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Electronic supplementary information

Enhanced UV-Vis-NIR activated photocatalytic activity from Fe^{3+}-doped BiOBr: Yb^{3+}/Er^{3+} upconversion nanoplates: synergistic effect and mechanism insight

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Experiments

Materials

Er_2O_3 (4N), Yb_2O_3 (4N), $Bi(NO_3)_3.5H_2O$ (AR), KBr (AR), $Fe(NO_3)_3·9H_2O$ (4N), 1,4-benzoquinone (BQ), disodium ethylenediaminetetraacetate (EDTA-2Na), and tert-butyl alcohol (t-BuOH) were used as starting materials. $Er(NO_3)_3$ and $Yb(NO_3)_3$ were prepared by dissolving the corresponding rare earth oxide in HNO_3 under heating with agitation.

Synthesis

The BiOBr: 10%Yb^{3+}/1%Er^{3+}/$x$$Fe^{3+}$ (BYEF, x = 0, 1, 2, 3, and 4 mol%) nanoplates were prepared through a facile solvothermal process. Firstly, stoichiometric amounts of $Er(NO_3)_3$, $Yb(NO_3)_3$ and $Bi(NO_3)_3·5H_2O$ were dissolved in 30 mL mannitol solution with vigorous stirring for 30 min. Secondly, stoichiometric amounts of KBr solution (2.5 M/L) was slowly added to the above reaction solution, with vigorous stirring for 10 min. Thirdly, stoichiometric amounts of $Fe(NO_3)_3·9H_2O$ was slowly added to the above mixture. After 30 min of agitation, the mixture was transferred into a Teflon-lined stainless steel autoclave of 50 mL capacity, and the autoclave was then placed in an oven with a temperature of 160 °C for 12 h. Naturally cooled to room temperature, the precipitates were washed with absolute alcohol and deionized water for several times and dried at 70 °C in air. To improve the crystallinity of the sample, the final products were annealed at 450 °C for 2 h in the air. A pure BiOBr sample was prepared in the absence of $Er(NO_3)_3$, $Yb(NO_3)_3$ and $Fe(NO_3)_3·9H_2O$ under identical conditions.

Characterization

The crystal structures of the samples were characterized by X-ray diffraction (XRD) using a Rigaku Smartlab powder diffractometer with Cu Ka radiation. The morphologies of the samples were studied using scanning electron microscopy (SEM, FEI Quanta 400FEG) and transmission electron microscopy (TEM, FEI Tecnai G20). The compositional analysis was determined by energy dispersive X-ray spectroscopy (EDX) on the SEM (FEI Quanta 400FEG). The surface properties of the sample atoms were measured by X-ray photoelectron spectroscopy (XPS) (ESCALab250), and the binding energies of the elements in the sample were calibrated by 284.6 eV of C 1s. The UV–vis absorption spectra of the samples were analyzed with a UV-vis spectrophotometer (UV-3600, Shimadzu) using $BaSO_4$ as a reference material. The Brunauer–Emmett–Teller (BET) surface areas were measured by N_2 adsorption/desorption measurements (ASAP 2020, Micromeritics, USA) at 77 K. Photoluminescence spectra and decay profiles were recorded using an Edinburgh Instruments FLS980 spectrometer equipped with a 980 nm diode laser as the excitation source, and R928P and R5509-72 photomultiplier as detectors. The EPR (electron paramagnetic resonance) spectra were recorded on a JES FA-200 spectrometer (JEOL, Japan). All the measurements were performed at room temperature.

Photocatalytic activity experiment

Photocatalytic efficiency of samples for RhB decomposition was tested under UV, ($\lambda < 400$ nm), Vis (400 nm < $\lambda < 760$ nm), NIR light (760 nm < $\lambda < 1100$ nm) and

full spectra light irradiation with a 500 W Xe lamp (CEL-LXX500, Beijing China Education Au-light Co., Ltd). In a typical process, 10 mg photocatalyst was added into RhB aqueous solution (30 mL, 10 mg/L) under magnetically stirring for 1 hour in the darkness to guarantee the adsorption–desorption equilibrium. During the illumination process, 2 mL of suspension was taken out at given time intervals and centrifuged to remove the remaining photocatalyst. The UV–vis absorption spectra of the solutions were recorded by Shimadzu UV-1800 spectrophotometer, and then RhB concentration was calculated by analyzing the photoabsorption intensity at wavelength of 553 nm.

In addition, in order to detect the generated active species in the photocatalysis, BQ (10 mM), EDTA-2Na (10 mM) and *t*-BuOH (0.5 mL) were used as superoxide radical ($\bullet O_2^-$), hole (h^+) and hydroxyl radical (•OH) scavengers, respectively, under the same experimental conditions.

Photocurrents Measurements

The photocurrents were measured using an electrochemical workstation (Bio-Logic SP-300) with a standard three-electrode system with a Pt wire as the counter electrode, saturated Hg/ Hg_2Cl_2 (in saturated KCl) as the reference electrode, and Na_2SO_4 (0.5 M) aqueous solution as the electrolyte. A 980 nm laser diode was utilized as the light source. The working electrodes were prepared on fluorine-doped tin oxide (FTO) conductor glass. Typically, the sample (40 mg) was Wet mill with anhydrous ethanol, then 40 mg of this sample was transferred to a glass bottles containing 400 μL of deionized water, 0.08 mL Nafion and 300 μL of Isopropyl alcohol, and

ultrasonic dispersion evenly to obtain the suspension solution. The suspension was spread on the ITO glass with the side protected by Scotch tape and dried at 90 °C for 10min to obtain the final working electrodes. The transient photocurrent responses with time of the working electrodes were measured at a 1.2 V bias potential during repeated on/off illumination cycles with different excitation power of 980 nm laser diode.

Density functional theory (DFT) calculations

In the present work, the calculations are performed using the CASTEP module within the plane-wave pseudopotential method, along with the generalized gradient approximation (GGA) exchange and correlation functional in scheme of Perdew-Burke-Ernzerhof (PBE). The valence electronic configurations are the states of Bi 6s6p, O 2s2p and Br 3d4s4p for the ground-state electronic structure calculations. The convergence tests regarding the cut-off energy have been made before the calculations to the properties and a plane wave cutoff energy of 380eV is used. Ultrasoft pseudopotential is adopted in the reciprocal space, and 2×2×2 Monkhorst–Pack mesh grid is sufficient to reach convergence for 2×2×1 supercell calculations. All the atoms of the pure and Fe^{3+}-doping BiOBr are fully relaxed to their equilibrium positions with an energy convergence of 5×10^{-6} eV while he force applied on each atom is less than 0.01 eV/Å and the stress is less than 0.02 GPa. In addition, the atomic displacement is less than 5×10^{-4} Å and the self-consistentfield (SCF) tolerance is 5×10^{-7} eV.

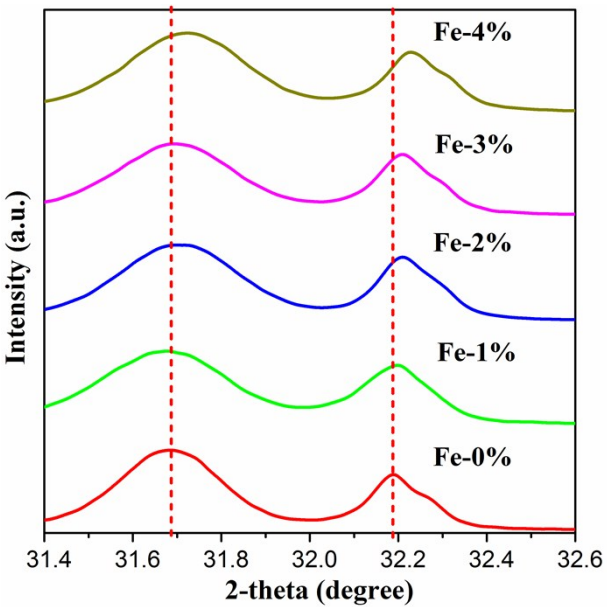

Fig. S1. The main diffraction peak near 2θ = 31.4º~32.6º with different Fe^{3+} concentrations.

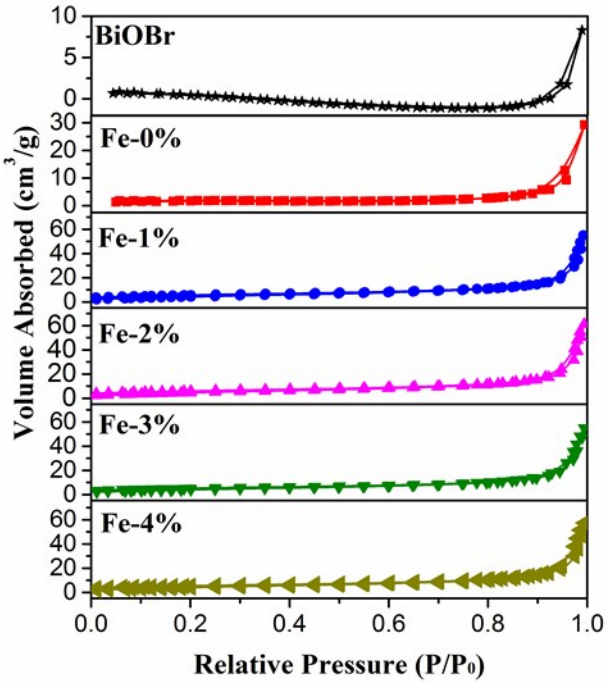

Fig. S2. N_2 adsorption-desorption isotherms of pure BiOBr and BYE nanoplates with different Fe^{3+} concentrations.

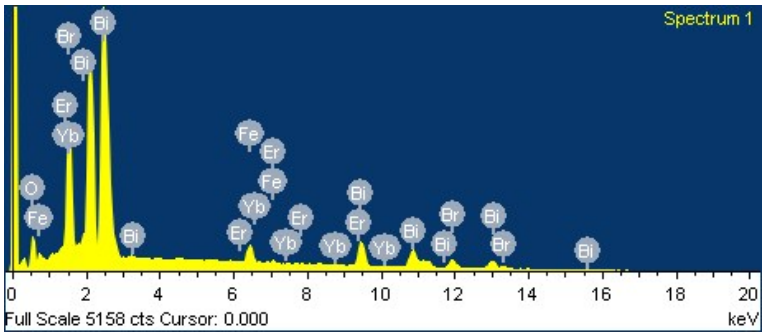

Fig. S3. EDX spectrum of BYE-4%Fe.

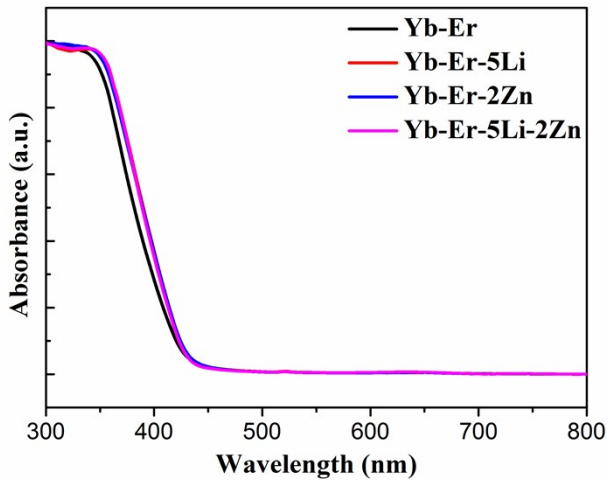

Fig. S4. UV–Vis absorption spectra of BiOBr: Yb^{3+}/Er^{3+} nanoplates single-doped or co-doping Li^{+} and Zn^{2+} ion.

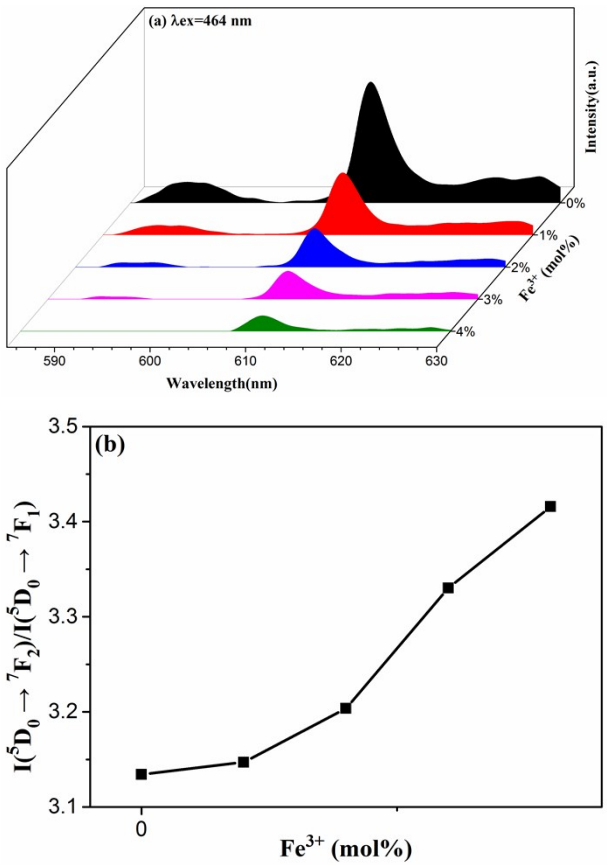

Fig. S5. (a) Emission spectrum; (b) The intensity ratio of $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ in BiOBr: 1%Eu^{3+}, *x*Ca^{2+} (*x* = 0, 1, 2, 3, 4 mol%) under 464 nm.

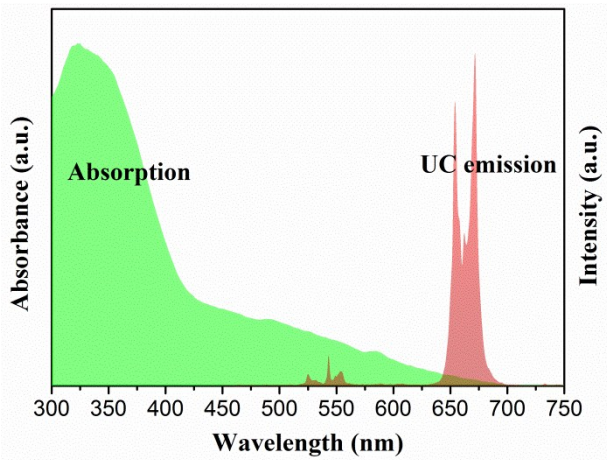

Fig. S6. UV–Vis absorption spectra of and UC spectra of BYE-3% nanoplates.

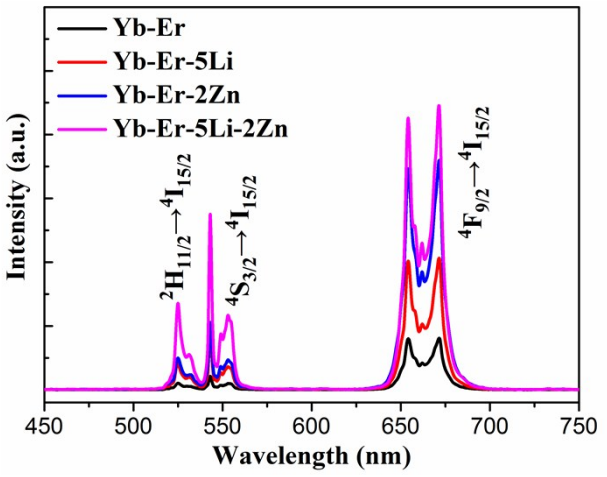

Fig. S7. UC spectra of BiOBr: Yb^{3+}/Er^{3+} nanoplates single-doped or co-doping Li^{+} and Zn^{2+} ion.

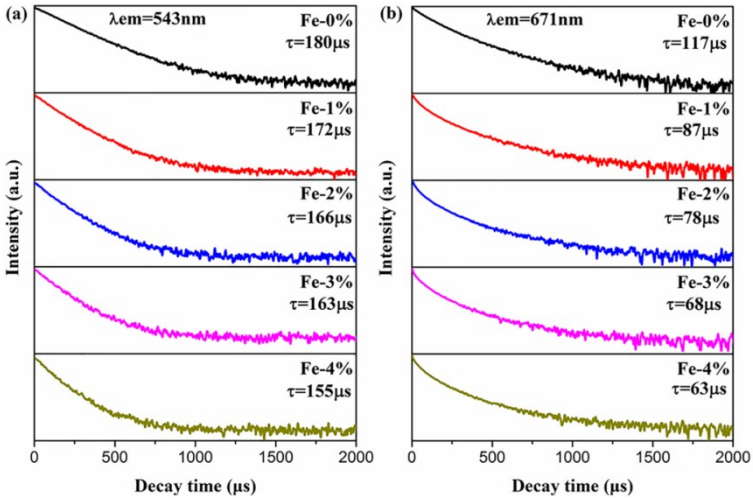

Fig. S8. The lifetime decay curves of (a) $^4S_{3/2}$ and (b) $^4F_{9/2}$ level of BiOBr: Yb^{3+}/Er^{3+} nanoplates doped with different Fe^{3+} concentrations under 980 nm excitation.

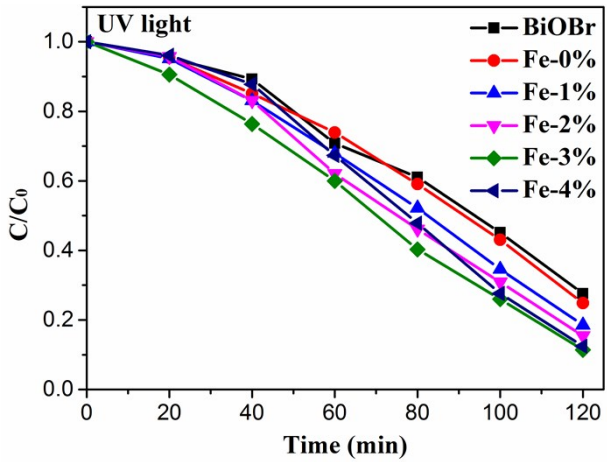

Fig. S9. Photocatalytic degradation of RhB and kinetics rates over different photocatalysts under UV light irradiation.

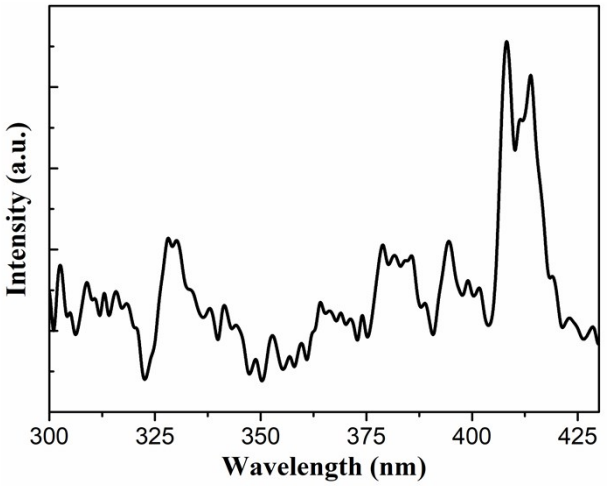

Fig. S10. UV UC spectra of BiOBr: Yb^{3+}/Er^{3+} nanoplates under 980 nm excitation.

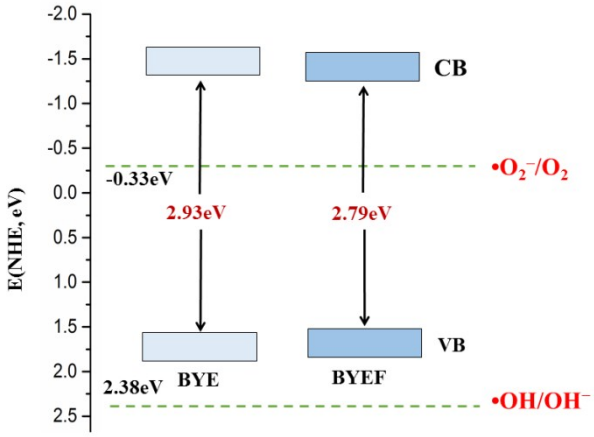

Fig. S11. Band gap structures for BYE-0% and BYE-4%