Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

Boosting the photocatalytic activity of BiOX under solar light via the selective crystal facet growth

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Experimental section

Preparation of BiOX (X=Cl, Br, I)

0.5 g polyvinylpyrrolidone K30 (PVPK30) was completely dissolved in 50 mL distilled water to form a homogeneous solution (Marked A). Then 5 mmol KX (X=Cl, Br, I) and 5 mmol $Bi(NO_3)_3{\cdot}5H_2O$ were dissolved in the above solution (A) to form another homogeneous solution (Marked B and C), respectively.

Under magnetic stirring condition, KX (X=Cl, Br, I) solution (B) was added into $Bi(NO_3)_3{\cdot}5H_2O$ solution (C) drop by drop to form a mixed solution. After continuously stirring for 4 h, the mixed solution was filtrated. The filter residue was washed using distilled water and absolute ethanol several times. The washed filter residue was dried at 80℃ for 10 h to obtain three-dimensional(3D) BiOX/PVP microspheres.

For comparison, the pure BiOX was prepared using the above-mentioned similar method without the introduction of PVP.

It is worth noting that the preparation method reported in this work is easy to achieve large-scale application due to its simple and environmentally friendliness. Meanwhile, this method has good application prospects for organic dye wastewater treatment.

Materials Characterization

The phase and structure of samples were identified using X-ray Diffractometer (Shimadzu, XRD-6000, Kyoto, Japan), and Fourier transform infrared spectroscopy 5DX FTIR (5DX, Nicolet. Co., USA). The samples' morphology was observed by scanning electron microscopy (SEM, FEI, F50, ZEISS, Oberkochen, Germany) and transmission electron microscopy (TEM, FEI, Tecnai G2 F20, Hillsboro, OR, USA). The optical properties of samples were examined by ultraviolet-visible diffuse reflectance spectrophotometer (UV-vis DRS, TU1901, Beijing, China). Ultraviolet photoelectron spectroscopy (UPS) measurements (Thermo Fisher ,EscaLab 250Xi, Massachusetts, USA) were performed with an unfiltered HeI (21.22 eV) gas discharge lamp and a total instrumental energy resolution of 100 meV. The measurement of N_2 absorption performance of samples was performed on an adsorption instrument (ASAP-2020, Micromeritics, USA). Photoluminescence (PL) spectra and time-resolved photoluminescence (TRPL) spectra were recorded using a Full-functional Steady/Transient Fluorescence Spectrometer (FLS980, Edinburgh, UK). Electron spin resonance (ESR) signals of radical species trapped by 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) were detected on a JES FA200 (JEOL, Japan) spectrometer. Zeta Potential of samples were tested by Zeta Potential Analyzer (Nanoplus, Micromeritics, USA).

Photocatalytic performance evaluation

The photocatalytic performance was evaluated by using a 300 W Xenon lamp with ultraviolet cut-off filter as simulation visible-light irradiation ($\lambda > 420$ nm, the optical power density was 1000 mW/cm^2) and real solar light irradiation (optical power density was tested using a photometer) to photodegrade RhB solution. The distance between liquid surface and Xenon lamp light source kept to 20 cm.

The following are test procedures. 100 mg of the photocatalyst was added into a 50 mL, 10 mg/L RhB solution. The mixture was fully stirred in the dark for 2 h to reach adsorption equilibrium. At given irradiation time intervals, a series of the reaction solution was sampled and measured the absorption with the UV-vis spectrophotometer (UV-vis DRS, TU1901, Beijing, China). It was worth mentioning that the magnetic photocatalyst in reaction solution was separated using an external magnet. The following is the formula for calculating degradation rate:

$$Degradation\ rate(\%) = \frac{A_0 - A_t}{A_0} \times 100\%$$

where, A_0 is the absorption of initial solution, A_t is the solution absorption after different reaction time.

Computational Method

In this work, density functional theory (DFT) calculations were performed in the Vienna Ab Initio Simulation Package (VASP) code[1,2]. The generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) functionals were used to treat the exchange-correlation functional of electrons[3]. Projector augmented wave (PAW) method was used to solve the ion-electron interactions in the periodic boundary conditions[4]. A Monkhorst-Pack mesh with a grid of (9

× 9 × 1) k-points was chosen for the optimization and projected density of states (PDOS) calculations of BiClO (001) and (110) surface. The kinetic energy cut-off for the plane waves was set to 300.0 eV. The surface slab model was constructed on the basis of Orthorhombic phase BiClO, the slab was separated by a vacuum layer of about 15 Å to avoid interaction between periodic structures. During the geometry optimizations, all self-consistent field (SCF) calculations were converged to 10^{-4} eV and the forces were smaller than 0.05 eV/Å. The molecular graphics viewer VESTA was used to plot molecular structures.

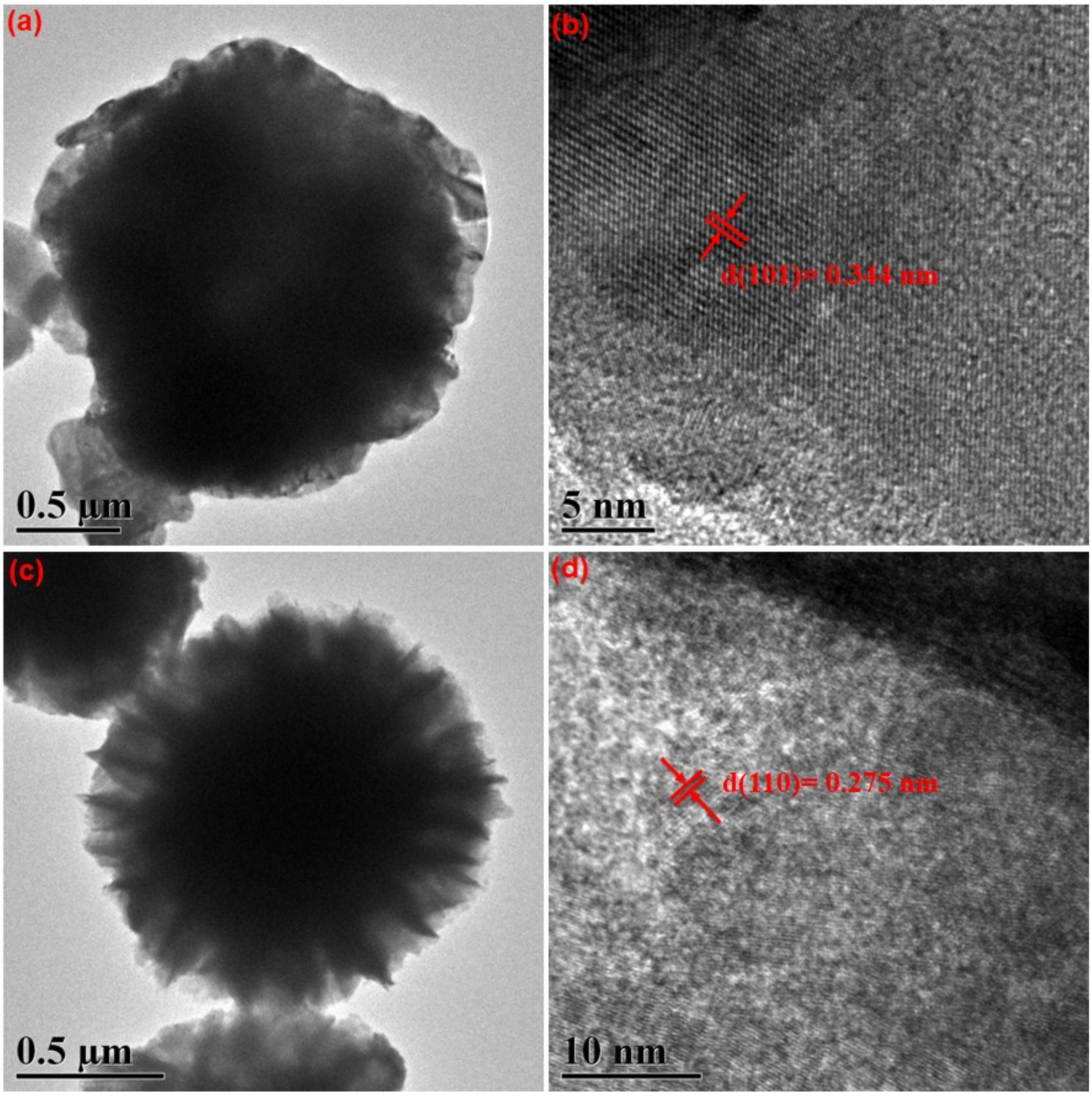

Fig.S1 TEM and HRTEM images of BiOCl (a, b) and BiOCl/PVP(c,d)

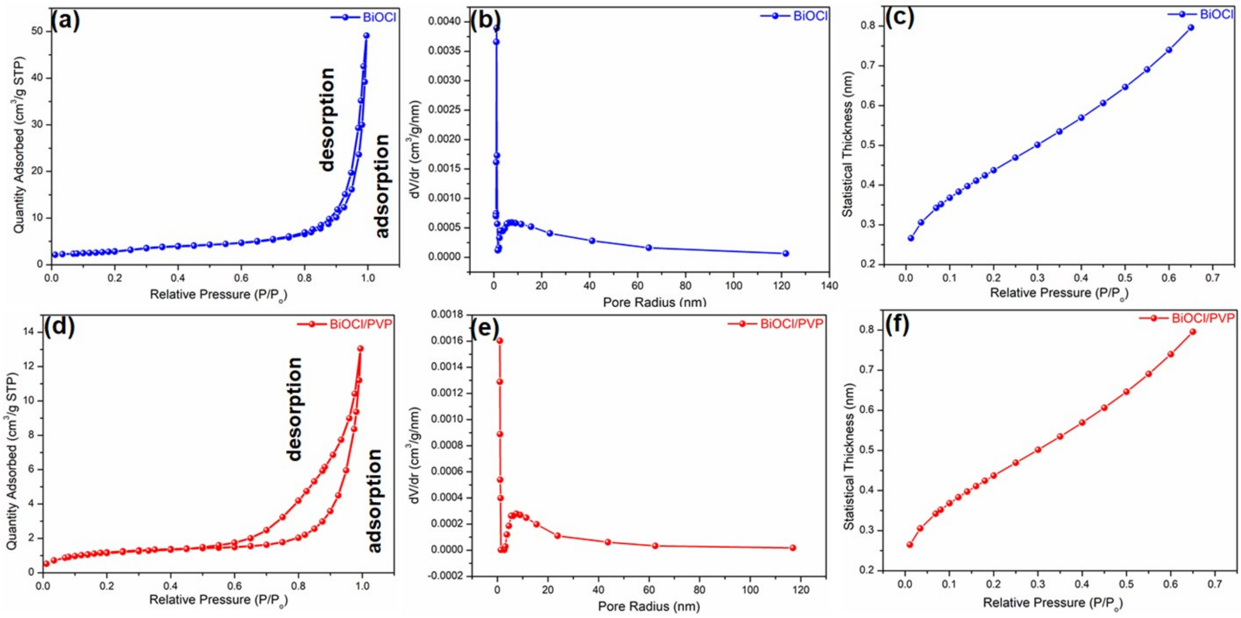

Fig. S2 (a, d) The N_2 adsorption-desorption isotherms; (b, e) pore properties; (c, f) variation curve of statistical thickness with.

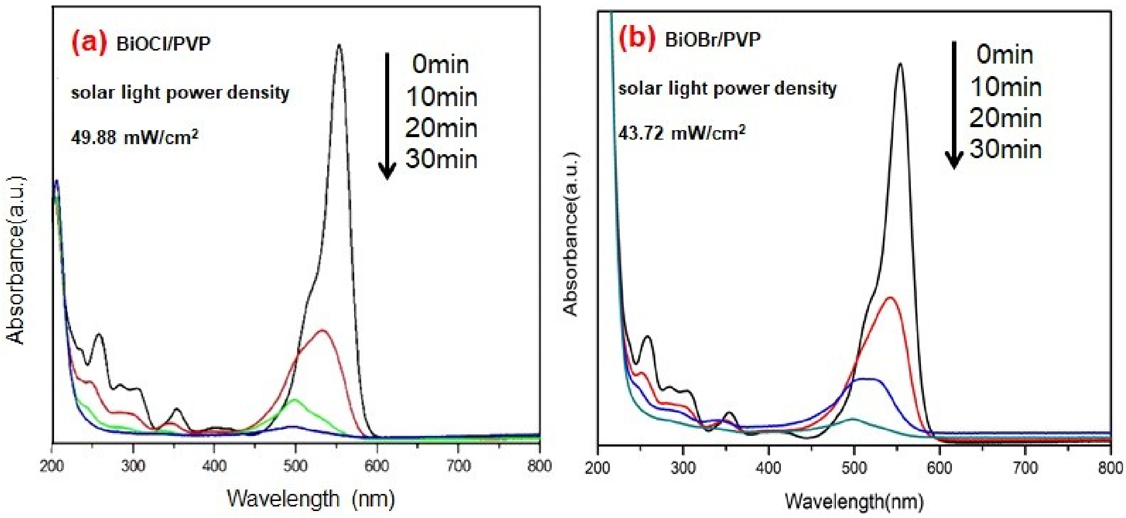

Fig.S3 Photocatalytic degradation spectra of RhB under sunlight with BiOCl/PVP(a) and BiOBr/PVP(b)

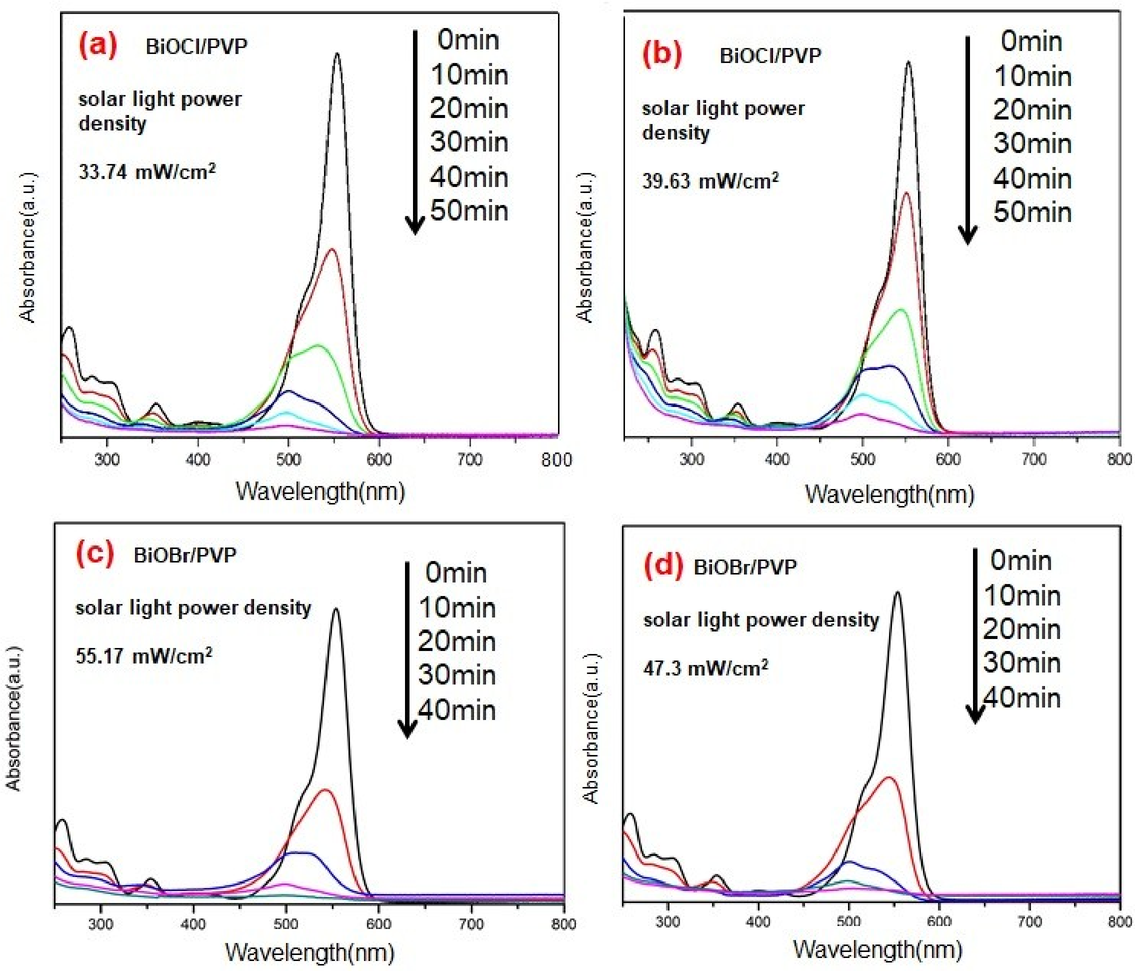

Fig.S4 Photocatalytic degradation spectra of RhB under sunlight with BiOCl/PVP (a, b) and BiOBr/PVP (c, d) in different days

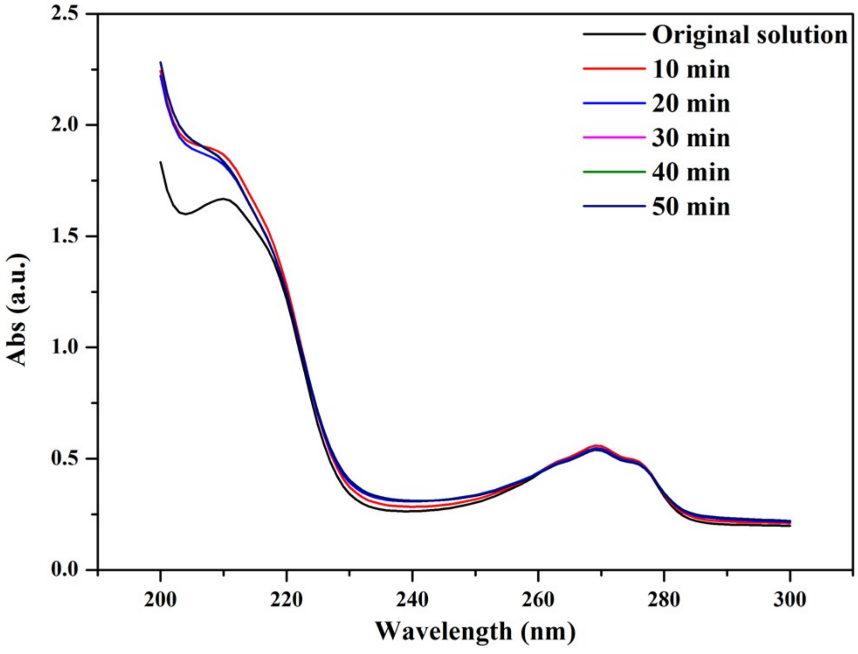

Fig. S5 Temporal evolution of the absorption spectra during the phenol photodegradation over BiOCl/PVP

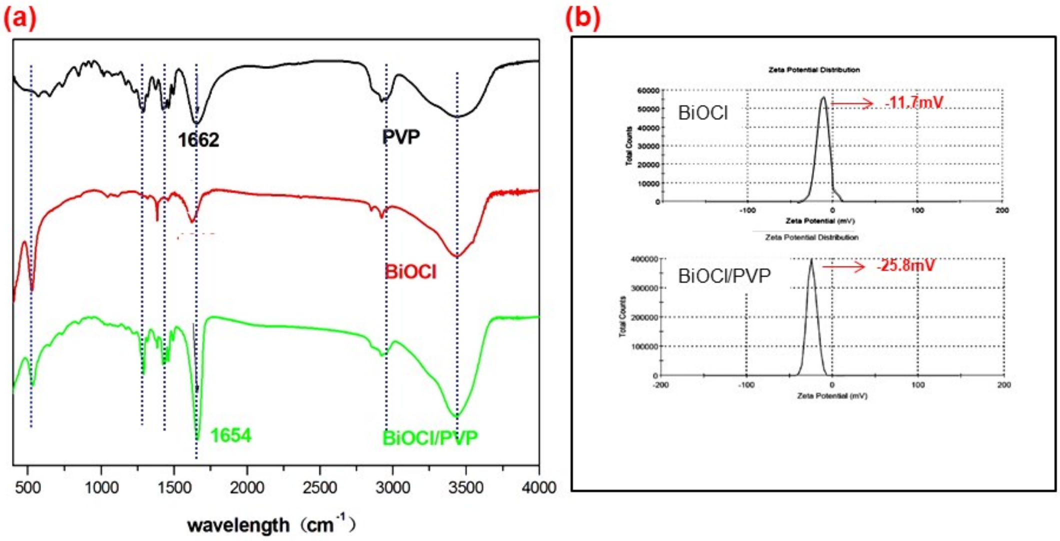

Fig.S6 FT-IR spectra of PVP, BiOCl and BiOCl/PVP(a), Zeta potential(b)

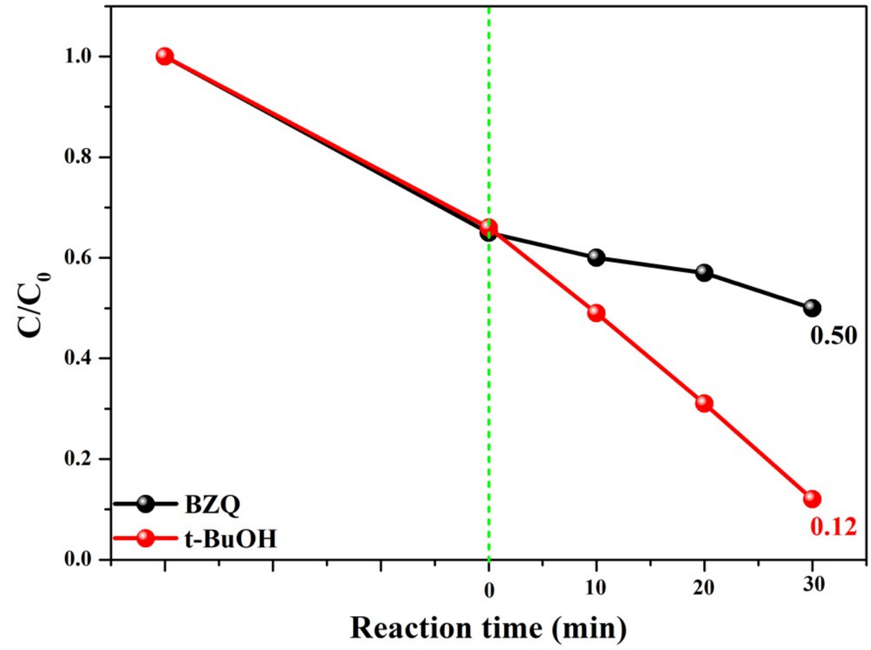

Fig.S7 The photodegradation rate of RhB using BiOCl/PVP with different scavengers.

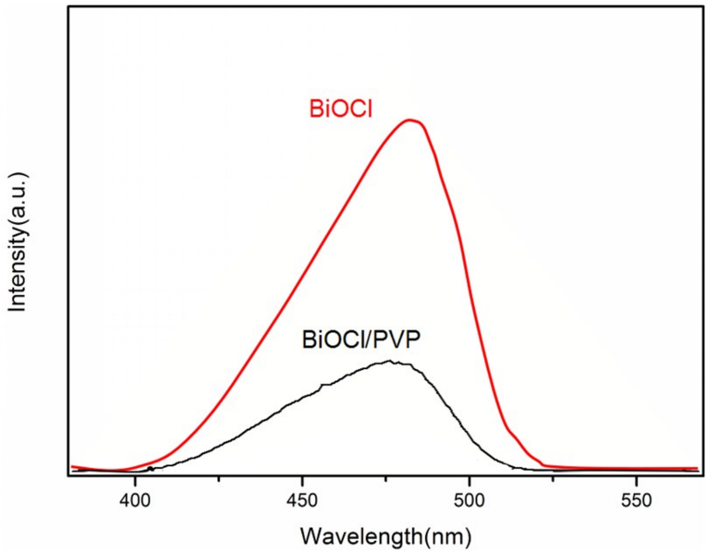

Fig.S8 PL spectra of BiOCl and BiOCl/PVP

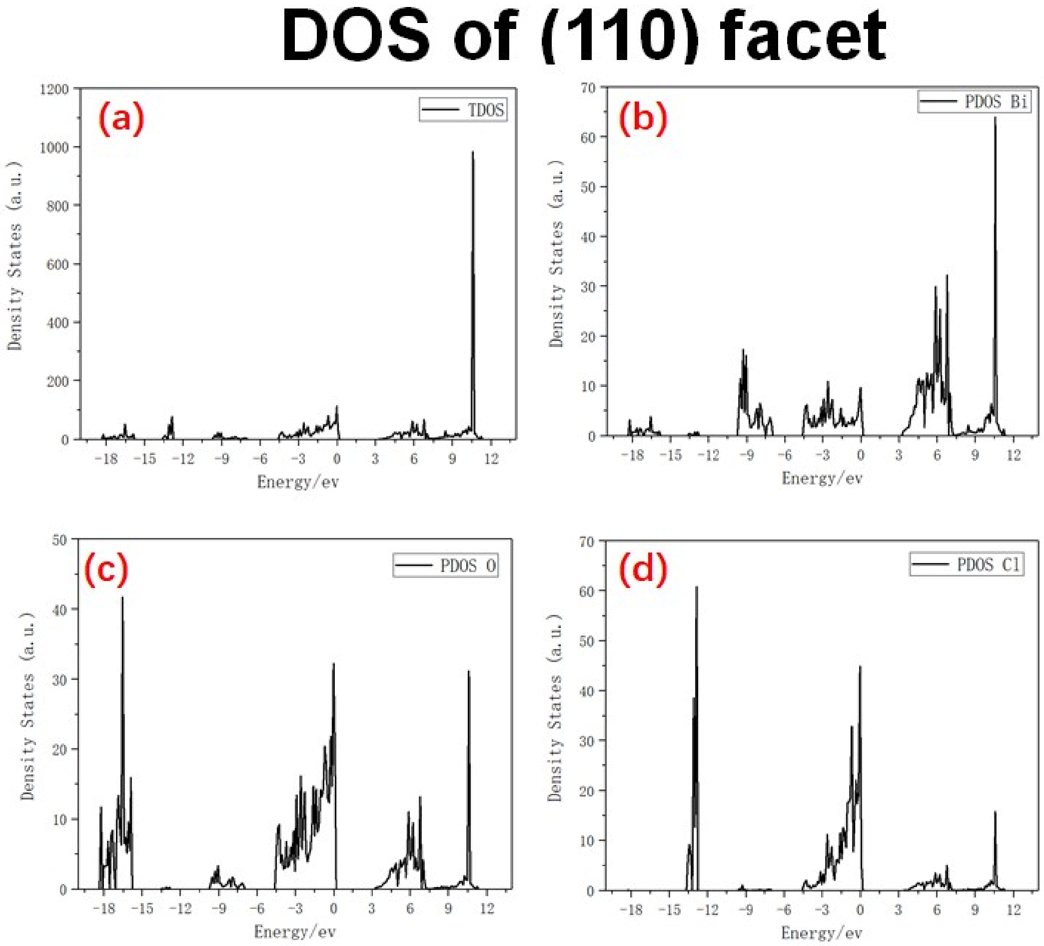

Fig. S9 Total density of states of (110) facet of BiOCl and corresponding atomic density of states

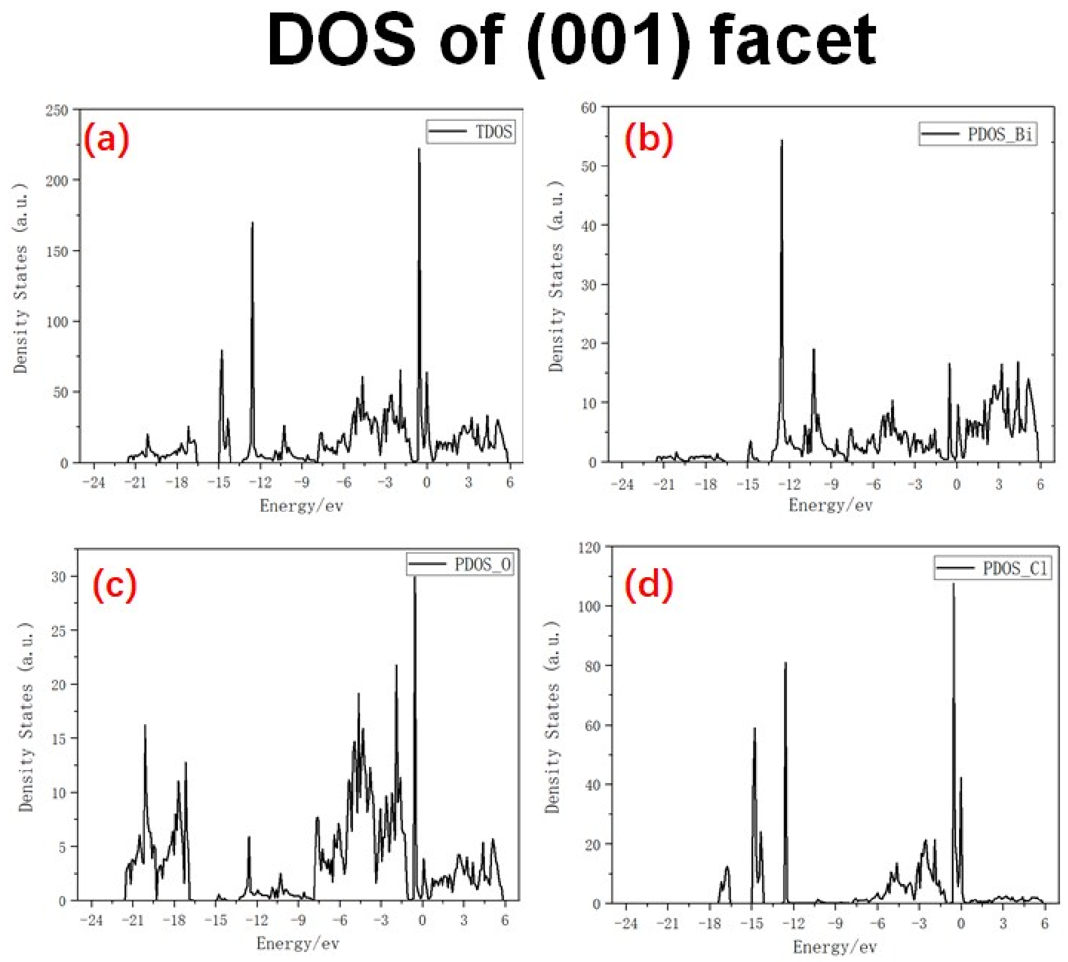

Fig. S10 Density of States of (001) facet of BiOCl and corresponding atomic density of states

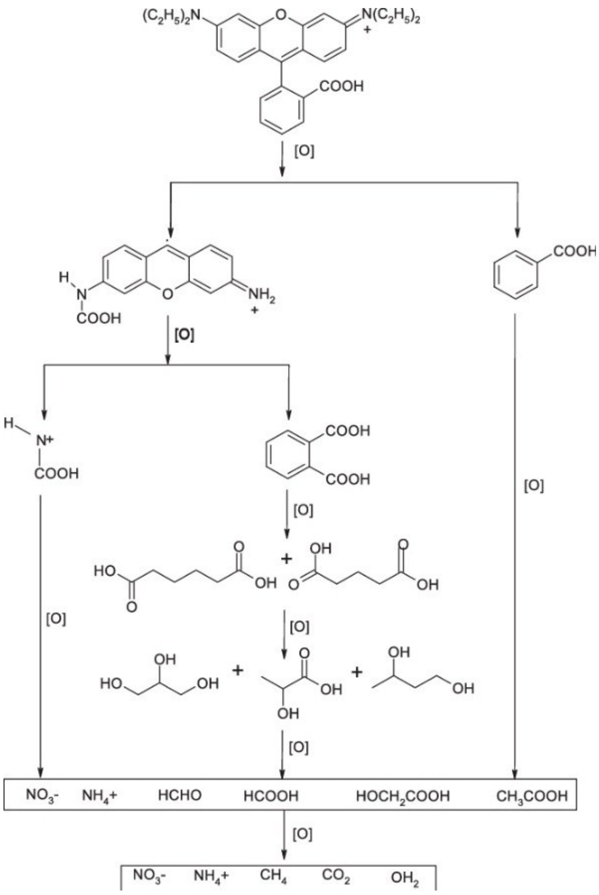

Fig. S11 RhB photodegrade reaction pathways [5], [O]=[•O^{2-}].

References

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