Supporting Information

Bi_2S_3-decorated three-dimensional BiOCl as a Z-scheme heterojunction with highly exposed {001} facets of BiOCl for enhanced visible-light photocatalytic performance

Mingming Sun,[abcd] Ruixiao Gao,[e] Bowei Wang,*[abcd] Jiayi Li,[a] Zijing Zhang,[a] Guoyi Bai,[f] Xilong Yan,[abcd] Yang Li[abcd] and Ligong Chen*[abcd]

[a] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, P. R. China.
[b] Institute of Shaoxing, Tianjin University, Zhejiang 312300, P. R. China.
[c] Guangdong Laboratory of Chemistry and Fine Chemical Industry Jieyang Center, Guangdong Province 522000, P. R. China.
[d] Tianjin Engineering Research Center of Functional Fine Chemicals, Tianjin 300350, P. R. China.
[e] Oilfield Chemicals R&D Institute, China Oilfield Services Limited, Langfang 065201, P. R. China.
[f] Key Laboratory of Chemical Biology of Hebei Province, College of Chemistry and Environmental Science, Hebei University, Baoding 071002, P. R. China
*Corresponding authors. E-mail: bwwang@tju.edu.cn (Bowei Wang); lgchen@tju.edu.cn (Ligong Chen)

1.1. Characterizations of photocatalysts

The patterns of X-ray diffraction (XRD) were collected on a X'Pert Pro (Panalytical, Netherlands) using a Cu-Kα X-ray source in the range of 5°-70° (5°·min^{-1}). SEM images were recorded on an S-4800 microscope (Hitachi, Japan). Transmission electron microscope (TEM) and high-resolution transmission electron microscopy (HRTEM) were carried out on a JEM-200 (JEOL, Japan) at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was recorded on an ESCALAB-250Xi (Thermo Fisher, UK). UV-vis diffuse reflectance spectra (DRS) were collected on a Lambda 750 spectrophotometer (Perkin Elmer, USA) by using $BaSO_4$ as a reflectance standard. Photoluminescence (PL) spectra were measured using a Fluorolog3 spectrophotometer (HOR1BA JOB1N YVON, USA) with excitation wavelength of 320 nm. The electron spin resonance (ESR) measurements were carried out by using a JES-FA200 spectrometer (JEOL, Japan).

1.2. Photoelectrochemical measurements

Electrochemical impedance spectra (EIS) were recorded on an electrochemical system (CHI-660e, Shanghai) in three-electrode quartz cells with 0.5 M Na_2SO_4 electrolyte solution. Platinum wire and Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. Work electrode was prepared by depositing photocatalyst onto the glassy carbon electrode.

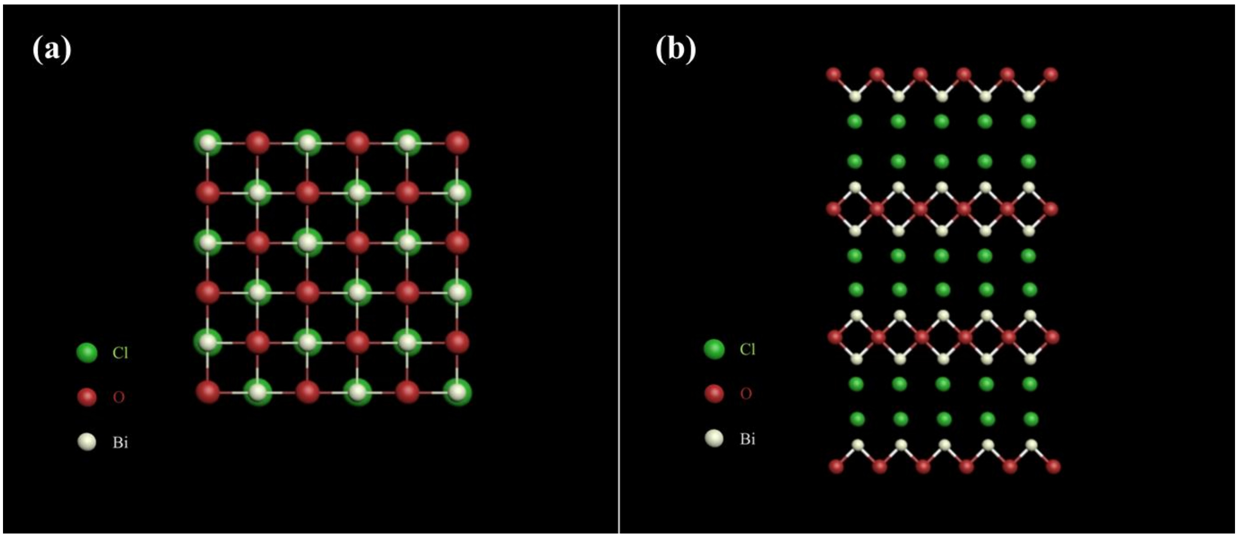


Fig. S1. The structure model of BiOCl crystals: (a) {001} facets and (b) {110} facets

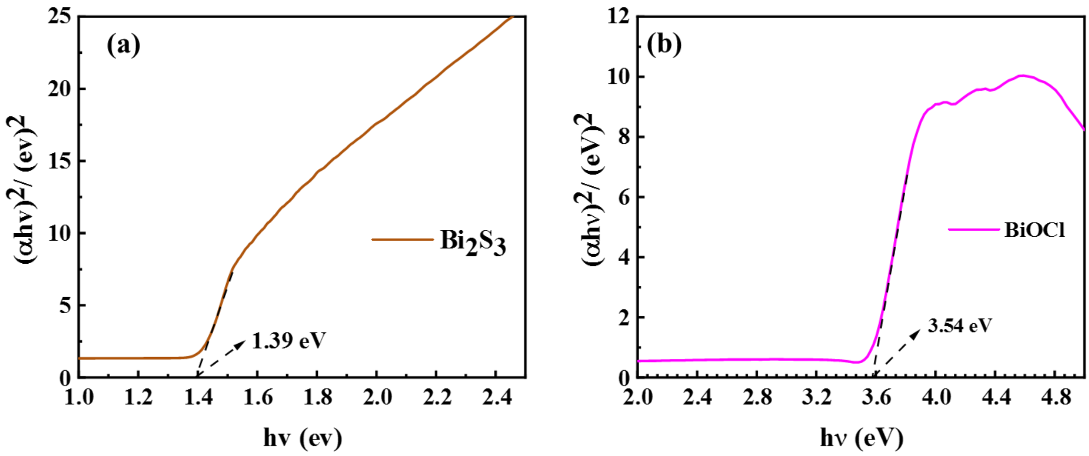


Fig. S2. plots of (αhν)2 versus the photon energy (hν) for (a) BiOCl and (b) Bi_2S_3.

The band gap energies (Eg) of the samples were estimated by Kubelka-Munk expression: $\alpha h\nu = A(h\nu - Eg)^{n/2}$, where Eg, α, h, ν, and A are band gap energy, light absorption coefficient, Planck's constant, photon frequency, and constant, respectively. As shown in Fig. S2, the band gaps of BiOCl and Bi_2S_3 are 3.54 and 1.39 eV, respectively.

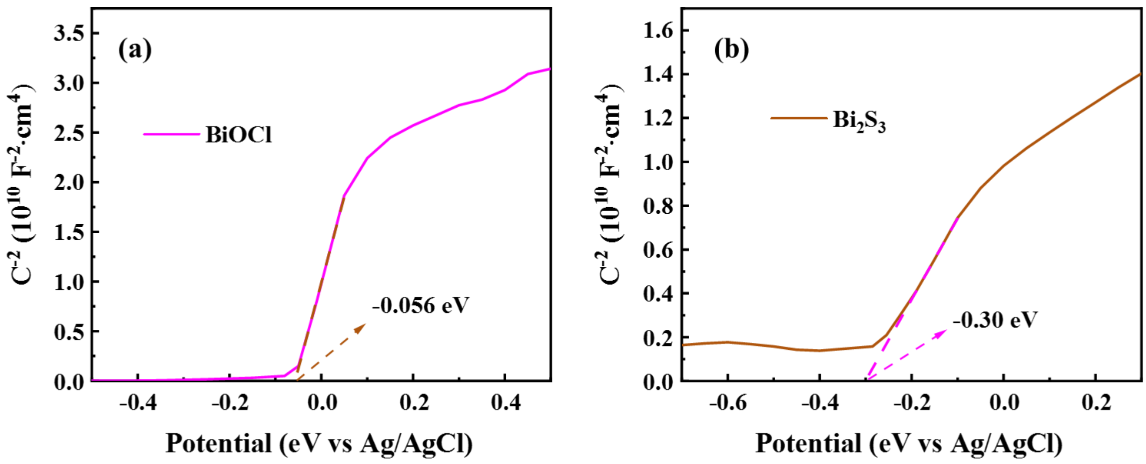


Fig. S3. Mott-Schottky curves of (a) BiOCl and (b) Bi_2S_3.

Furthermore, the potential of valence band (VB) and conduction band (CB) of BiOCl and Bi_2S_3 were extrapolated from the Mott-Schottky curves. As shown in Fig. S3, the value of the E_{CB} relative to Ag/AgCl electrode can be obtained via extrapolating the linear part of the curve to $C^{-2} = 0$. Moreover, the values of Eg, E_{CB} and E_{VB} of BiOCl and Bi_2S_3 are displayed in Table S1.

Table S1. The values of Eg, E_{CB} and E_{VB} of BiOCl and Bi_2S_3.

Sample	Eg (eV)	E_{CB} (eV vs. Ag/AgCl)	E_{CB} (eV vs. NHE)	E_{VB} (eV)[a]
BiOCl	3.54	-0.056	0.164	3.704
Bi_2S_3	1.39	-0.30	-0.08	1.31

a: $E_{VB}=E_{CB}+Eg$

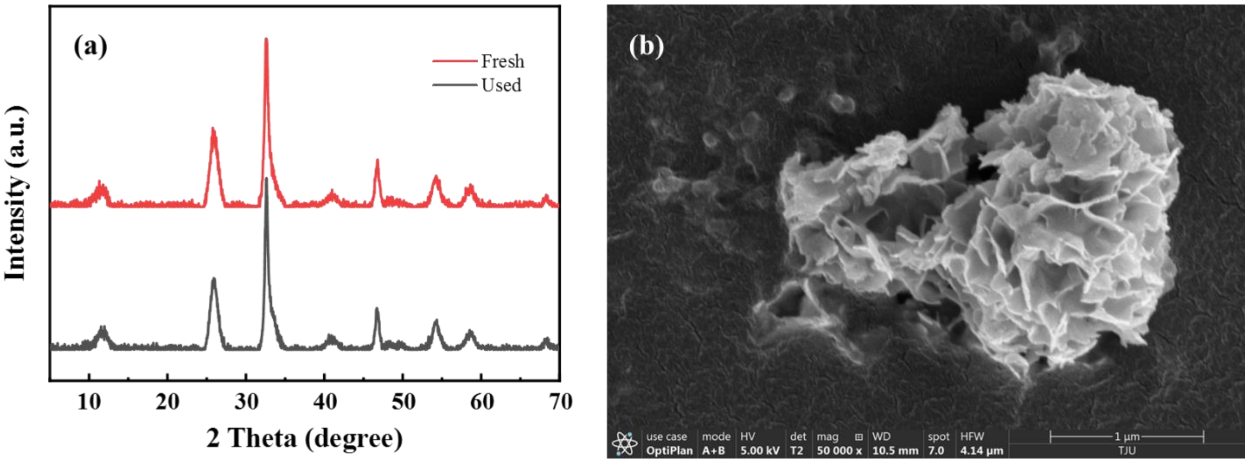


Fig. S4. The XRD patterns and SEM image of BOC-BS-5 after four cyclic experiments.

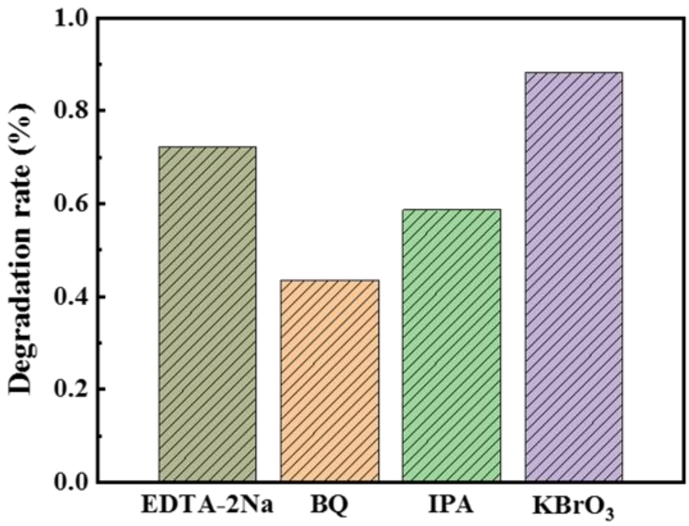
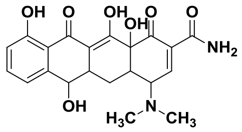
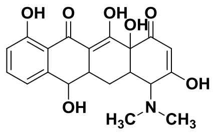
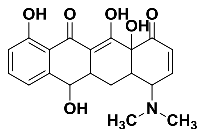
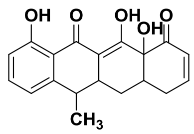
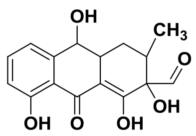
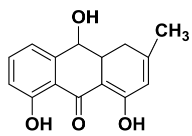
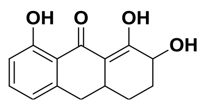
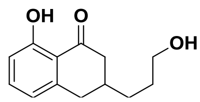


Fig. S5. Effects of different scavengers to photocatalytic degradation.

Table S2. Major intermediates identified by LC-MS.

Compounds	m/z	formula	Proposed structure
TC	445	$C_{22}H_{24}N_2O_8$	
Product 1	415	$C_{21}H_{24}N_2O_7$	
Product 2	388	$C_{20}H_{21}NO_7$	
Product 3	372	$C_{20}H_{21}NO_6$	
Product 4	327	$C_{19}H_{18}O_5$	
Product 5	305	$C_{16}H_{16}O_6$	
Product 6	259	$C_{15}H_{14}O_4$	
Product 7	247	$C_{14}H_{14}O_4$	
Product 8	221	$C_{13}H_{16}O_3$	
Product 9	177	$C_{10}H_8O_3$