h. After cooling down to room temperature, the powders were collected by filtration, washed with H_2O and ethanol, and then dried under vacuum.

Table S1. The comparison of elemental analysis, band gaps and specific surface area for NU-1000，BNU-1 ,BNU-2and BNU-3.

Sample	Zr_6:Bi (atomic ratio)	Band gap (eV)	BET surface area (m^2/g)
NU-1000	None	2.58	2001
BNU-1	1.2:1	2.52	1117
BNU-2	2.3:1	2.54	1665
BNU-3	3.3:1	2.56	1084

Zr_6:Bi atomic ratio were measured by ICP-OES.

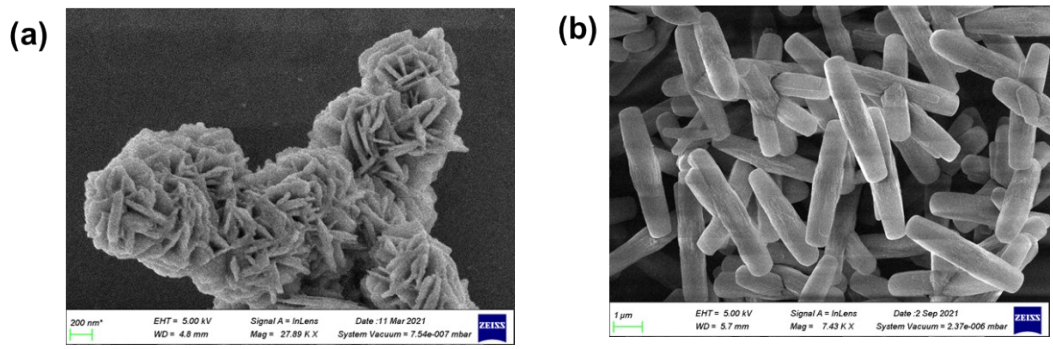

Figure S1. SEM images of BiOBr and (b) NU-1000.

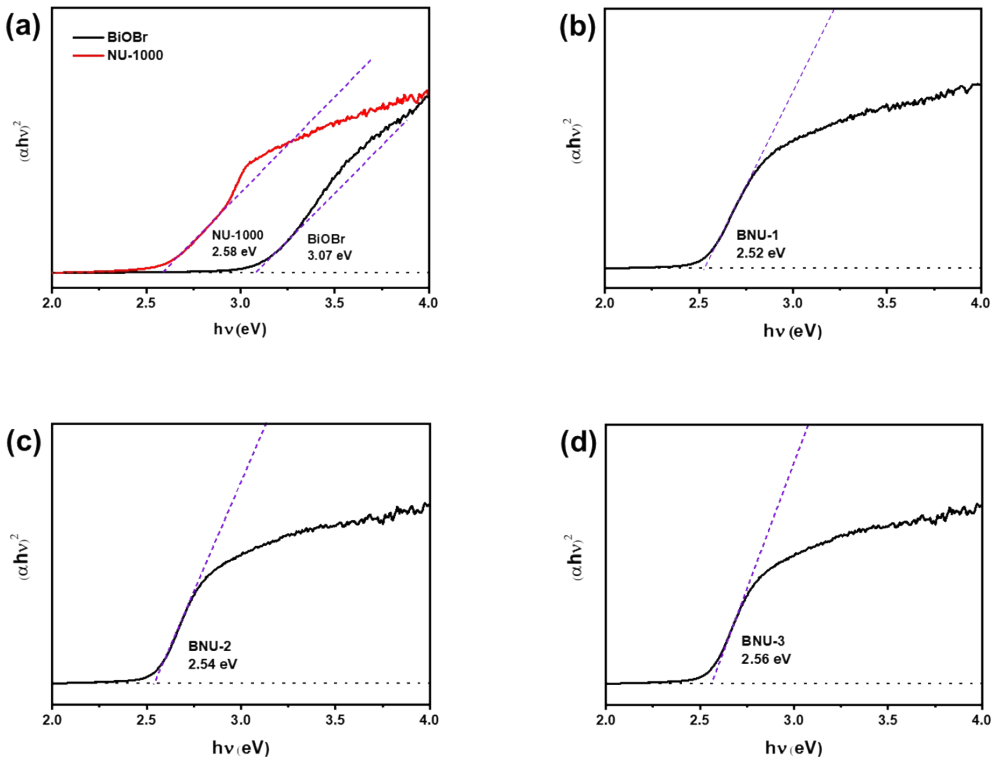

Figure S2. The Tauc plots of (a) BiOBr and NU-1000, (b) BNU-1 (c) BNU-2 and (d) BNU-3

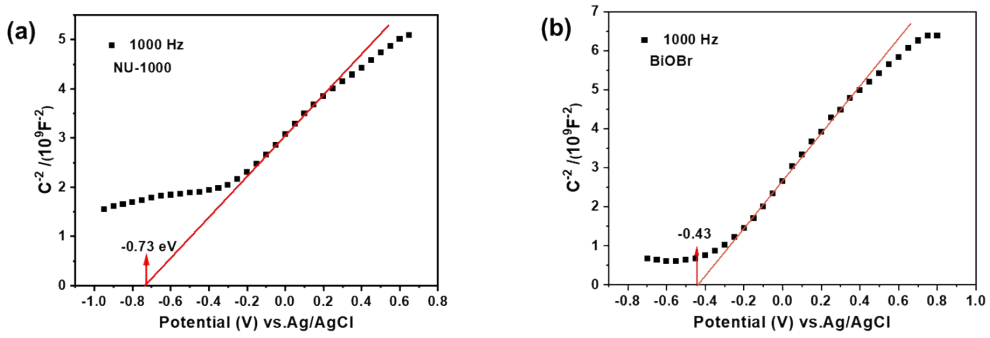

Figure S3. The Mott-Schottky of (a) NU-1000 and (b) BiOBr

Calculation method

Comparison of the rate constants k for the photocatalytic degradation of TC according to the pseudo-first-order kinetic equation $\ln(C_t/C_0) = k_0 t$ (C_t is the concentration of TC at time t during photocatalytic process, C_0 is the initial concentration of TC after adsorption, k_0 stands for the pseudo-first order reaction rate constant (min^{-1}) and t is the photocatalytic reaction time (min).

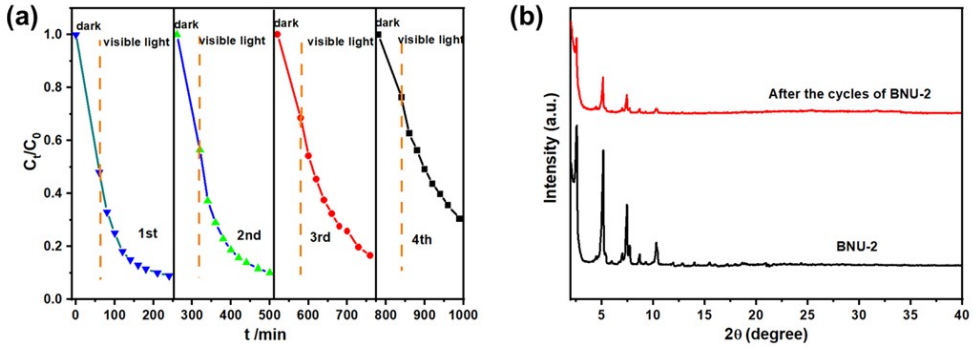

Figure S4 Comparation of the adsorption and photocatalytic degradation of TC over BNU-2 in four cycles; (b) XRD image of BNU-2 after four cycles.

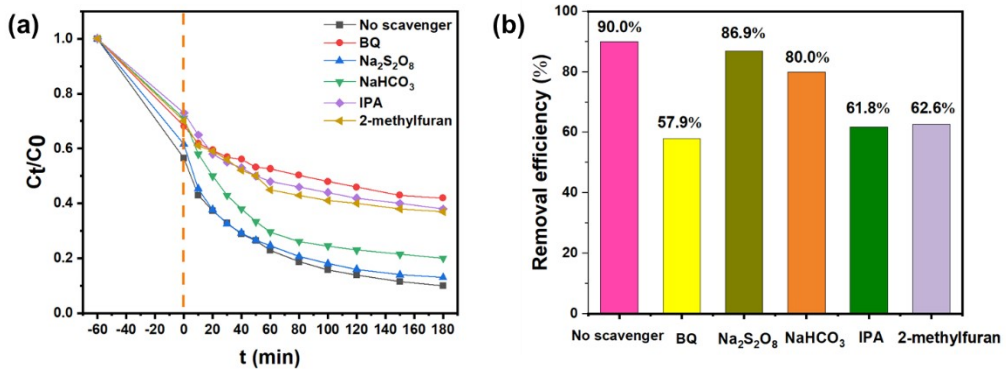

Figure S5. Photocatalytic degradation of TC with the reactive species scavenger

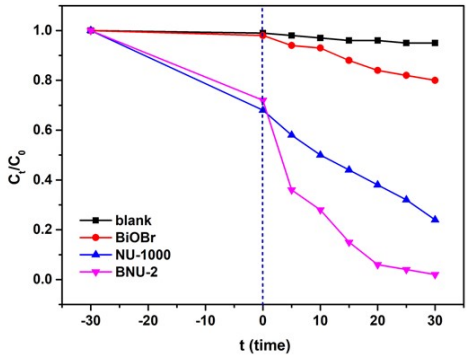

Figure S6. Degradation curves of RhB by different catalysts under visible light irradiation

Table S2 Compared with other photocatalytic tetracycline degradation systems

Photocatalytic Materials	Mass of Photocatalyst (mg)	C_0 (mg/L)	Time (min)	Light source (wavelength)	Efficiency (%)	Ref.
BiOI/MIL-121	40	20	120	300wXe	68	1
$CoFe_2O_4$/MIL-101(Fe)	10	10	120	300wXe	80	2
g-C_3N_4/UiO-66-NH_2/CdS	50	20	180	300wXe	83	3
V_2O_5/MIL-101(Fe)	50	100	120	300wXe	88	4
ZIF-67/BiOCl	60	10	120	250wXe	78	5
BNU-2	**10**	**100**	**120**	**100wLED**	**87**	**This work**

References

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