Study on the Synergistic Enhancement of Photocatalytic Degradation of Carbendazim by Co doped BiOBr induced Spin Polarization and OVs

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Text S1. Reagents

Carbendazim (≥98%), Ciprofloxacin (≥98%), Levofloxacin (≥98%), Tetracycline (≥98%), Methyl Orange (≥98%), $Bi(NO_3)_3 \cdot 5H_2O$, KBr, $AgNO_3$, $KBrO_3$, ethylene glycol (EG), L-Histidine ($C_6H_9N_3O_2$), ammonium oxalate [$(NH_4)_2C_2O_4$], isopropyl alcohol (C_3H_8O), 4-Hydroxy-TEMPO ($C_9H_{18}NO_2^*$)， NaCl, Na_2SO_4, $NaHCO_3$, Na_2HPO_3 and Na_2CO_3 were supplied by Macklin Biochemical Technology Co., Ltd. The deionized water was purified by the laboratory Millipore-Q System.

Text S2. Characterization

The crystalline structures were analyzed by X-ray diffraction (XRD, UltimaIV) with the Cu Kα radiations. The structure and chemical bond of the catalysts were analyzed by Fourier transform infrared spectroscopy (FT-IR, Nicolet NEXUS 670). The micromorphology, lattice information, and elemental distribution of the catalysts were observed by scanning electron microscopy (SEM, Zeiss Sigma 300) and and transmission electron microscopy (TEM, FEI Tecnai G2 F20). The valence state of each element in the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientifc K-Alpha, China). The UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS, Shimadzu UV-3600i Plus) was used to measure the light absorption performance. The emission spectra photoluminescence spectra (PL, PerkinElmer-LS55) at excitation wavelength of 280 nm were measured to investigate the separation ability of photocarriers. Measurement of total organic carbon (TOC, Shimadzu TOC-L CPN CN200) was quantified with a TOC analyzer. The impedance (EIS) was tested on an electrochemical workstation (Shanghai Chenhua CHI660E). Time-resolved photoluminescence decay spectra were measured using a steady-state/transient fluorescence spectrometer (TRPL, Edinburgh FLS1000). Electron spin resonance (ESR) spectra were collected using a Bruker A300 instrument.

Text S3. Theoretical calculations

The density functional theory (DFT) calculations were carried out using the Cambridge Serial Total Energy Package (CASTEP) module. The geometry optimization and electronic structures of BiOBr, BiOBr-Ov and Co-BiOBr were calculated by the Generalized Gradient Approximation

(GGA) with Perdew-Burke-Ernzerhof (PBE) functional, with the considerations of spin-orbit polarization. For all calculations, the electronic states were expanded using a plane-wave basis set with a kinetic energy cut-off of 489.80 eV. The K-grid points was set to 1×1×1 and the electronic energy, the maximum displacement, the precision of interatomic interaction force, the precision of crystal internal stress were 2.0×10^{-5} eV, 0.002 Å, 0.05 eV/Å and 0.1 GPa, respectively.

Table S1. Crystallite size of BiOBr and 5% Co-BiOBr samples by using Debye-Scherrer.

lattice plane of BiOBr	FWHM	crystallites size	average crystallite size	lattice plane of 5% Co-BiOBr	FWHM	crystallites size	average crystallite size
(102)	0.18502	43.50754		(102)	0.28215	28.53527	
(110)	0.23713	34.44091		(110)	0.37709	21.66211	
(200)	0.18057	45.28657	39.64738	(200)	0.24384	33.54391	27.90368
(212)	0.20388	41.89814		(212)	0.27292	31.30949	
(101)	0.27026	33.10375		(101)	0.36579	24.46761	

Table S2. Comparison of the photocatalytic performance of related catalysts in the degradation of CBZ.

Catalyst	**Catalyst weight**	**Details of Catalytic Experiments**	**Removal efficiency**	**Ref.**
5% Co-BiOBr	20 mg	Xe lamp (300 W, λ >350 nm),10 mg/L CBZ	92.1% (60min)	This work
Cu_2O/ZnO@ PET	20 mg	UV,T=52℃,1.0 mg/L CBZ	98.1% (160min)	[1]
Bi_2S_3/$BiFeO_3$	50 mg	Xe lamp (150 W, λ > 400 nm). 10 mg/L CBZ	95% (120min)	[2]
Fe/TiO_2	200 mg	Sunlight,T=25℃, 8 mg/L CBZ	98.5% (60min)	[3]
$Gd_2(WO_4)_3$	60 mg	A Philips projection lamp (250 W, 532 nm),10 mg/L CBZ	98% (140min)	[4]
ZnO-GQD	20 mg	natural sunlight irradiation 1.91 mg/L CBZ	94% (70min)	[5]
$SrTiO_3$/Mo_2AlB_2	20 mg	Halogen lamp(500W) 15 mg/L CBZ	87.5% (80min)	[6]

Table S3. Fluorescence lifetime parameters of the samples.

Samples	A_1	τ_1 (ns)	A_2	τ_2 (ns)	Ave. τ (ns)
BiOBr	0.65329	0.85818	0.48171	0.85819	0.858184244
5% Co-BiOBr	1.03974	0.7886	0.05243	4.97058	1.797215

$$I_{(t)} = I_{(0)} + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \qquad (\text{Eq.S1})$$

$$\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2) \qquad (\text{Eq.S2})$$

where t represents time, A_1 and A_2 are exponential prefactors, τ_1 represents the carrier lifetime of the radiative energy-transfer process and τ_2 represents the carrier lifetime of the non-radiative energy-transfer process.

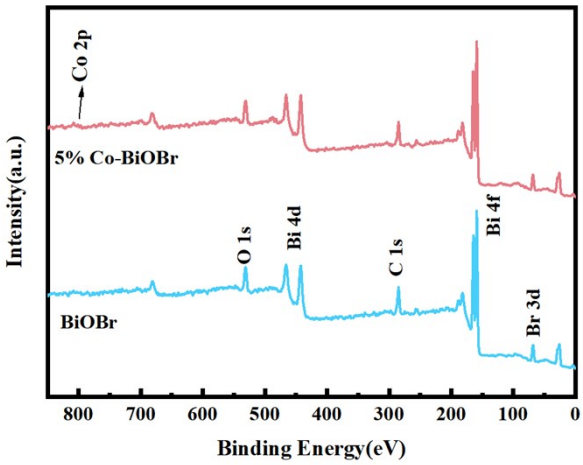

Figure S1. XPS survey spectra of BiOBr and 5% Co-BiOBr.

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