Supporting Information

The {001} Facets-dependent High Photoactivity of BiOCl Nanosheets

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Experimental Section

The molecular precursors were prepared from BiCl₃ and Thiourea (Tu) according to the following reaction:

 $nBiCl_3 + mTu \rightarrow Bi_n(Tu)_xCl_{3n} \downarrow$ (1)

0.004 mol BiCl3 was added to 50 mL ethanol and sonicated for 10 min, then 0.004 (or 0.008, or 0.012) mol Tu was added slowly into the solution. The color of solution was becoming yellow after sonication for 1 min, and then changed into yellow or jacinth precipitations after another 10 min of sonication. The solution was filtered and dried at 60 °C for 12 h, being denoted as 1:1 (for 0.004 mol Tu), 1:2 (for 0.008 mol Tu) and 1:3 (for 0.012 mol Tu) precursor, respectively.

The BiOCl NSs were obtained by adding 0.5 g precursors in 400 mL of deionized water with pH = 4.00 for 20 min of sonication, followed by filtration and drying at 80 °C for 12 h. Then, all samples were calcined at 400 °C in air for 2 h. 1:1 BiOCl nanosheet (BiOCl NS-1), 1:2 BiOCl nanosheet (BiOCl NS-2) and 1:3 BiOCl nanosheet (BiOCl NS-3) were derived from the hydrolysis of above 1:1, 1:2 and 1:3 precursors, respectively. For comparison, the aschistic BiOCl with a little {001} facets was derived from the pyrolysis of BiCl₃ at 400 °C for 2 h under air atmosphere with a heating rate of 5 °C/min.

X-ray diffraction patterns (XRD) were recorded on a Bruker D8 advance X-ray diffractometer by using Cu K α radiation and 2 θ scan rate of 6 [°]/min. TEM images were obtained by a tecnaiG² 20S-TWIN transmission electron microscope with operating at an accelerating voltage of 200 kV. HRTEM image was obtained by a JEOL JEM-2010FEF field emission electron microscope with operating at an accelerating voltage of 200 kV. FESEM images were obtained by a JEOL JEM-6700F field emission scanning electron microscope with operating at an accelerating voltage and applied current of 5 kV and 10 mA, respectively. EPR spectra were obtained on JEOL JES-FA300 electron spin resonance spectrometer with micro frequency at 8982 MHz. The spectra were calibrated to the diphenylpicrylhydrazyl (DPPH) signal at 2.002. A low temperature EPR spectrum was directly measured with 1 h UV light irradiation. In order to facilitate the collection of room temperature EPR signal, all BiOCl samples with 1 h UV light irradiation were heated in argon at 300 °C for 2 h before testing.^{S1} Photoluminescence (PL) spectra of BiOCl samples were obtained on a Jasco FP-6500 with $\lambda_{exc} = 320$ nm. The thermo gravimetric analyses (TGA) of the precursors were performed by using an NETZSCH STA 449 C TGA thermal analyzer with a heating rate of 10 °C min-1 and the range of temperature from 50 to 800 °C in air atmosphere. X-ray photoelectron spectroscopy (XPS) measurements were carried out by a VG Multilab 2000 spectrometer (Thermo Electron Corporation) with an Mg Ka X-ray source, and the spectra calibrated to the C 1s peak at 284.6 eV. The Brunauer-Emmett-Teller (BET) surface areas were measured using quantachrome autosorb-1 automated gas sorption systems at 77 K.

The photocatalytic activity was examined by the Rhodamine B (RhB) degradation under UV light irradiation ($\lambda = 365$ nm). The UV light was obtained by a 300 W high-pressure mercury lamp (Changzhou Yuyu Electro-Optical Device Co., Ltd. China). 100 mL aqueous suspension containing 10 mg/L RhB and 20 mg photocatalysts was placed in a quartz glass beaker. Prior to irradiation, the suspension was sonicated for 10 min and then magnetically

stirred in dark for 30 min to get adsorption equilibrium, and then kept under magnetically stirring and constant air-equilibrated conditions during the irradiation. At certain time intervals, 4 mL suspension was sampled and centrifuged to remove the particles. The upper clear liquid was analyzed by recording the maximum absorption band (554 nm for RhB) and UV-visible spectra using a Shimadzu UV-3600 spectrophotometer.



Fig. S1 The structure model illustration of BiOCl crystals (3×3 lattices): (a) three-dimensional



projection; (b) {110} facets; and (c) {001} facets.

Fig. S2 TEM images: a) 1:2 precursor; and b) 1:3 precursor.



Fig. S3 XRD patterns of precursors and BiOCl NS-3 with different hydrolysis time from 1:3 precursor.

Fig. S3 shows XRD pattern of the precursors. As can be seen, all samples are well crystallized, and the feed molar ratio determines the chemical composition of the precursor. The XRD patterns for 1:1 and 1:2 precursors can be assigned to $Bi_3(Tu)_7Cl_9$ (JCPDS No.53-0072), while the 1:3 precursor can be assigned to $Bi(Tu)_3Cl_3$ (JCPDS No.53-0073). The XRD patterns of the hydrolyzed products were presented at the top of Fig. S3. No apparent difference was observed between 30 sec and 30 min of hydrolyzing, indicating a fast hydrolysis process of the precursor. Further, the TGA curve of BiOCl NS-3 shows no decline before 600 °C as shown in Fig. S4 that indicates the complete transformation from the precursors to BiOCl.



Fig. S4 TGA curve of BiOCl NS-3.



Fig. S5 a) top view HRTEM images of BiOCl NS-3; b) side view HRTEM images of BiOCl





Fig. S6 FESEM of images: (a) aschistic BiOCl; (b) BiOCl NS-1; (c) BiOCl NS-2; and (d)

BiOCl NS-3.



Fig. S7 TEM of images: (a) aschistic BiOCl; (b) BiOCl NS-1; (c) BiOCl NS-2; and (d)

BiOCl NS-3.



Fig. S8 XRD pattern $(10^{\circ}-14^{\circ})$ of BiOCl NSs.

The XRD pattern ($10^{\circ}-14^{\circ}$) of BiOCl NSs (Fig. S8) shows that the half width of (001) peak increases from BiOCl NS-1 to BiOCl NS-3. From Scherer formula, the d₍₀₀₁₎ is 36.5, 23.2 and 14.0 nm for BiOCl NS-1, BiOCl NS-2 and BiOCl NS-3, respectively.^{S2} This result is in agreement with FESEM data and also can support the difference of the thicknesses.



Fig. S9 UV-vis absorption spectral of RhB under UV light irradiation ($\lambda = 365$ nm) over

BiOCl NS-3.



Fig. S10 Percentage removal of BiOCl and P25 got at t = 32 min.



Fig. S11 XRD pattern of BiOCl NS-3 without or with UV irradiation.



Fig. S12 High-resolution XPS spectra of Bi4f: (a) BiOCl NS-3 with 1 h UV irradiation; (b) BiOCl NS-2 with 1 h UV irradiation; (c) BiOCl NS-1 with 1 h UV irradiation; (d) aschistic

BiOCl with 1 h UV irradiation; and (e) BiOCl NS-3 without UV irradiation.

Fig. S12 shows the Bi4f high-resolution XPS spectra of BiOCl NSs after 1h UV irradiation. 165.8 eV and 160.5 eV are indexed Bi^{3+} from BiOCl.^{S3,S4} The new peaks appear at lower binding energy 163.7 eV and 158.2 eV which can be indexed lower valence state of Bi due to the existence of oxygen vacancies. The same phenomenon had been happened in TiO₂

system.^{S5-S7} The appearance of oxygen vacancies induced a lower binding energy peak which due to Ti^{3+} . Furthermore, the area percentage of the peak at 163.7 and 158.2 eV of Bi4f increases with the {001} facets percentage increasing. It is consistent with oxygen vacancies concentration.

Table S1. The relation between the percentage of {001} facets and photoactivities.

Samples	BET (m²/g)	thickness	percentage of {001} facets	$k (\underset{^{I} \cdot s^{-1}}{\text{mol} \cdot L})$	$(C_0 - C_t)/C_0$ [b]
aschistic BiOCl	6.0	NA	NA	0.0030	9.6%
BiOCl NS-1	13.9	36 nm	ca. 71%	0.0107	33.6%
BiOCl NS-2	13.8	29 nm	ca. 75%	0.0151	48.1%
BiOCl NS-3	14.3	13 nm	ca. 87%	0.0255	81.1%

[a] The thickness was measured from FESEM images. [b] $(C_0 - C_t)/C_0$ was got at t = 32 min. **Table S2.** Bond energy (kJ/mol) of metal-oxygen.^{S8}

Samples	Zr-O	Ti-O	Sn-O	Al-O	Bi-O	Zn-O
bond energy	766.1	666.5	528.0	501.9	337.2	250.0

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