Supporting information

Increasing visible-light absorption for photocatalysis with black BiOCl

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Experimental Section

$BiCl_3$, isopropanol, triethanolamine (TEOA) p-benzoquinone (BQ), nitroblue tetrazolium (NBT), ethanol, NaOH were analytical pure and from Sinopharm Chemical Reagent Co., Ltd. Nano-TiO_2 (Degussa P25, 70% in anatase phase and 30% in rutile, particle diameters: 30-50 nm) was from Degussa Corp. Rhodamine B (RhB) was analytical pure and used without further purification.

White BiOCl was prepared by hydrolyzing $BiCl_3$. 0.01 mol $BiCl_3$ were added in 200 mL H_2O and sonicated for 10 min, then magnetically stirred in dark for 2 h. At the end, BiOCl was filtered and washed several times by ethanol and then dried at 80 °C for 12 h. The color of pure BiOCl was white.

Black BiOCl was prepared as follow 0.5 g pure white BiOCl were added in 100 mL H_2O and sonicated for 10 min, then irradiated 3 h under UV light (λ = 365 nm) with boosting Ar gas. Then samples were filtered and washed several times by deionized water and then dried at 80 °C for 12 h.

Electron spin resonance (EPR) spectra were obtained on JEOL JES-FA300 electron spin resonance spectrometer at room temperature with micro frequency at

8982 MHz. X-ray diffraction (XRD) patterns of the samples recorded at room temperature, by a Bruker D8 advance X-ray diffractometer using Cu Kα radiation and 2θ scan rate of 6 min^{-1}. Diffraction pattern were taken over the 2θ range 10-80°. High resolution transmission electron microscope (HRTEM) images were obtained by a JEOL JEM-2010FEF field emission electron microscope with operating at an accelerating voltage of 200 kV. UV-vis diffuse reflectance spectra (DRS) were obtained using a Shimadzu UV-3600 spectrometer by using $BaSO_4$ as a reference. X-ray photoelectron spectroscopy (XPS) measurements were carried out by a VG Multilab 2000 spectrometer (Thermo Electron Corporation) with an Al Kα X-ray source, and the spectra calibrated to the C 1s peak at 284.6 eV. Photoluminescence (PL) of the samples were obtained on a Jasco FP-6500 with λexc = 300 nm.

The photocatalytic activities of as-prepared samples were evaluated by the degradation of RhB (10 mg/L) under visible light (λ ≥ 400 nm) irradiation. The visible light was obtained by a 500 W high pressure xenon lamp with a 400 nm cutoff filter to ensure the needed irradiation light. The xenon lamp was bought from Changzhou Yuyu Electro-Optical Device Co., Ltd. China. Typical photocatalytic degradation process is arranged in such a way: 100 mL aqueous suspensions of 10 mg/L RhB placed in a quartz beaker, and then 20 mg photocatalyst were added. Prior to irradiation, the suspensions were sonicated for 10 min and then magnetically stirred in dark for 30 min to get desorption-adsorption equilibrium. The suspensions were kept under constant air-equilibrated conditions during irradiation. A magnetic stirrer was employed for continuous mixing. At certain time intervals, 4 mL suspensions were sampled and centrifuged by TGL-16G centrifuge (Shanghai Anting Scientific Instrument Factory, China) at 10 000 rpm for 15 min to remove the particles. The upper clear liquid was analyzed by recording the maximum absorption band (554 nm

for RhB) and UV-visible spectra of dyes using a Shimadzu UV-3600 spectrophotometer.

The stability measurements of black BiOCl were conducted initially for 9 consecutive days (one cycle per a day). Black BiOCl was filtered and saved in oxygen/air circumstance after per photocatalytic experiment.

For detecting the active species during photocatalytic reactivity, hydroxyl radicals (•OH), superoxide radical (O_2•$^-$) and holes (h^+) were investigated by adding 1.0 mM isopropanol (a quencher of •OH), BQ (a quencher of O_2•$^-$) and TEOA (a quencher of h^+[17]), respectively. The method was similar to the former photocatalytic activity test. The NBT (5×10^{-5} mol L^{-1}, exhibiting an absorption maximum at 259 nm) was used to determine the amount of O_2•$^-$ generating from BiOCl photocatalytic system.[17] The production of O_2•$^-$ in BiOCl suspensions was quantitatively analyzed by detecting the concentration of NBT with Shimadzu UV-3600 spectrophotometer. The method was similar to the former photocatalytic activity test with NBT replacing the RhB.

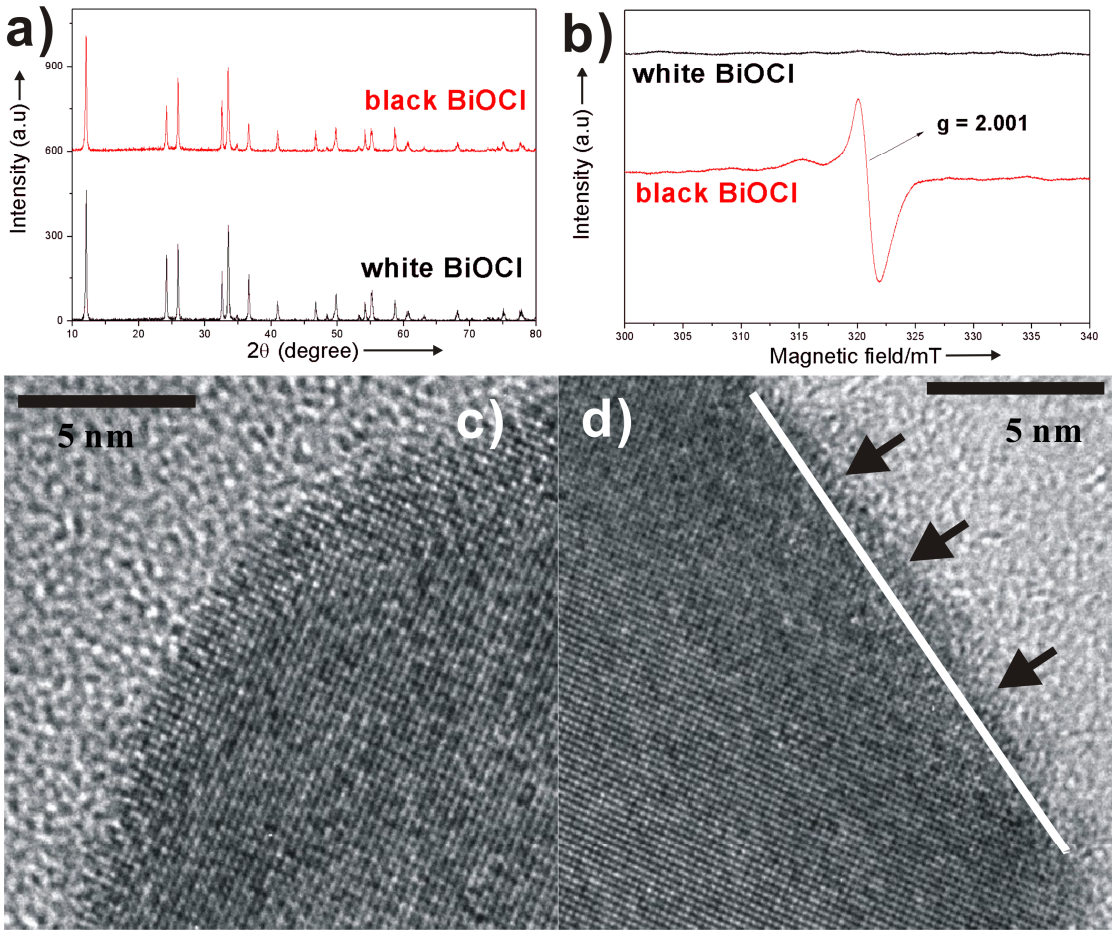

Fig. S1. Enlarged Fig. 1.

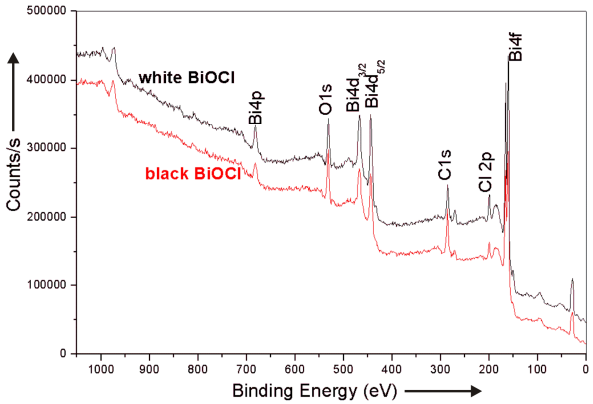

Fig. S2. Survey XPS spectrum of white BiOCl and black BiOCl.

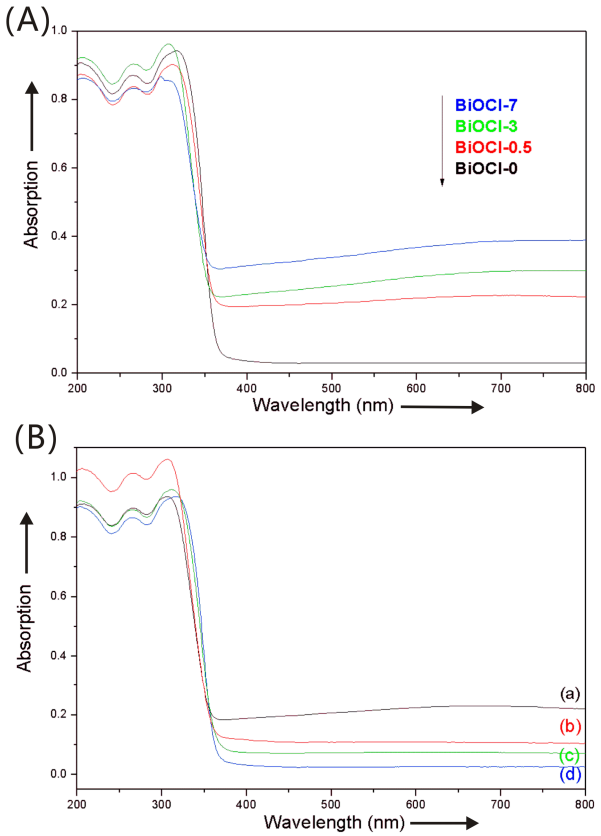

Fig. S3 DRS spectra of control experiments for the transformation of white BiOCl to black BiOCl. (A) UV irradiation time from 0.5 h to 7 h; and (B) irradiation wavelength and gas type factor: (a) boosting Ar under UV irradiation for 0.5h; (b) boosting Air under UV irradiation for 0.5h; (c) boosting Ar under visible light irradiation ($\lambda \geq 400$ nm) for 0.5h; and (d) white BiOCl.

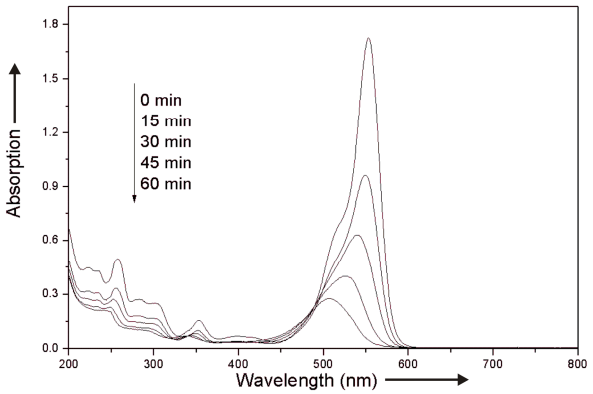

Fig. S4. UV-vis absorption spectral of RhB photocatalytic degradation with black BiOCl.

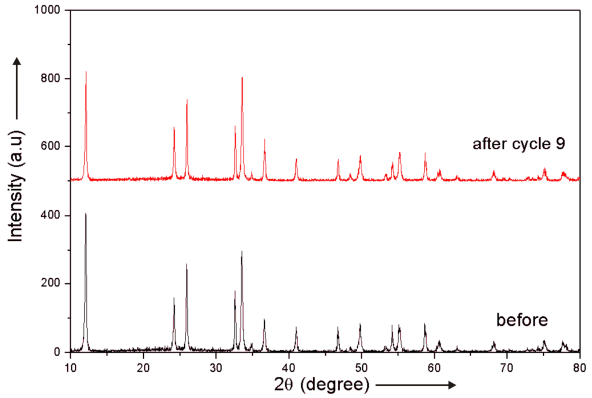

Fig. S5 XRD pattern of black BiOCl: before and after photodegradation of RhB.

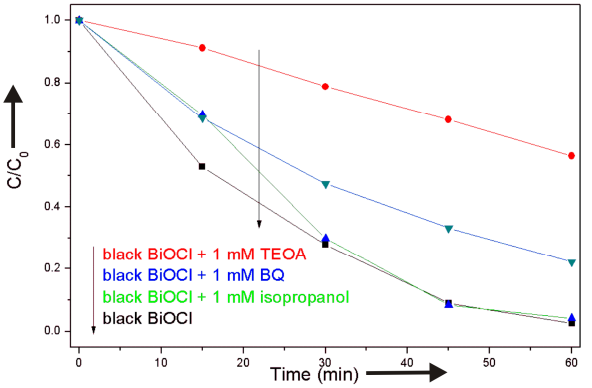

Fig. S6 Plots of photogenerated active species trapping in the system of photodegradation of RhB.

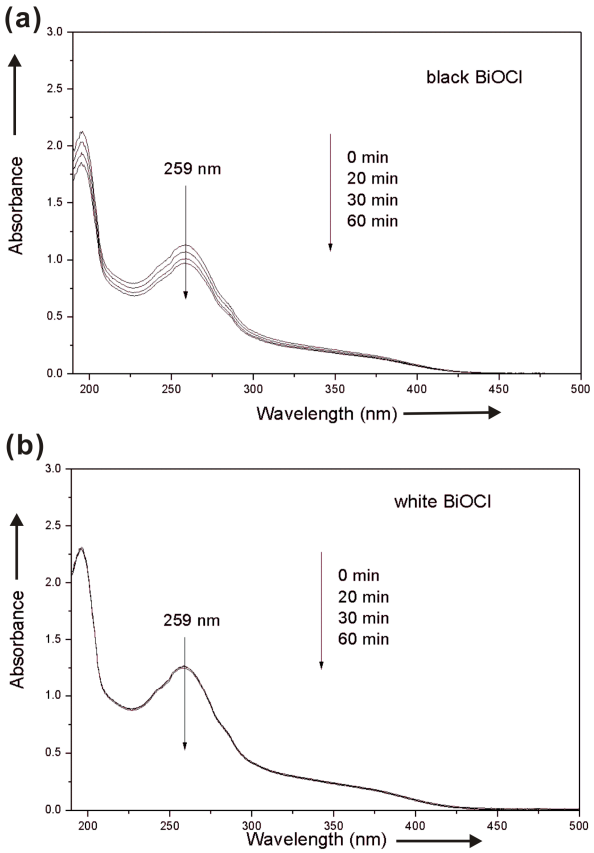

Fig. S7 (a) UV-Vis absorption spectra of NBT in black BiOCl suspension; and (b) UV-Vis absorption spectra of NBT in white BiOCl suspension.

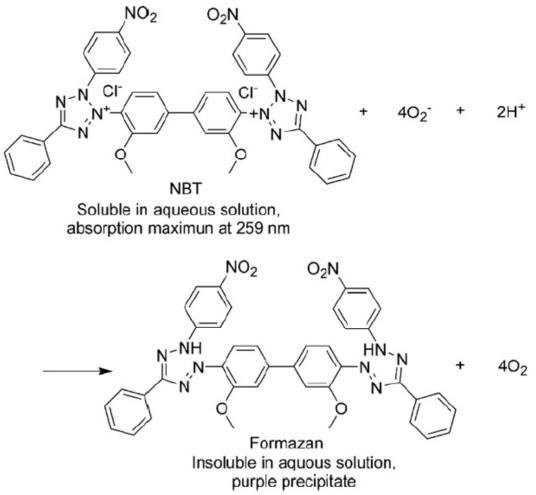

Fig. S8 Reaction of NBT with superoxide ion.