

Electronic Supplementary Information

Iodide Surface Decoration: A Facile and Efficacious Approach to Modulating the Band Energy Level of Semiconductors for High-Performance Visible-Light Photocatalysis

Hongwei Huang,^{*a} Ke Xiao,^a Shixin Yu,^a Fan Dong,^b Tierui Zhang,^c Yihe Zhang^{*a}

^a Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China

^b Chongqing Key Laboratory of Catalysis and Functional Organic Molecules, College of Environmental and Bio-logical Engineering, Chongqing Technology and Business University, Chongqing, 400067, China

^c Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Experimental Section

1. Synthesis

All chemicals are analytical reagents and used without further treatment. First, the pristine $\text{Bi}_2\text{O}_2\text{CO}_3$ is hydrothermally obtained. Typically, a mixture of 2 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 2 mmol of urea are totally dissolved in 25 ml distilled water. Then, the suspensions are transferred into a 50 ml Teflon-lined stainless steel autoclave and heated at 160 °C for 20 h. When the procedures end, the products are filtrated, washed and dried at 70 °C for 12 h.

Iodide modified $\text{Bi}_2\text{O}_2\text{CO}_3$ are prepared by a secondary hydrothermal route, and potassium iodide (KI) is selected to decorate $\text{Bi}_2\text{O}_2\text{CO}_3$. 0.5 mmol $\text{Bi}_2\text{O}_2\text{CO}_3$ is dispersed in the KI solutions under ultrasound and stirring. Next, they are hydrothermal maintained at 180 °C for 5 h. After that, the as-prepared samples are collected by the same procedures with above preparation. The as-obtained samples with different molar ratios of KI to $\text{Bi}_2\text{O}_2\text{CO}_3$ of 0, 0.1, 0.2, 0.5, 1 and 2 are denoted as BOC, IB-1, IB-2, IB-3, IB-4 and IB-5, respectively. To exclude formation of other crystalline phases, the molar ratio of KI to $\text{Bi}_2\text{O}_2\text{CO}_3$ is increased to 100:1. The as-prepared sample is denoted as BI-100.

2. Characterization

Phase structure of $\text{Bi}_2\text{O}_2\text{CO}_3$ and modified $\text{Bi}_2\text{O}_2\text{CO}_3$ was characterized by a D8 Advance X-ray diffractometer with Cu $\text{K}\alpha$ radiation (Bruker AXS, Germany). Fourier-transform infrared (FTIR) spectra were recorded by a Bruker spectrometer in the frequency range 500-4000 cm^{-1} . X-ray photoelectron spectroscopy (XPS) was

carried out to determine the chemical states and composition on a VGMPK II X-ray instrument. Scanning electron microscope (SEM, S-4800) and transmission electron microscopy (TEM, 2100F) were used to investigate the microstructure and morphology of $\text{Bi}_2\text{O}_2\text{CO}_3$ and modified $\text{Bi}_2\text{O}_2\text{CO}_3$. A Varian 710-ES (Varian, Shanghai, China) inductively coupled plasma optical emission spectrometer (ICP-OES) with Sepex Certiprep standards was used to analyze the element of IB-4. UV-vis diffuse reflectance spectra (DRS) were acquired on a UV-visible-NIR spectrophotometer (Cary 5000), and photoluminescence (PL) spectra were obtained by using a Hitachi F-4600 fluorescence spectrophotometer. To trap the active radicals, the spin trapping electron spin resonance (ESR) experiments were carried out by using a ESR spectrometer (Bruker JES FA200). A xenon lamp serves as visible light source, and DMPO (5,5'-dimethyl-1-pyrroline-N-oxide) was utilized as a spin-trap reagent. Photoelectrochemical measurements were performed on a CHI-660E electrochemical system (Shanghai, China) with a standard three-electrode cell. The light source of is a 150 w xenon lamp coupled with 420 nm filters. Platinum wire, saturated calomel electrodes (SCE) and photocatalyst film were, respectively, employed as the counter electrode, reference electrodes, and working electrode. 0.1 M Na_2SO_4 was used as electrolyte solution. Potentials are measured with reference to the SCE. The photoresponse of the photocatalysts as light on and off were measured at 0.0 V.

3. Photocatalytic evaluation

Degradation of Rhodamine B (RhB): The photocatalysis activity of $\text{Bi}_2\text{O}_2\text{CO}_3$ and modified $\text{Bi}_2\text{O}_2\text{CO}_3$ were evaluated by degrading (Rhodamine B) RhB under visible light (500 W Xe lamp, $\lambda > 420$ nm). In the test, 50 mg of photocatalyst was dispersed into 50 mL of RhB solution under strong ultrasonic. Before irradiation, to reach an adsorption-desorption equilibrium, the suspensions were adequately stirred in darkness for 1 h. Afterwards, about 2.5 ml aliquots were sampled at given time intervals, and separated through centrifugation. The concentration of upper centrifuged liquid was determined on a UV-vis spectrophotometer (U-3010).

Removal of NO: The photocatalysis performance of $\text{Bi}_2\text{O}_2\text{CO}_3$ and modified $\text{Bi}_2\text{O}_2\text{CO}_3$ were also studied by removal of NO at ppb levels in a continuous flow reactor at normal temperature. A 150 W commercial tungsten halogen lamp is vertically put outside the reactor with coupling a cutoff filter (420 nm) to remove UV light in the light beam.

In every photocatalytic activity test, a sample dish with a diameter of 12.0 cm containing 0.20 g photocatalyst was placed in the center of the reactor. The rectangular reactor are made of stainless steel and covered with Saint-Glass with a volume of 4.5 L (30 cm \times 15 cm \times 10 cm). The initial concentration of NO was diluted to approximately 600 ppb by mixed with flowing air, and the flow rate was set to be 2.4 mL/min by a mass flow controller. After equilibrium, the lamp was turned on. The NO concentration was continuously measured by a NO_x analyzer, and the NO (η) removal ratio was calculated by equation $(\eta\%) = (1-C/C_0) \times 100\%$, here C_0 and C represent the inlet and outlet NO concentrations, respectively.

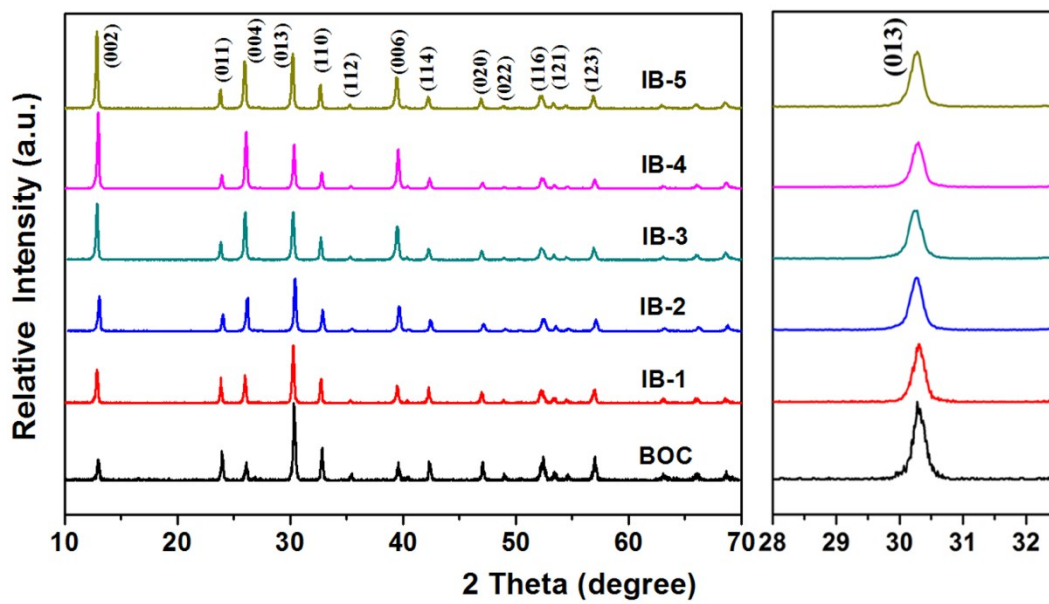


Fig. S1 XRD patterns of Bi₂O₂CO₃ (BOC), IB-1, IB-2, IB-3, IB-4 and IB-5.

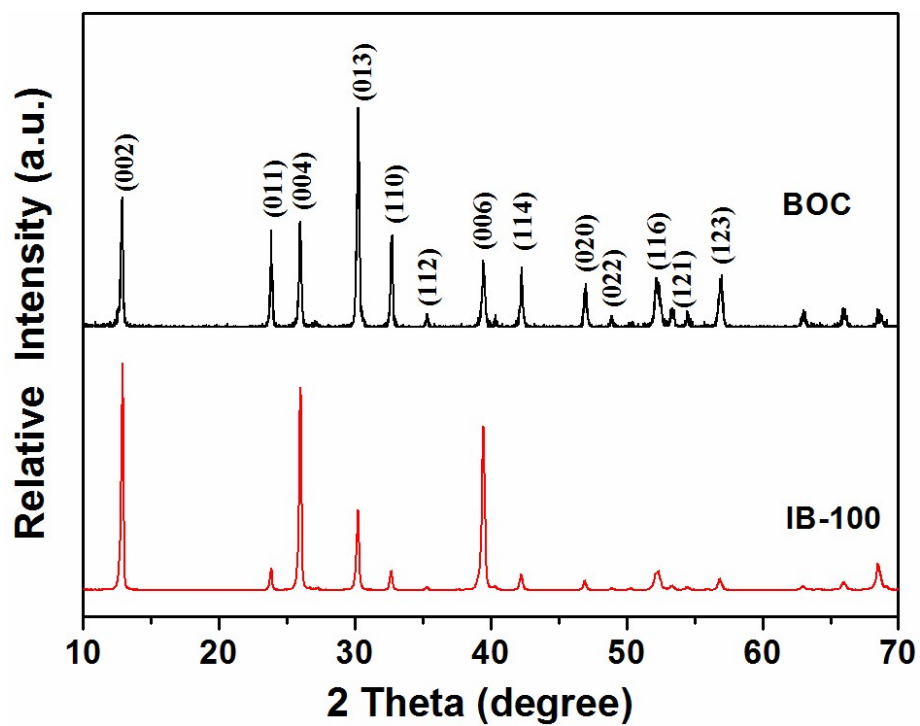


Fig. S2 XRD patterns of $\text{Bi}_2\text{O}_2\text{CO}_3$ (BOC) and IB-100.

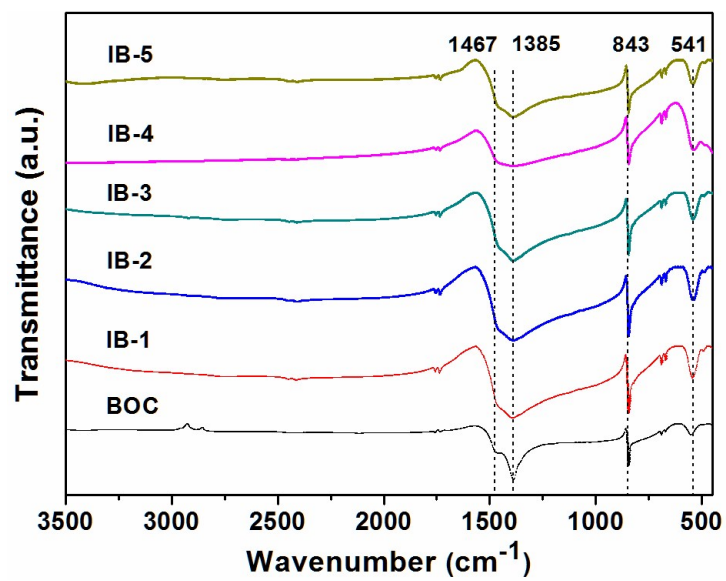


Fig. S3 FT-IR spectra of Bi₂O₂CO₃, IB-1, IB-2, IB-3, IB-4 and IB-5.

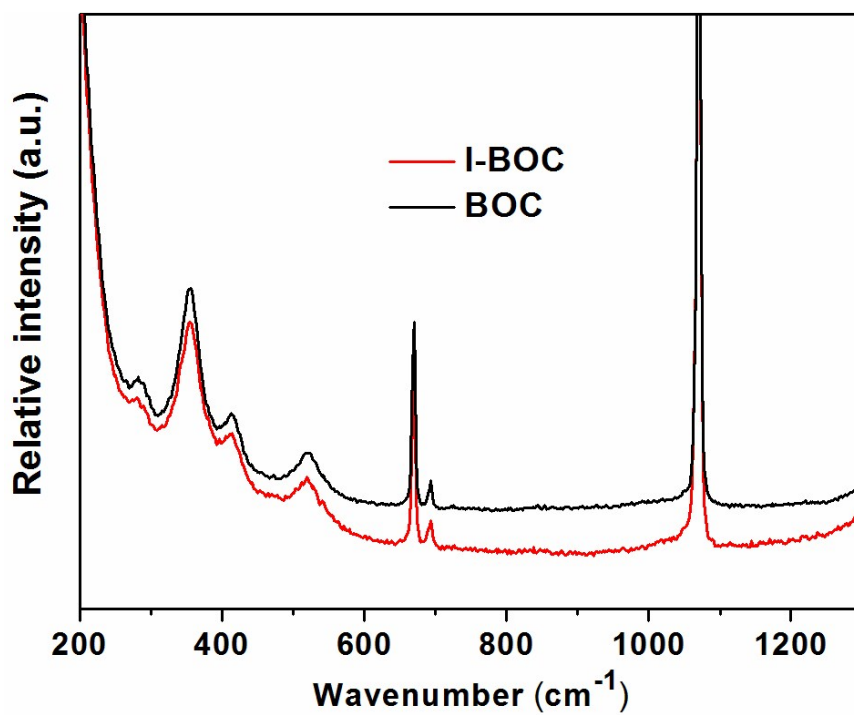


Fig. S4 Raman spectra of Bi₂O₂CO₃ and IB-4.

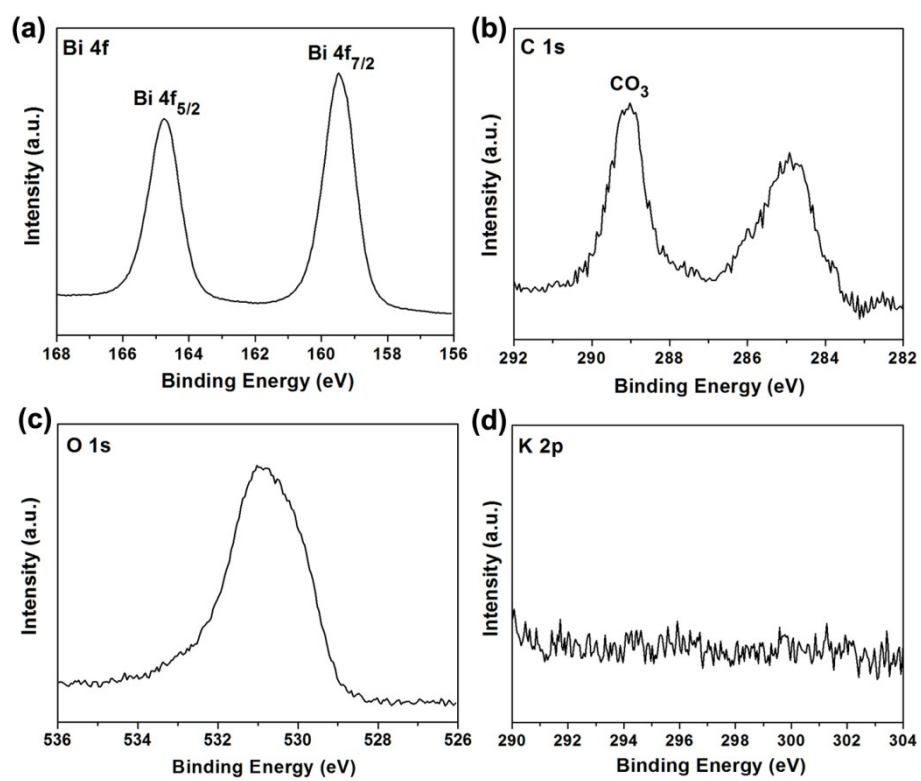


Fig. S5 High-resolution XPS spectra of (a) Bi 4f, (b) C 1s, (c) O 1s, and (d) K 2p.

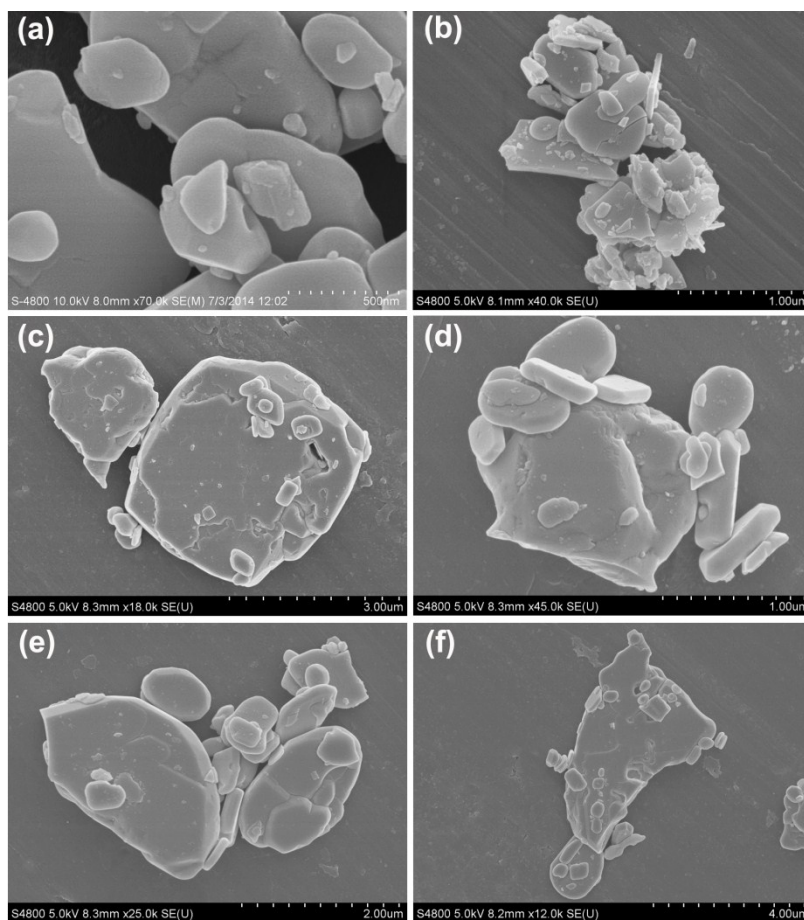


Fig. S6 SEM images of (a) Bi₂O₂CO₃, (b) IB-1, (c) IB-2, (d) IB-3, (e) IB-4 and (f) IB-5.

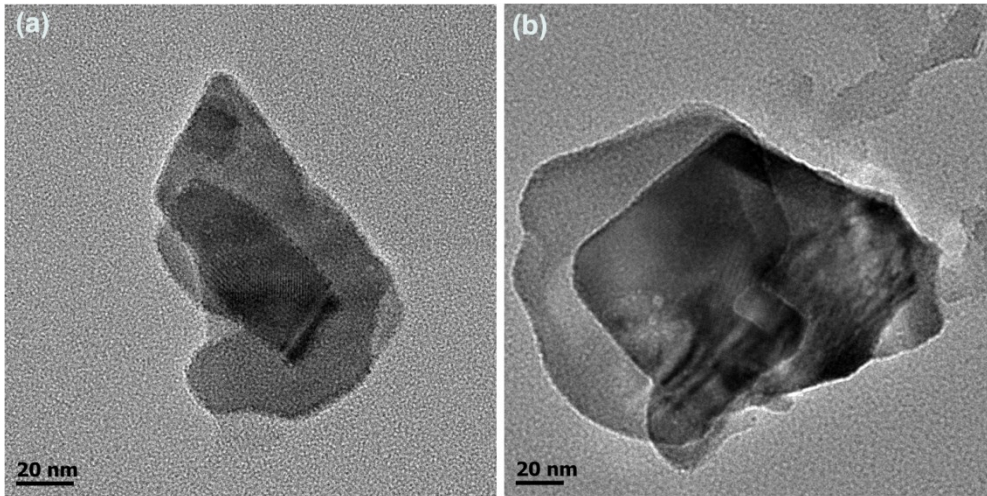


Fig. S7 TEM images of (a) $\text{Bi}_2\text{O}_2\text{CO}_3$ and (b) I-BOC (IB-4).

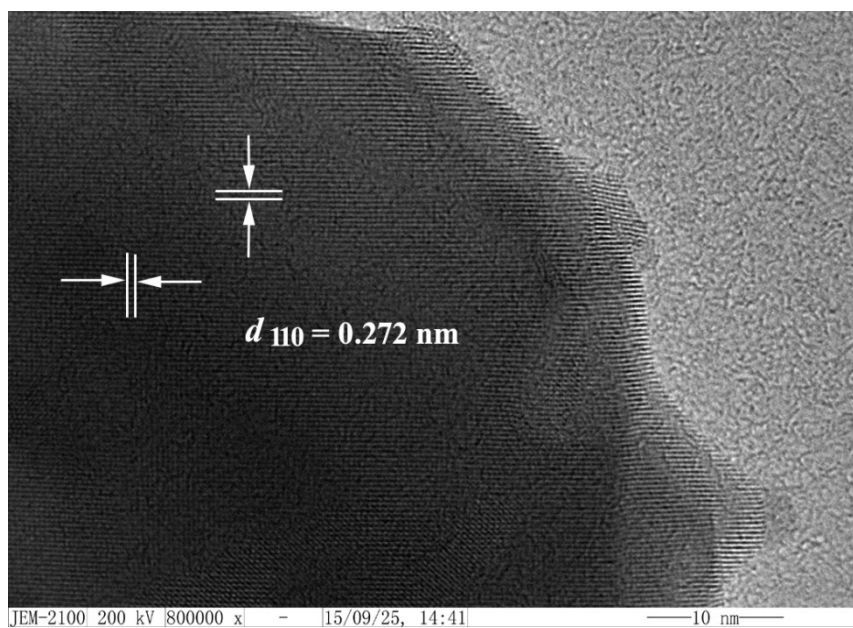


Fig. S8 HRTEM image of I-BOC (IB-4).

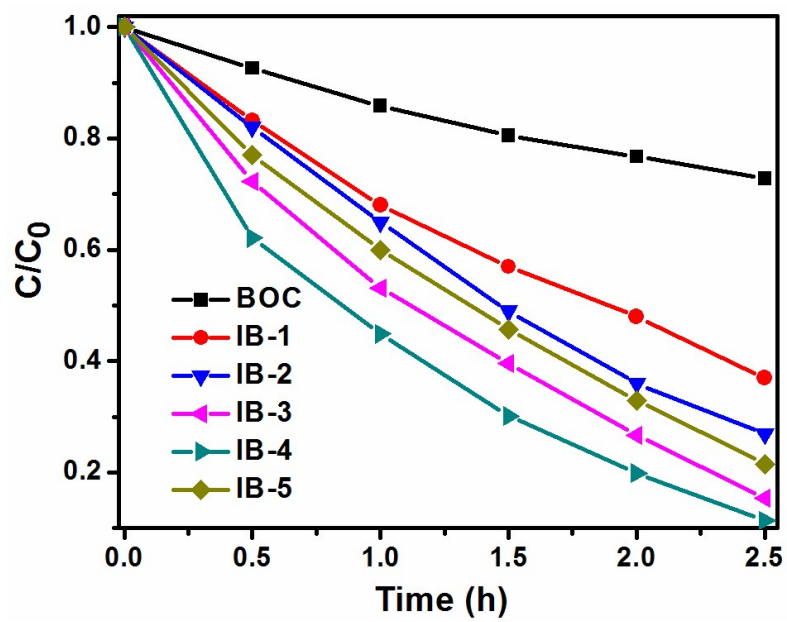


Fig. S9 Degradation curves of RhB over Bi₂O₂CO₃, IB-1, IB-2, IB-3, IB-4 and IB-5

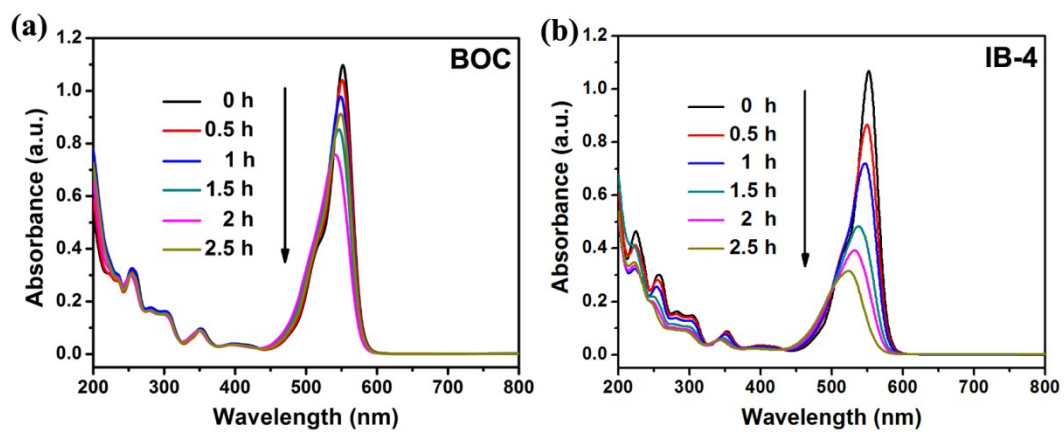


Fig. S10 Absorption spectra of RhB over (a) $\text{Bi}_2\text{O}_2\text{CO}_3$ and (b) IB-4.

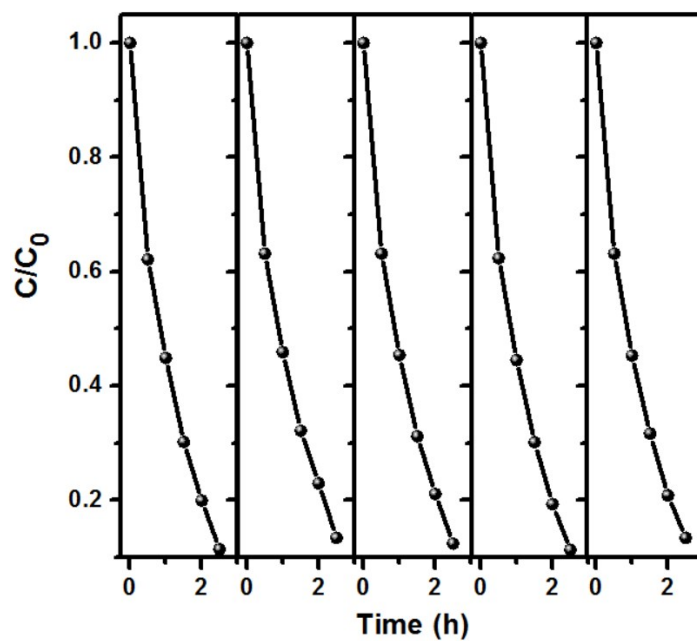


Fig. S11 Recycling test for photodegradation of RhB over IB-4 under visible light ($\lambda > 420$ nm).

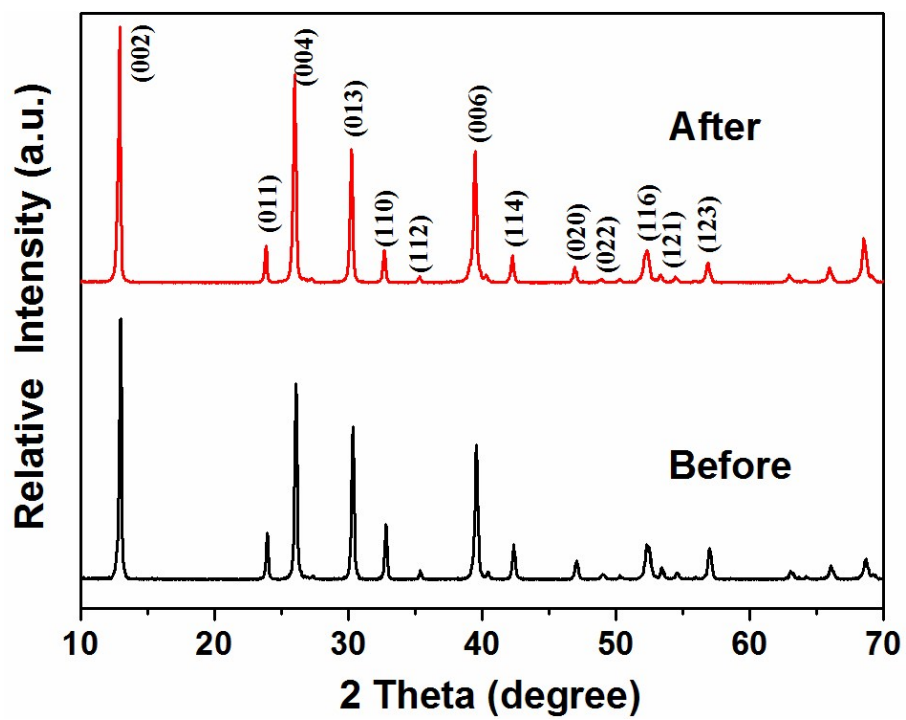


Fig. S12 XRD patterns of IB-4 sample before and after irradiation.

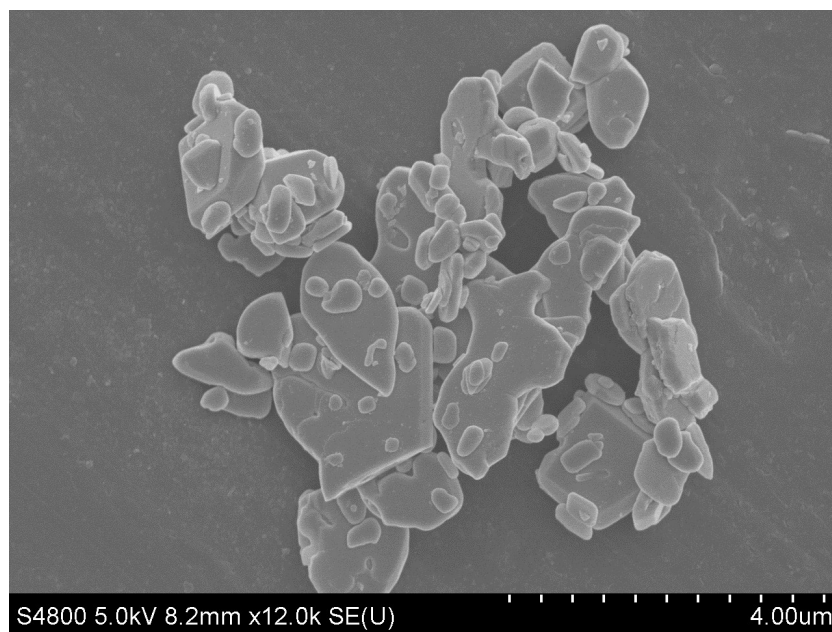


Fig. S13 SEM image of recovered IB-4 sample after irradiation.

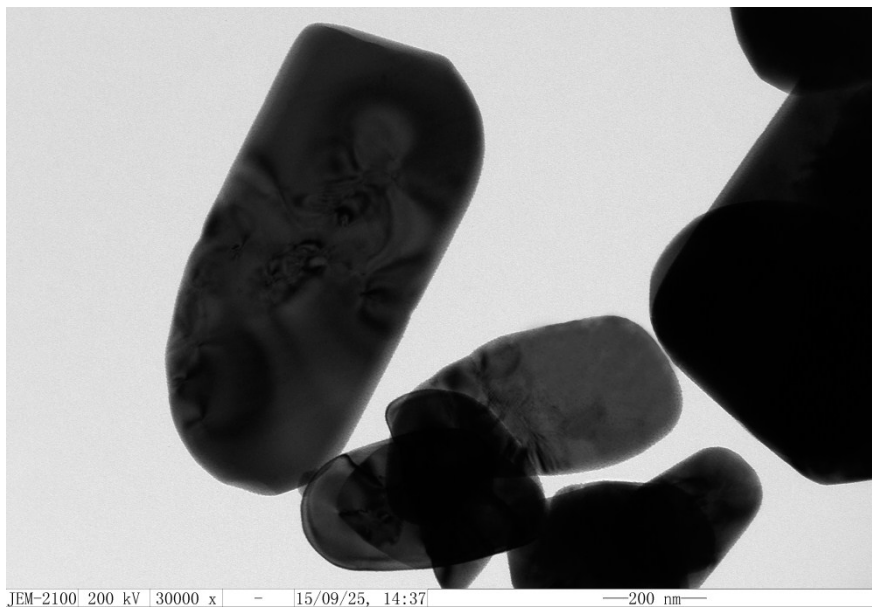


Fig. S14 TEM image of recovered IB-4 sample after irradiation.

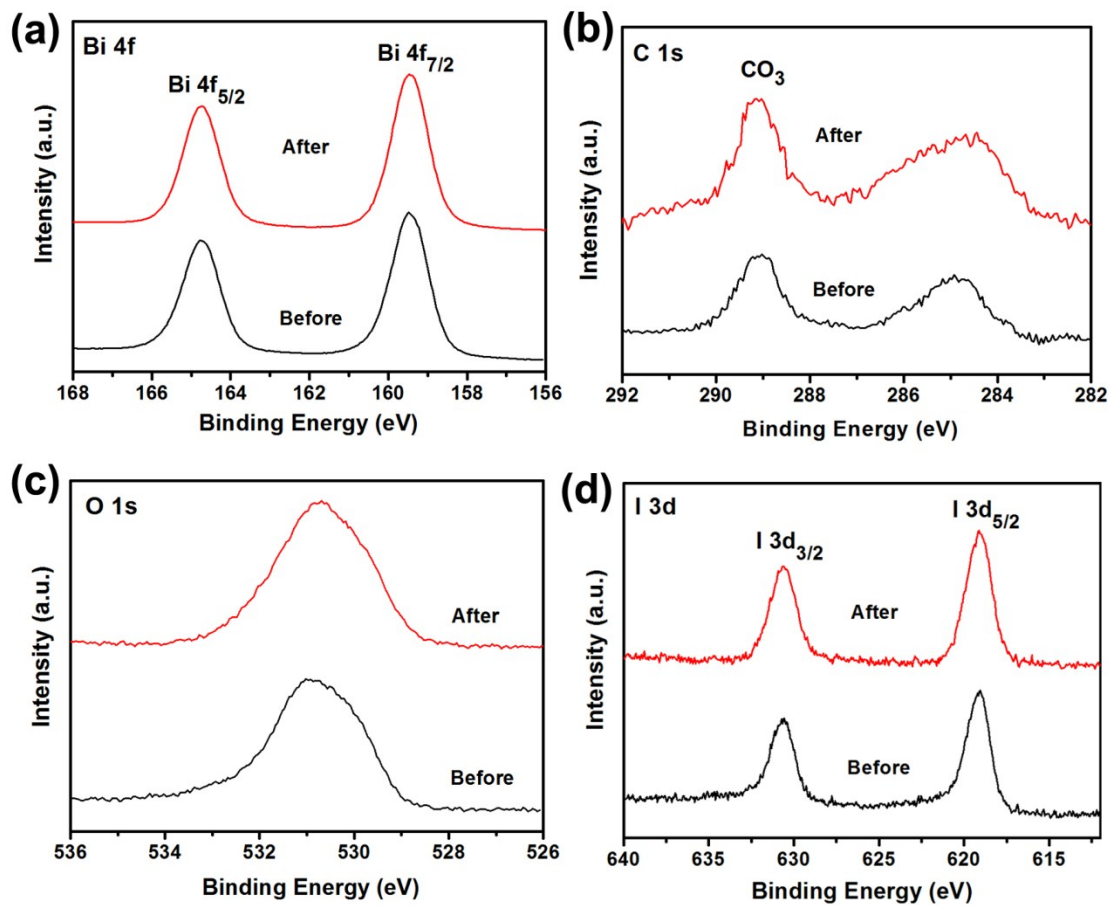


Fig. S15 XPS of IB-4 sample before and after irradiation.

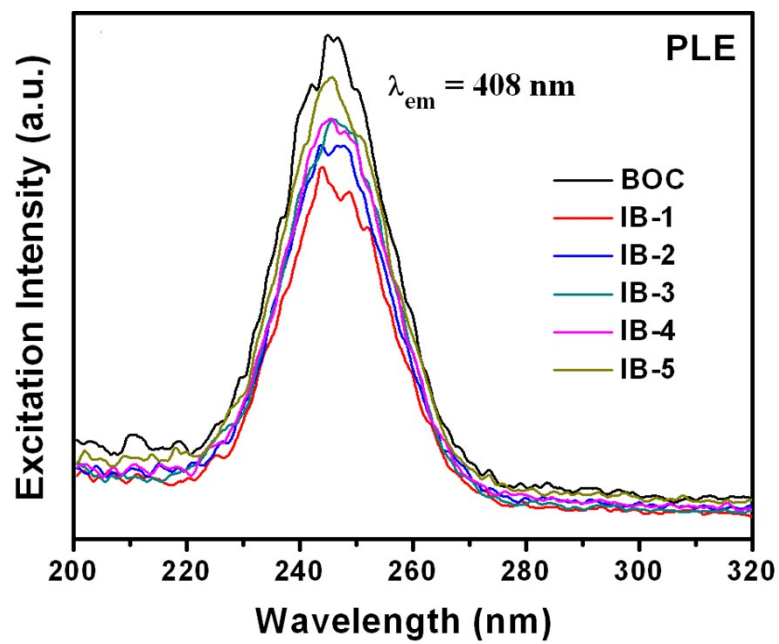


Fig. S16 PL spectra of $\text{Bi}_2\text{O}_2\text{CO}_3$ and Γ modified $\text{Bi}_2\text{O}_2\text{CO}_3$ samples.

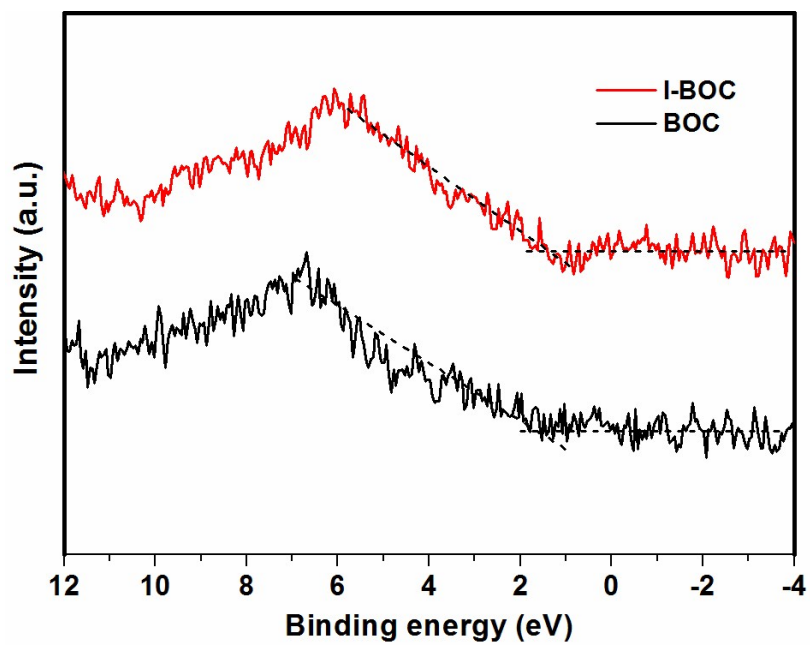


Fig. S17 VB XPS of $\text{Bi}_2\text{O}_2\text{CO}_3$ and I-BOC (IB-4).