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Supplementary information

Efficient charge separation and transfer in CdS/BiOBr/Bi_2S_3 heterojunction via dual S-scheme and photothermal effect for enhanced Cr(VI) photoreduction

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1. Chemicals

Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$, AR, 98%), Potassium bromide (KBr, AR, 98%), Chromium nitrate ($Cd(NO_3)_2$, AR, 99%), Mannitol (AR, 98%), Sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$, 99.99%), Urea (AR, 99%), Ethanol (AR, 99.5%), Potassium dichromate standard solution ($K_2Cr_2O_7$, 0.02 M), Diphenylcarbazide (DPC), Ethanol (AR, 99.5%), Silver nitrate ($AgNO_3$, AR, 99%), Sodium sulfate anhydrous (Na_2SO_4, AR, 99%), Benzoquinone (AR, 99.5%) and Isopropanol (AR, 99.9%) were all purchased from Aladdin Reagent.

2. Preparation of photocatalysts

The CBOS dual S-scheme heterojunctions were synthesized using a straightforward ion exchange method followed by in situ growth. First, 2 mmol of BiOBr was dissolved in 30 mL of deionized water and magnetically stirred for 30 min to achieve uniform dispersion. Next, 2 mL of 1 M $Na_2S_2O_3$ solution was added to the BiOBr suspension, followed by stirring for additional 10 min. Subsequently, an appropriate amount of $Cd(NO_3)_2$ (0 mmol, 0.5 mmol, 1 mmol, or 1.5 mmol) was introduced into the suspension, and the mixture was stirred continuously for another 20 min. The uniformly mixed suspension was then transferred to a 50 mL reaction vessel and heated in an oven at 180 °C for 6 h. After the reaction, the autoclave was allowed to cool naturally to room temperature. The resulting products were collected via centrifugation, washed several times with ethanol and deionized water, and dried at 70 °C under ambient conditions.

The BiOBr nanosheets were prepared by a solvothermal method in Mannitol solution (0.1 M). First, $Bi(NO_3)_3 \cdot 5H_2O$ (5 mmol) was dissolved in 30 ml mannitol solution and stirred magnetically for 30 min. Subsequently, 2 ml KBr solution (2.5 M) was added to stir vigorously for 30 min. Finally, the suspension was transferred into a 50 mL Teflon-lined autoclave and heated to 160 °C for 12 h. After the reaction, the autoclave was allowed to cool naturally. The resulting products were collected and separated through centrifugation, washed with ethanol and deionized water several times, and then dried at 70 °C in ambient air.

The Bi_2S_3 nanorods were prepared by hydrothermal method. First, $Bi(NO_3)_3 \cdot 5H_2O$ (5 mmol) was dissolved in 15ml deionized water and stirred magnetically for 30 min, then 15 ml $Na_2S_2O_3$ solution (1 M) was added to stir vigorously for 20 min. Next, 0.5 g of urea was added to the solution and stirred for 10 min. Finally, the suspension was transferred into a 50 mL Teflon-lined autoclave and heated to 160 °C for 12 h. After the reaction, the autoclave was allowed to cool naturally. The resulting products were collected and separated through centrifugation, washed with ethanol and deionized water several times, and then dried at 70 °C in ambient air.

The CdS nanoparticles were synthesized using a hydrothermal method. First, 5 mmol of $Cd(NO_3)_2$ was dissolved in 20 ml of deionized water and stirred magnetically for 30 minutes. Then, 10 ml of $Na_2S_2O_3$ solution (0.5 M) was added, and the mixture was vigorously stirred for another 30 minutes. The suspension was then transferred into a 50 ml autoclave and heated to 180 °C, maintaining this temperature for 6 h. After the reaction, the mixture was naturally cooled. The obtained product was collected by centrifugation, washed three times with ethanol and deionized water, and dried at 70°C for 12 h.

3. Characterization

The phase structures were observed by the X-ray diffraction measurements using an Ultima IV diffractometer with Cu Kα radiation (λ=1.5406 Å, U=40 kv, I=40 mA). The morphologies and high angle angular dark field-scanning transmission electron microscopy (HAADF-STEM) images of the sample were examined by transmission electron microscopy (TEM, FEI Tecnai G20). The morphology and microstructure were examined by field emission scanning electron microscope (Hitachi Regulus8100, Japan). X-ray photoelectron spectra (Thermo Scientific K-Alpha, America) were tested on a monochromatic Al Kα source and the C(1s) binding energy is 284.8 eV. The absorption edges of samples were tested by a UV-vis spectrophotometer (Hitachi U-4100), with a 150 W xenon lamp as the excitation source, using $BaSO_4$ as a reference. Electrochemical properties were characterized by an electrochemical workstation (Gamry, Reference 600+) with a Pt counter electrode, an $Hg/HgCl_2$ as reference electrode, and 0.5 $mol\cdot L^{-1}$ Na_2SO_4 solution as the electrolyte. Photoluminescence spectra and decay profiles were recorded using an Edinburgh Instruments FLS980 spectrometer equipped. The EPR (electron paramagnetic resonance) spectra were recorded on an Electron Paramagnetic Resonance (Bruker A300). The KPFM characterization was performed under ambient conditions using an atomic force microscope (AFM, SPM-9600, Shimadzu). The content of metal ions in the reaction solution was measured by inductively coupled plasma-Mass Spectrometry (ICP-MS) technology (Agilent 7700(MS))

4. Theoretical calculations

The calculations of band structure were performed based on the density functional theory (DFT) simulations with the DS-PAW. The core-valence interactions were treated by the projector augmented wave (PAW) method, where the plane wave expansion was truncated with a cutoff energy of 420 eV. The BiOBr, Bi_2S_3 and CdS used (6 x 6 x 1), (6 × 2 × 1) and (3 × 4 × 1) K-point grid for structural optimization in the self-consistent calculations, respectively. The vacuum space is adopted 15 Å above the surfaces to avoid periodic interactions.

5. Photocatalytic and photothermocatalytic performance

The photocatalytic performance of the photocatalyst was evaluated under full-spectrum light ($300\ \text{nm} \leq \lambda \leq 2000\ \text{nm}$) and NIR light ($800\ \text{nm} \leq \lambda \leq 2000\ \text{nm}$) using a 300 W Xe lamp. In a typical experiment, 20 mg of photocatalyst was dispersed in 40 mL of Cr(VI) solution ($10\ \text{mg}\cdot\text{L}^{-1}$). The suspension was equilibrated in darkness for 2h to achieve an adsorption-desorption equilibrium (pH value of reaction environment was 5.25). Under illumination, the ambient temperature of the reaction was controlled to about 20°C by circulating water, 3.5mL suspension was taken regularly, and the supernatant was obtained by centrifugation; the Cr(VI) concentration of the supernatant was analyzed using the diphenylcarbazide (DPC) method. The photocatalytic stability cycle experiment adopts the above steps of the photocatalytic experiment. The difference is that after each reaction, all the photocatalytic reaction suspensions are collected, centrifuged, washed (once with deionized water and alcohol to minimize the loss of the catalyst), and the next photocatalytic experiment is carried out after drying, which is repeated five times.

For the photothermocatalytic experiment, the catalytic environment was temperature controlled using a Jacketed beaker with water circulation to maintain a stable temperature throughout the process.

6. Methods for detecting Cr(VI)

The diphenylcarbazide (DPC) method was used to determine the concentration of Cr(VI) ions in the supernatant solution obtained after photocatalytic experiment. 1 mL Cr(VI) solution obtained after photocatalytic reduction was mixed with 9 mL H_2SO_4 (0.2 M) aqueous solution in a 20 mL volumetric flask. Then, 0.2 mL of newly prepared 0.25% (w/v) DPC in acetone was added to the volumetric flask. After vortexing the mixture about 15-30 s, it was allowed to stand for 10-15 min to ensure full color development. The red-violet to purple color mixed solution was then measured at 540 nm by the UV-vis spectroscopy using deionized water as reference.

7. Apparent quantum yield (AQY) calculation equation:

$$AQY = \frac{3 \times \ number\ of\ reduced\ Cr(VI)}{N} \times 100\%$$

$$N = \frac{E\lambda}{hc}$$

N: the number of incident photons;

E: the accumulated light energy in the given area (J);

λ: the wavelength of the light;

h: the Plank constant (6.626×10^{-34}J•s)

c: the velocity of light (3×10^{8}m•s^{-1})

8. Additional figures

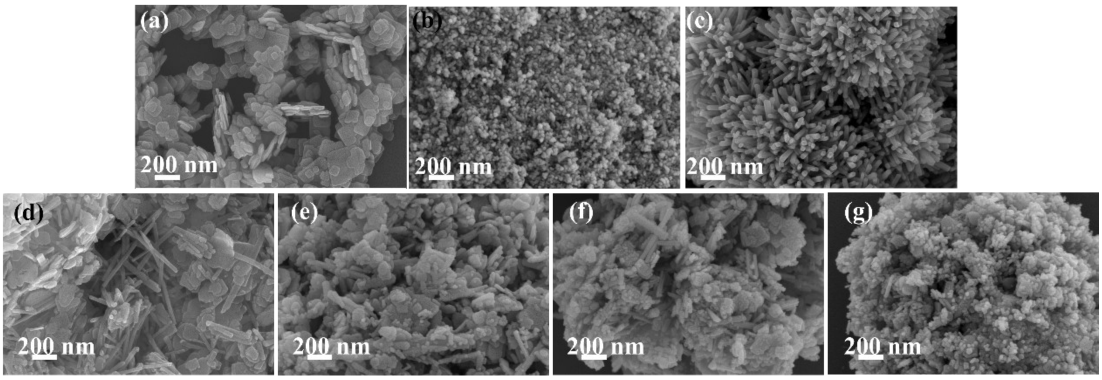

Fig. S1. SEM images of (a) BiOBr, (b) CdS, (c) Bi_2S_3, (d)BOS, (e) CBOS-0.5, (f) CBOS-1 and (g) CBOS-1.5.

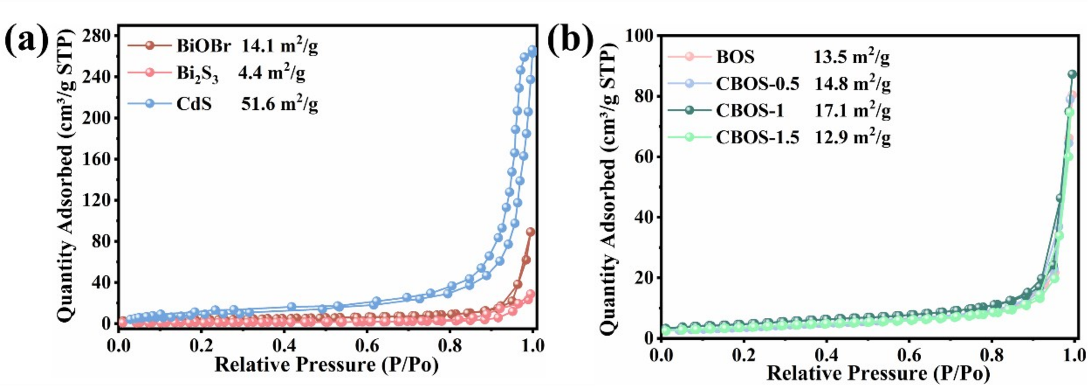

Fig. S2 Nitrogen adsorption-desorption isotherm curve of photocatalyst.

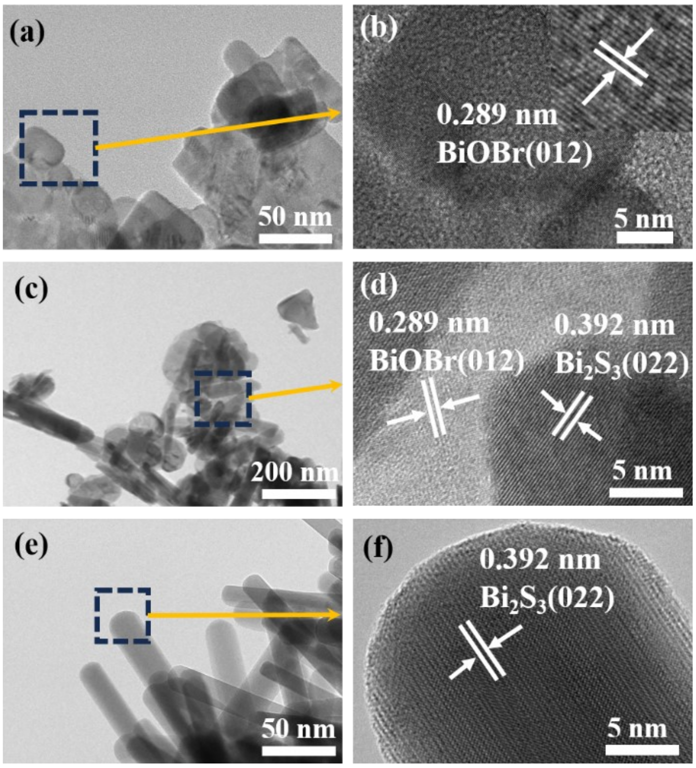

Fig. S3 TEM and HRTEM: (a, b) BiOBr, (c, d) BOS, (e, f) Bi_2S_3.

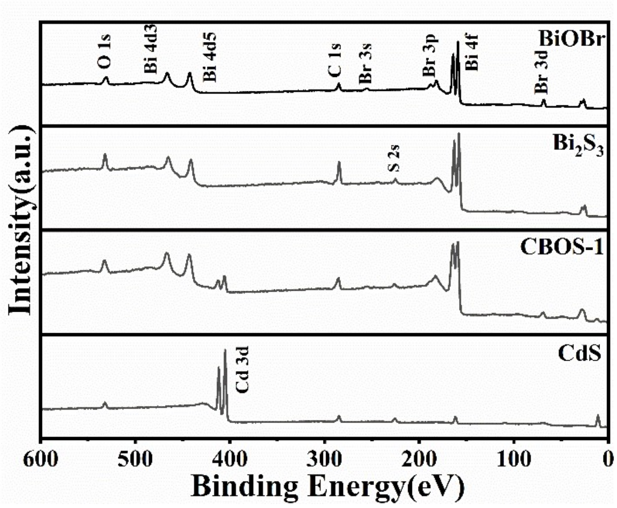

Fig. S4. XPS full spectrum of BiOBr, Bi_2S_3, CBOS-1 and CdS.

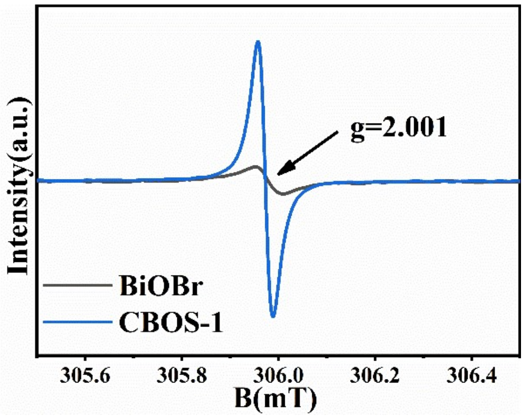

Fig. S5. EPR spectrum of BiOBr and CBOS-1.

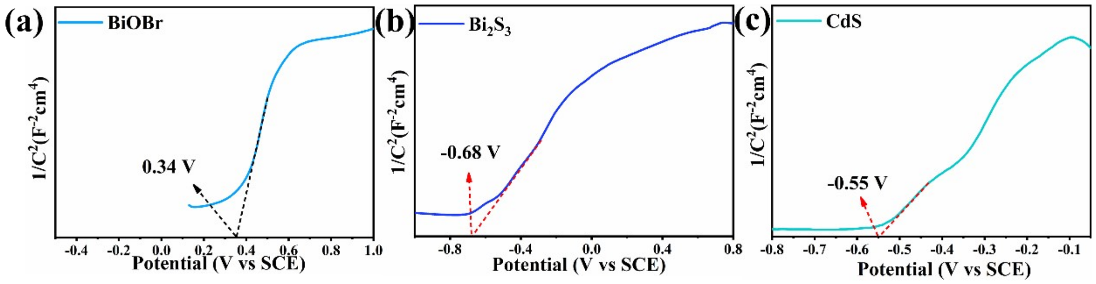

Fig. S6. Mott Schottky test of BiOBr,Bi_2S_3 and CdS.

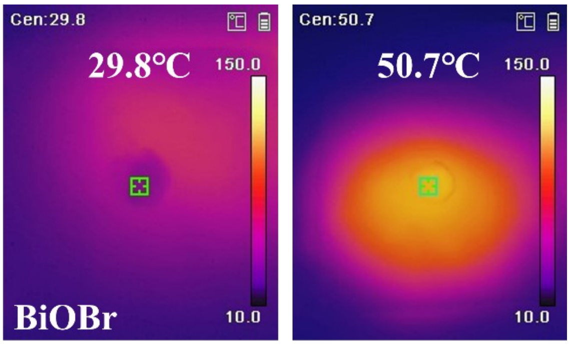

Fig. S7. Infrared thermal images of BiOBr powder (a) before and (b) after illumination.

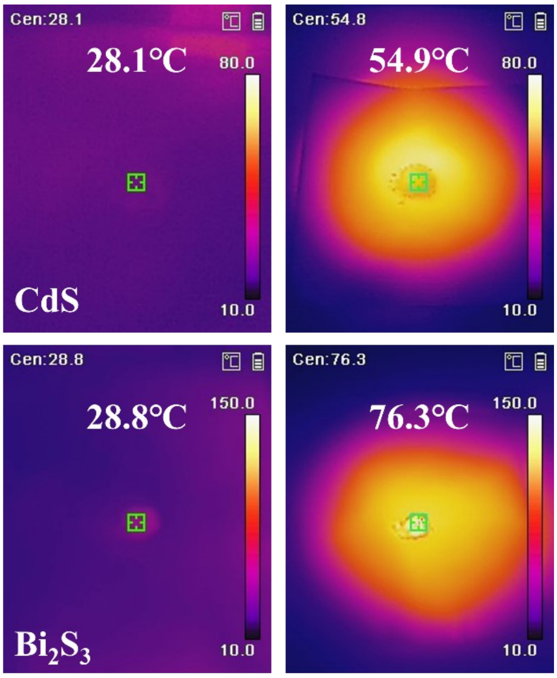

Fig. S8. Infrared thermal images of CdS and Bi_2S_3 powder.

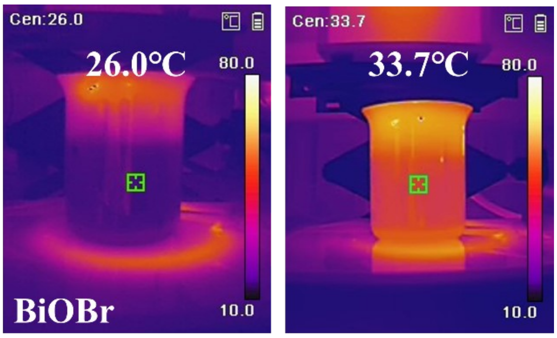

Fig. S9. Infrared thermal images of BiOBr suspension illumination.

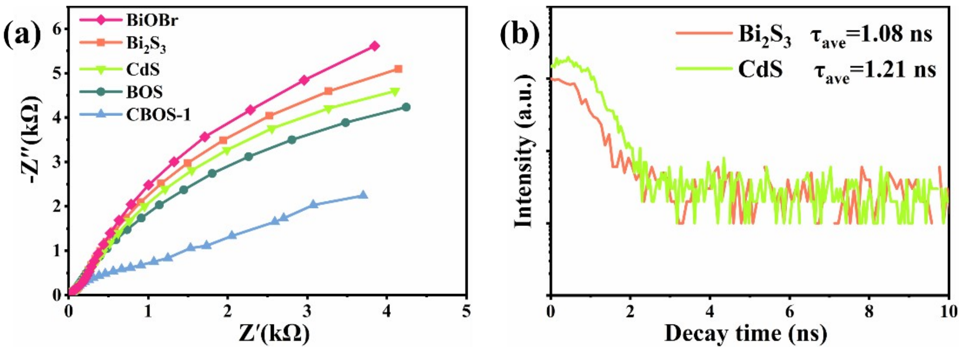

Fig. S10. (a) EIS test of BiOBr, Bi_2S_3, CdS, BOS and CBOS-1; (b) TRPL spectra

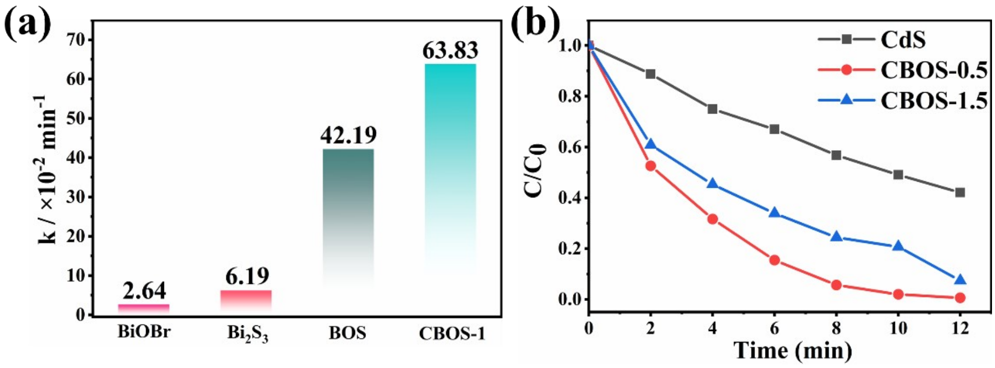

Fig. S11. (a) first-order reaction kinetic constants under full-spectrum irradiation; (b) photocatalytic performance of CdS, CBOS-0.5 and CBOS-1.5 under full-spectrum irradiation.

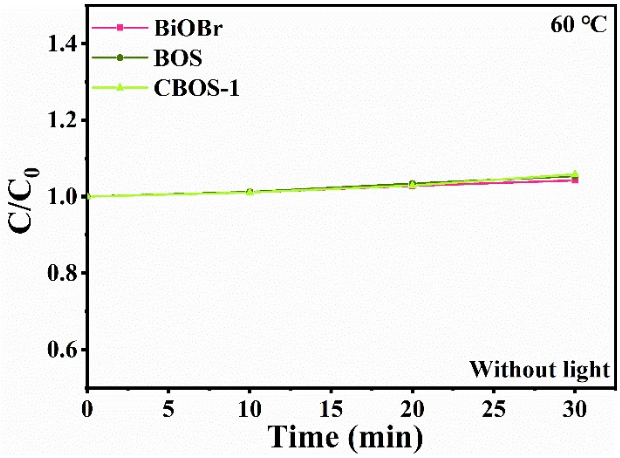

Fig. S12. Dark degradation curve of Cr(VI) by catalyst at 60 °C.

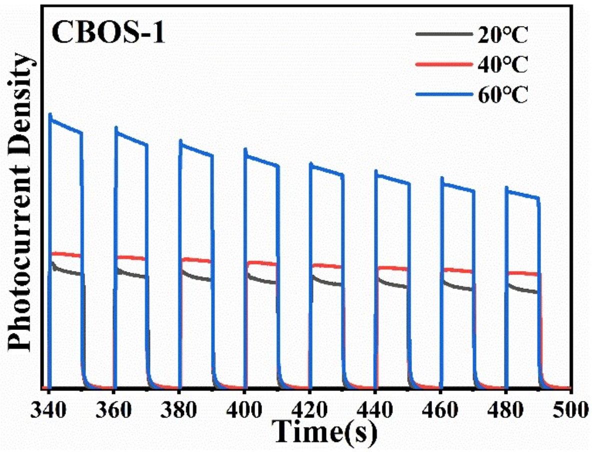

Fig. S13. Photocurrent response of CBOS-1 at different temperatures.

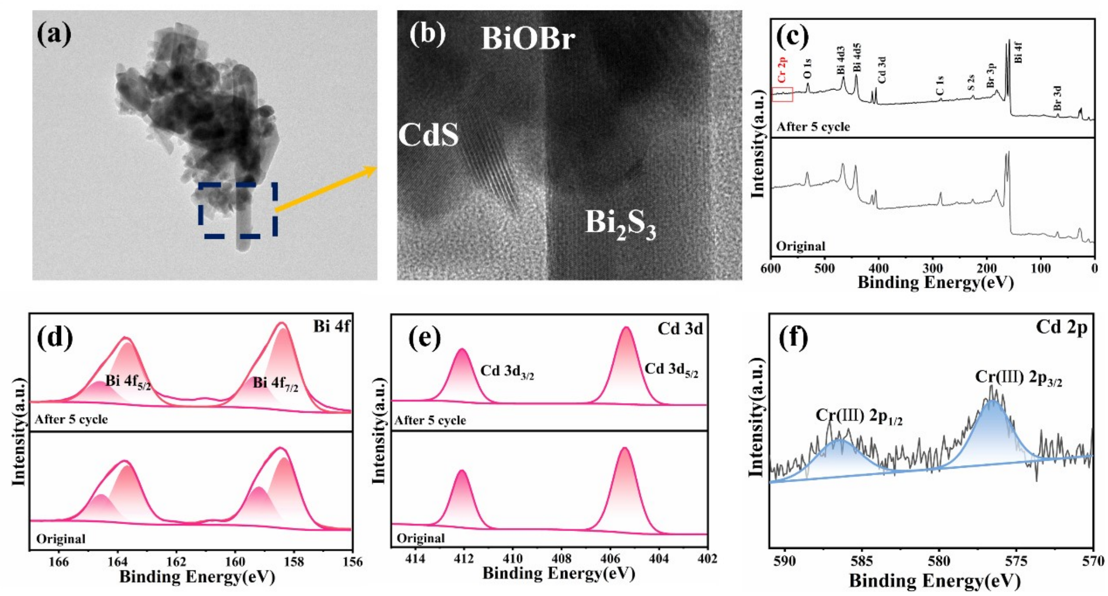

Fig. S14. (a, b) TEM images and (c-f) XPS test of CBOS-1 after five cycles.

Table S1. The content of metal ions in solution after photocatalytic reaction identified by ICP-MS analysis.

Sampling number	Test element	Primary solution element concentration C_0 (mg/L)	Average C_0 (mg/L)
1	Bi	0.5040	0.439
2		0.4163	
3		0.3987	
1	Cd	3.4587	3.391
2		3.3863	
3		3.3268	