

Supplementary Information

Plasmon Ag and CdS Quantum Dots Co-Decorated 3D Hierarchical Ball-Flower-Like Bi₅O₇I Nanosheets as Tandem Heterojunctions for Enhanced Photothermal-Photocatalytic Performance

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2 Experimental section

2.1 Materials

Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), potassium iodide (KI), silver nitrate (AgNO_3) and absolute ethanol (EtOH) were purchased from Guoyao Chemical Reagent Co. Ltd, China. Cadmium acetate dihydrate ($\text{Cd}(\text{AC})_2$) and sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) were ordered from Aladdin Reagent Company, China. All the reagents were not further purified. Deionized water was used throughout the experiment.

2.2 Synthesis

2.2.1 Synthesis of 3D ball-flower-like $\text{Bi}_5\text{O}_7\text{I}$

0.485g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was added into 60 mL ethanol absolute and was treated under ultrasonic condition for 2 h. Afterwards, 0.166g KI aqueous solution was slowly added into to form the red suspension. The PH of the red suspension was adjusted to 7 by dropping NaOH solution. Then the above reaction system was heated at 80 °C for 5 h under oil bath. After the reaction was cooled to room temperature, the BiOI precursor was obtained by washing with deionized water and ethanol absolute, then dried at 60°C for 10h. Finally, BiOI precursor was calcined at 450 °C for 3 h at a heating rate of 5 °C/min to obtain $\text{Bi}_5\text{O}_7\text{I}$.

2.2.2 Synthesis of 3D ball-flower-like $\text{Bi}_5\text{O}_7\text{I}/\text{Ag}$ nanoparticles

According to the optimal experiment results indicated that adding 3 mL of AgNO_3 (0.01 mol/L) exhibited the excellent photocatalytic activity (Figure S1). Therefore, we determined the optimal amount of silver to add. First of all, 100 mg as-

prepared $\text{Bi}_5\text{O}_7\text{I}$ powder was added into 45 mL deionized water and stirred for 20 min, 3 mL AgNO_3 (0.01 mol/L) solution was added to the $\text{Bi}_5\text{O}_7\text{I}$ suspension solution drop by drop. Then, $\text{Bi}_5\text{O}_7\text{I}$ suspension solution was irradiated with a 500 W xenon lamp for 30 min under continuous stirring in order that Ag^+ on the surface of $\text{Bi}_5\text{O}_7\text{I}$ was reduced to Ag^0 . To simplify writing, sample with optimal silver addition was named as $\text{Bi}_5\text{O}_7\text{I}/\text{Ag}$.

2.2.3 Synthesis of 3D ball-flower-like $\text{Bi}_5\text{O}_7\text{I}/\text{Ag}$ nanoparticles/CdS quantum dots

100 mg $\text{Bi}_5\text{O}_7\text{I}/\text{Ag}$ composite was added into 30 mL deionized water and stirred for 20 min. 0.01 mol/L of $\text{Cd}(\text{AC})_2$ (2, 4, 6 and 8 mL) aqueous solution and 0.01 mol/L of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (2, 4, 6 and 8 mL) aqueous solution were added to the above suspension solution drop by drop, successively. After 4 h of magnetic stirring, the mixed solution was transferred into a 100 mL Teflon-lined autoclave at 160 °C for 12 h. Final composite sample was labeled as $\text{Bi}_5\text{O}_7\text{I}/\text{Ag}/\text{CdS}(\text{X})$ (X = 2, 4, 6, and 8 mL). For comparison, the CdS quantum dots were prepared using a similar method except that $\text{Bi}_5\text{O}_7\text{I}/\text{Ag}$ composite was not added.

2.3 Characterization

The phase composition of as-prepared materials were analyzed by X-ray diffraction (XRD-D8 Advance, Bruker) with Cu K α radiation source (40 kV, 44 mA), scanning range 10° ~ 80°. The morphology of as-prepared materials were analyzed by scanning electron microscope (SEM, Hitachi S-4800), and the working voltage was 20 kV. Transmission electron microscope (TEM, JEOL JEM-2010) at the working voltage of 200 kV was used to observe the microstructure. The surface element state

was measured on a PHI-5700 ESCA X-ray photoelectron spectroscopy (XPS) with Al K α X-ray source. UV-vis diffuse reflection spectra (DRS) of the materials were obtained by UV-vis spectrophotometer (UV-2550, Shimadzu), BaSO₄ was used as the reference. The Fourier transform infrared spectra (FT-IR) of the samples were collected with a PerkinElmer spectrum one system. Scanning Kelvin probe (SKP) test (SKP5050 system, Scotland) was executed to evaluate the work function at ambient atmosphere. Electron spin response (ESR) spectra of active species captured by 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) were examined on an ER200-SRC spectrometer under visible-light illumination. The specific surface areas and pore sizes of as-prepared samples were measured by AUTOSORB-1 (Quantachrome Instruments) nitrogen adsorption apparatus. Photoluminescence (PL) spectra were measured with a PE LS 55 spectrofluoro-photometer at excitation wavelength of 325 nm. The water contact angles (CA) of the samples were determined by Contact angle meter (Dataphysics OCA 20, Germany), using 3 μ L water droplet as a probing liquid.

2.4 Photocatalytic degradation

Bisphenol A (BPA) was widely used in daily life and has become a substance that people can often contact. In addition, some datas show that bisphenol A has certain toxicity and teratogenicity in embryos. 2,6-dichlorophenol (2,6-DCP) was harmful to the environment and may cause pollution to water and soil, especially to mollusks, fish and mammals. Therefore, BPA and 2,6-DCP were selected to test the photocatalytic degradation performance. In a typical experiment, the photocatalyst (40 mg) was added to BPA solution (20 mL, 10 mg L⁻¹) or 2,6-DCP solution (20 mL, 10

mg L⁻¹). Then, the suspension was placed in the dark to ensure adsorption-desorption equilibrium. The suspension was irradiated with a 300 W Xenon lamp equipped with optical filter ($\lambda \geq 420$ nm). The residual BPA or 2,6-DCP concentration was analyzed by T6 UV-vis spectrophotometer.

2.5 Photoelectrochemical tests

Photoelectrochemical tests were recorded by an electrochemical workstation (CHI760E, Shanghai), employed a standard three-electrode cell with the different sample films as the working electrode, the counter electrode (Pt sheet) and the reference electrode (Ag/AgCl). An aqueous solution of Na₂SO₄ (0.1 M) water solution was used as the electrolyte, which was irradiated by an AM 1.5 solar power system.

2.6 Photocatalytic hydrogen evolution

The photocatalytic hydrogen evolution was tested in an online photocatalytic hydrogen evolution system (AuLight, Beijing, CEL-SPH2N) at room temperature. In a typical process, 50 mg of photocatalysts were suspended in 100 mL aqueous closed-gas circulation reaction cell which include 80 mL deionized water and 20 mL of methanol used as the sacrificial reagent. Afterward, the suspension was purged with N₂ for several times to remove O₂ and CO₂. After that, the suspension solution was irradiated by a 300W Xe-lamp equipped with an AM 1.5 G filter (Oriel, USA), and use an on-line gas chromatography (SP7800, TCD, molecular sieve 5 Å, N₂ carrier, Beijing Keruida, Ltd) to analyze the hydrogen periodically with the interval of every 1h.

2.7 Photothermal test

The photothermal test of as-prepared samples was carried out as follow. 0.1 g of samples was loaded on a white paper and the initial temperature was controlled at room temperature. The temperature of the sample was measured using the FLIR infrared thermal imager Testo 865. A 300 W xenon lamp was used as a light source.

2.8 Water temperature evolution test

1 mL (150mg/L) of the aqueous dispersion of $\text{Bi}_5\text{O}_7\text{I}$ or $\text{Bi}_5\text{O}_7\text{I}/\text{Ag}/\text{CdS}(4)$ were illuminated by 808-nm laser, and the corresponding temperature was recorded every 60 s by FLIR infrared thermal imager Testo 865.

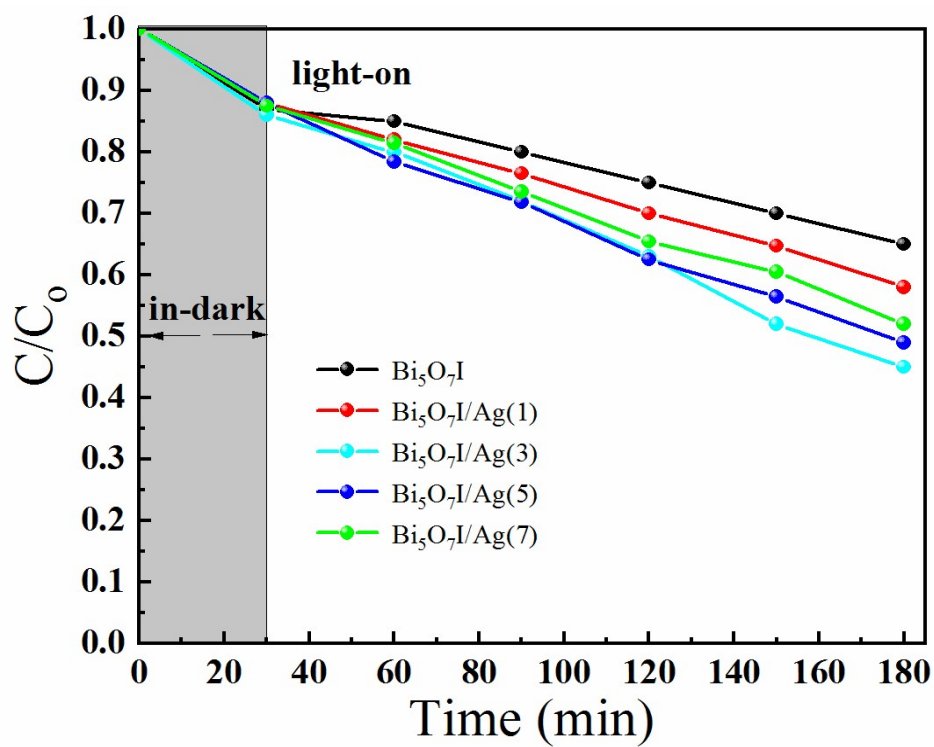


Fig. S1. Experimental results of optimum addition amount of Ag (Photocatalytic degradation of BPA).

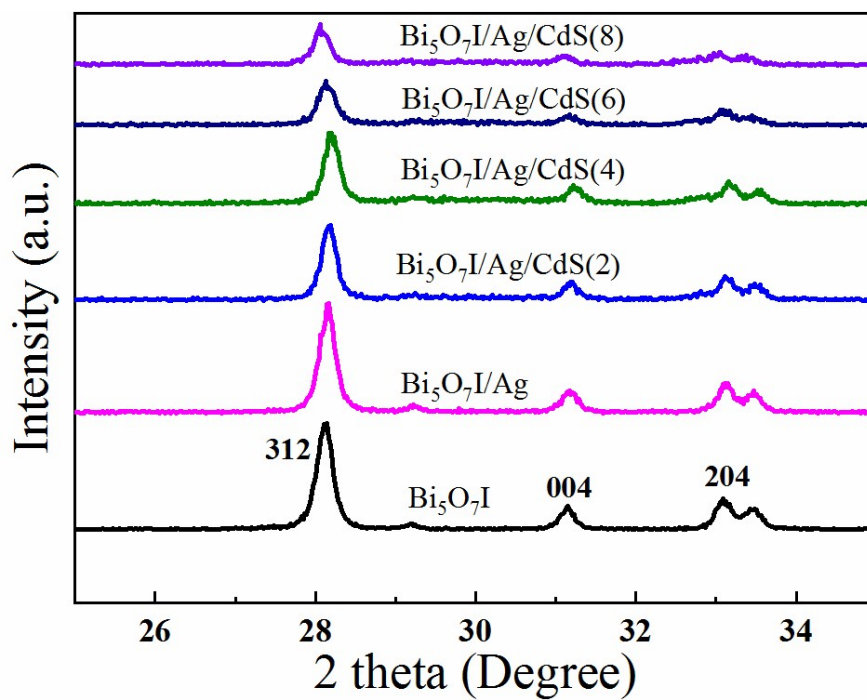


Fig. S2. Partially amplified XRD patterns of as-prepared samples.

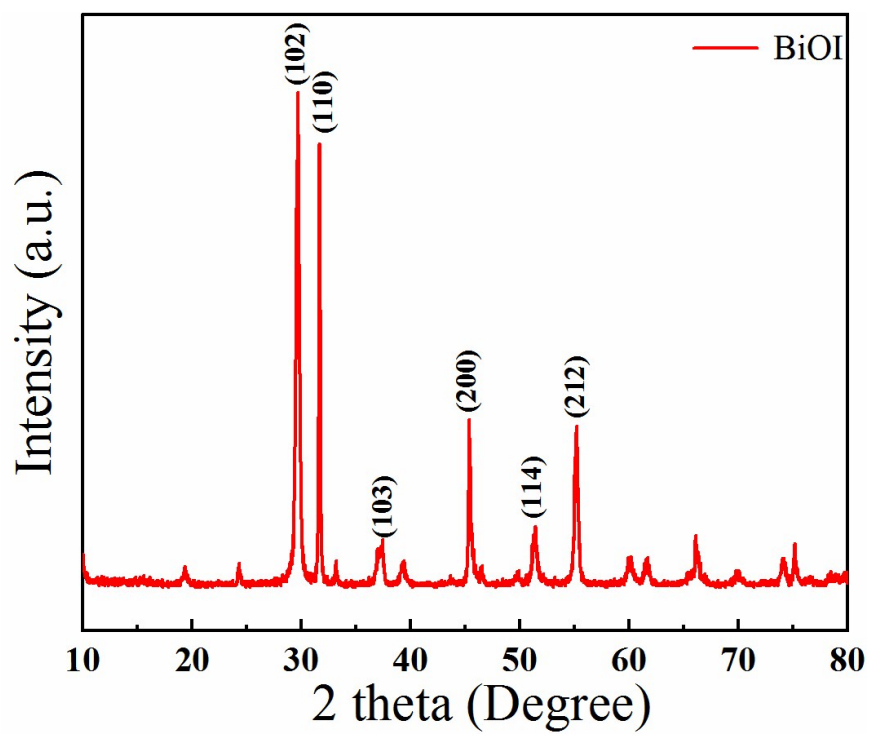


Fig. S3. XRD pattern of as-prepared BiOI precursor.

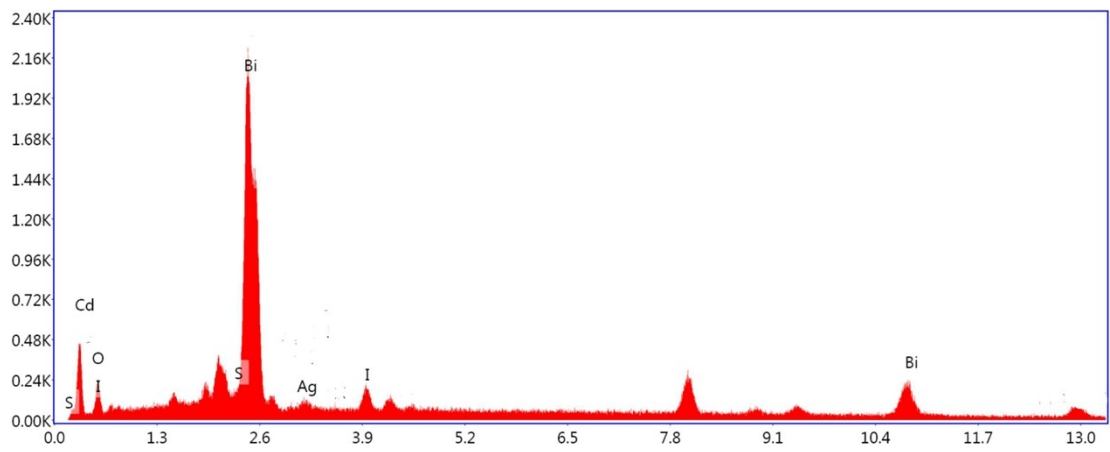


Fig. S4. EDS spectrum of as-prepared $\text{Bi}_5\text{O}_7\text{I}/\text{Ag}/\text{CdS}(4)$.

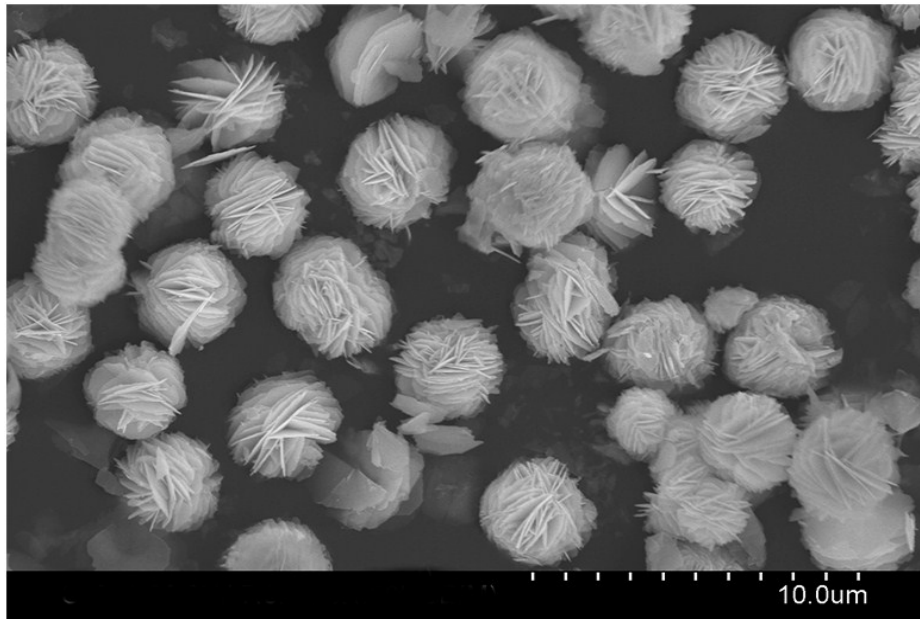


Fig. S5. SEM image of pure Bi₅O₇I.

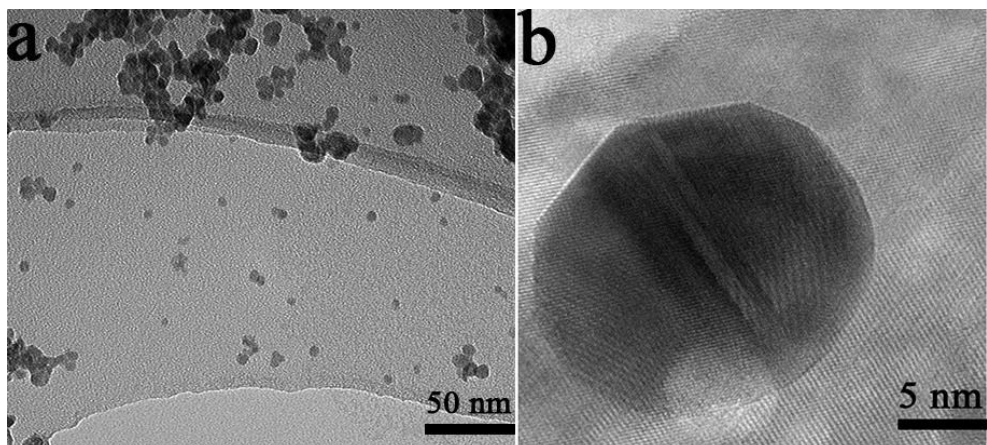


Fig. S6. TEM image of CdS quantum dots (a), and HRTEM image of the Bi₅O₇I/Ag (b).

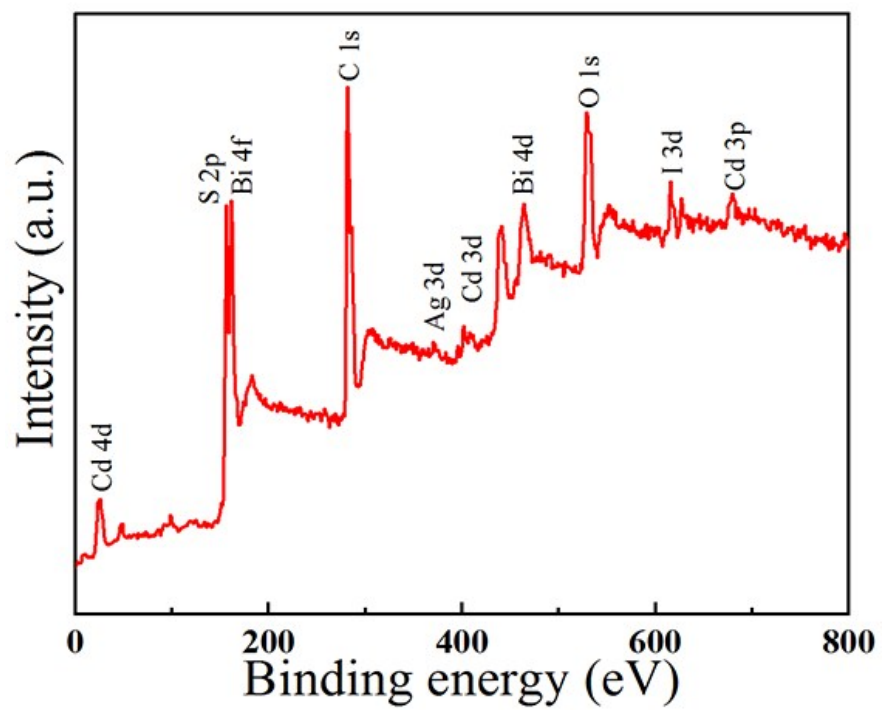


Fig. S7. XPS survey spectrum of $\text{Bi}_5\text{O}_7\text{I}/\text{Ag}/\text{CdS}(4)$.

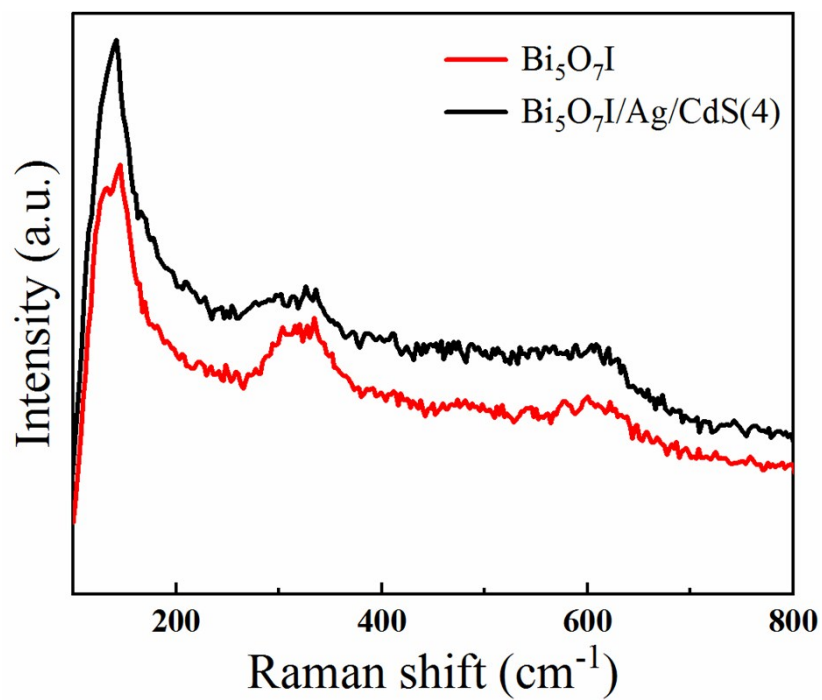


Fig. S8. Raman spectra of pure Bi₅O₇I and Bi₅O₇I/Ag/CdS(4) samples, respectively.

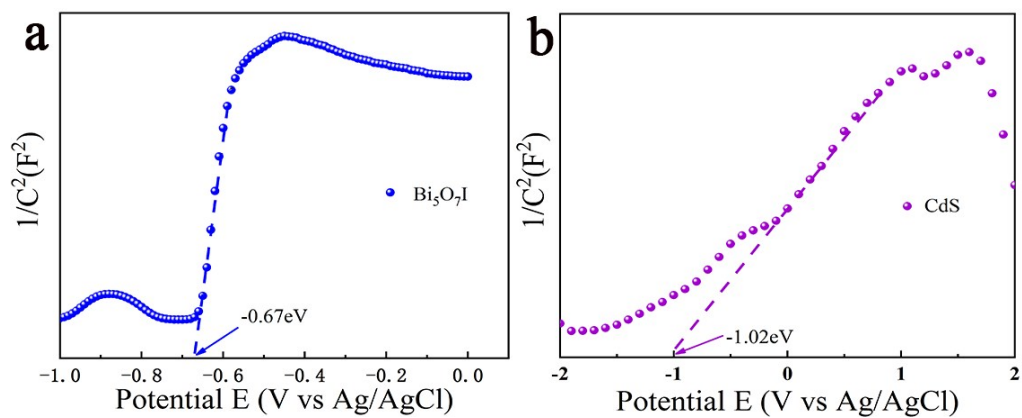


Fig. S9. Mott-Schottky plots of Bi₅O₇I (a), and CdS (b), respectively.

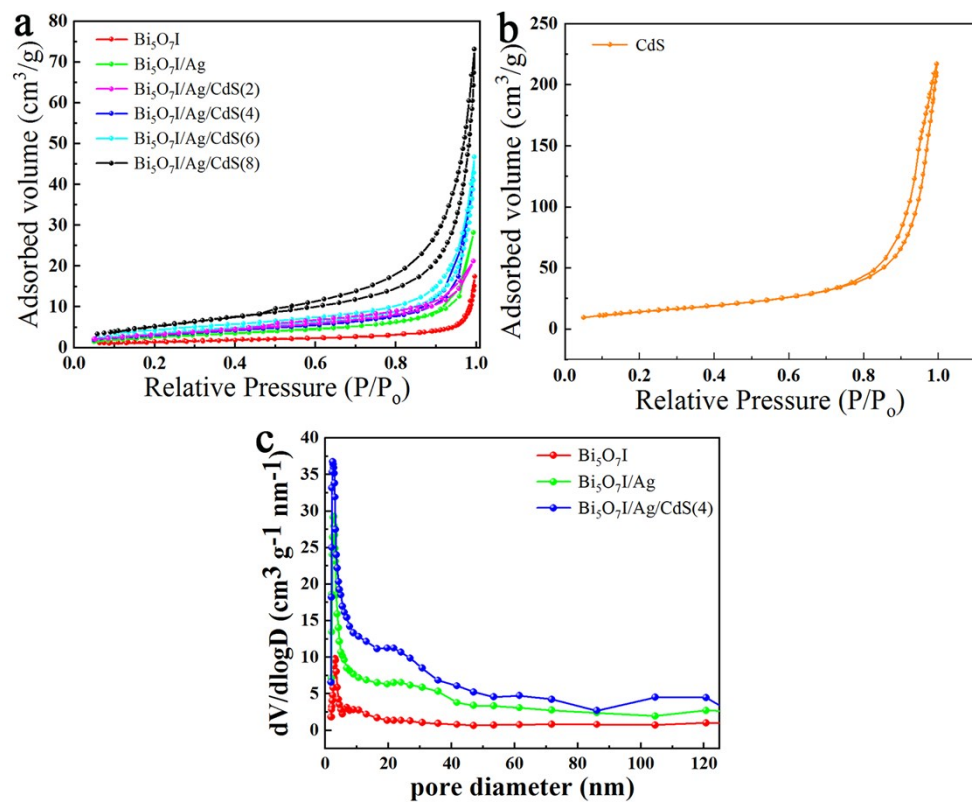


Fig. S10. N_2 adsorption-desorption isotherms and pore distribution plots of as-prepared samples.

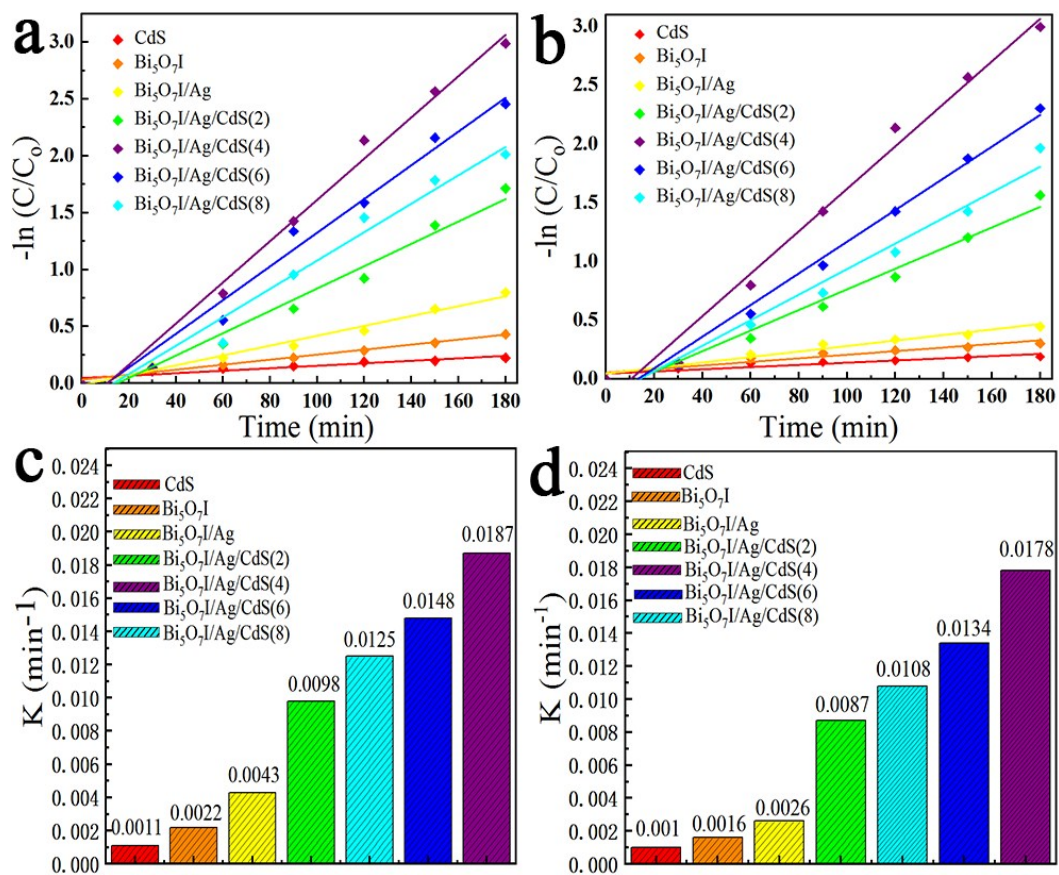


Fig. S11. Corresponding pseudo-first-order kinetic curves of photocatalytic degradation of BPA

(a) and 2, 6-DCP (b), reaction rate constants of photocatalytic degradation of BPA (c) and 2, 6-

DCP

(d).

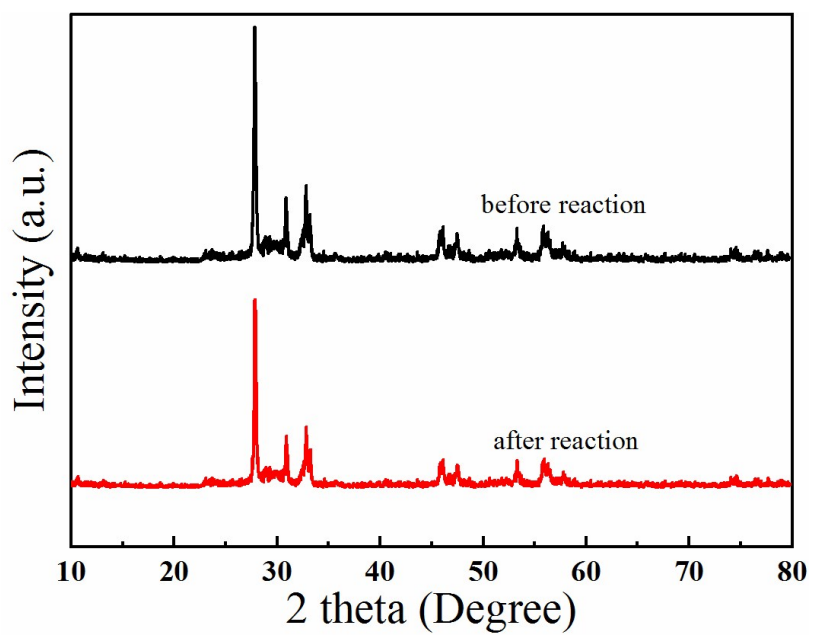


Fig. S12. XRD patterns of $\text{Bi}_5\text{O}_7\text{I} / \text{Ag} / \text{CdS}(4)$ composite before and after five cycles, respectively.

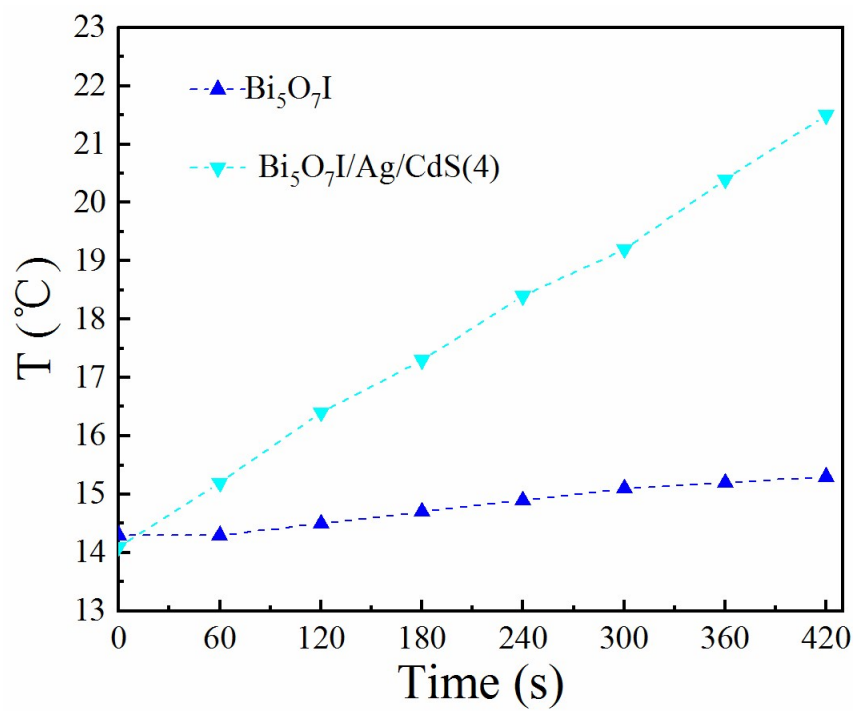


Fig. S13. Temperature evolution profiles of aqueous solution of Bi₅O₇I and Bi₅O₇I/Ag/CdS(4), respectively.

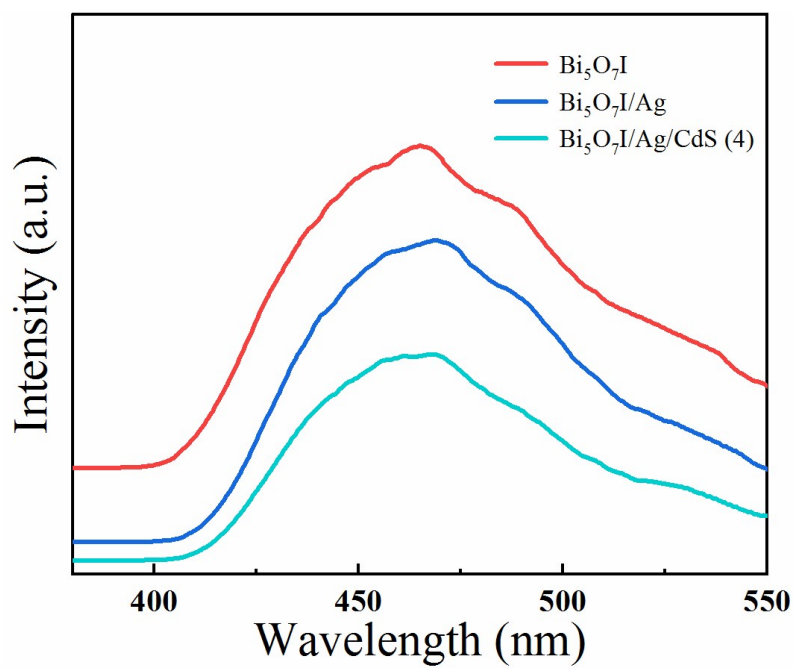


Fig. S14. Photoluminescence spectra of $\text{Bi}_5\text{O}_7\text{I}$, $\text{Bi}_5\text{O}_7\text{I}/\text{Ag}$, and $\text{Bi}_5\text{O}_7\text{I}/\text{Ag}/\text{CdS}(4)$, respectively.

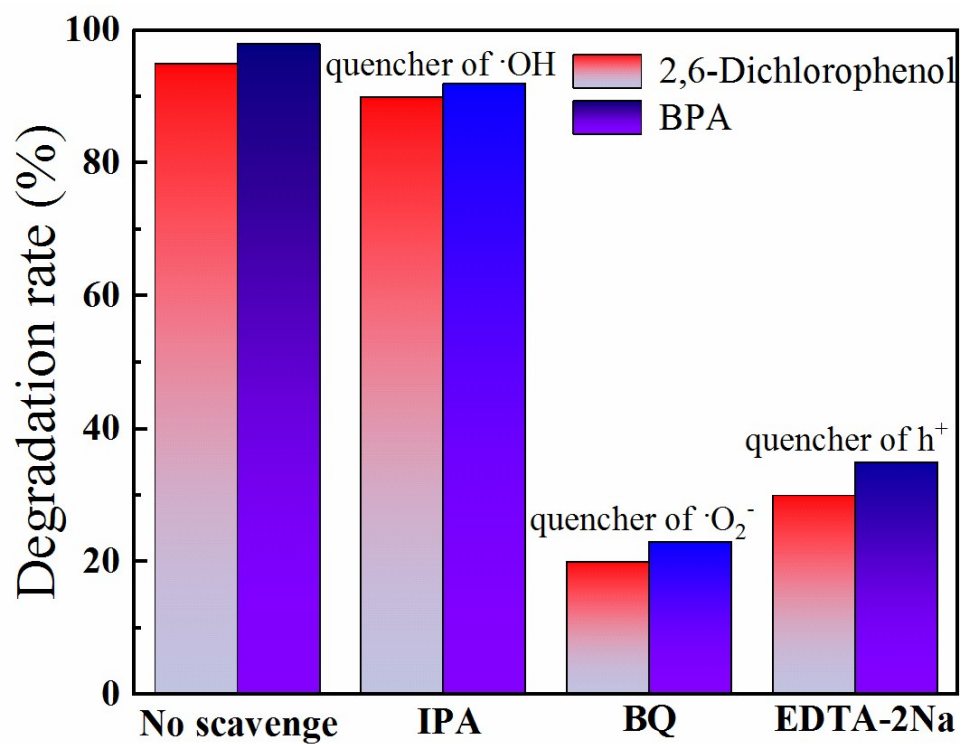


Fig. S15. The species trapping experiments for degradation BPA and 2, 6-DCP over Bi₅O₇I /Ag /CdS(4) photocatalyst under visible light irradiation.

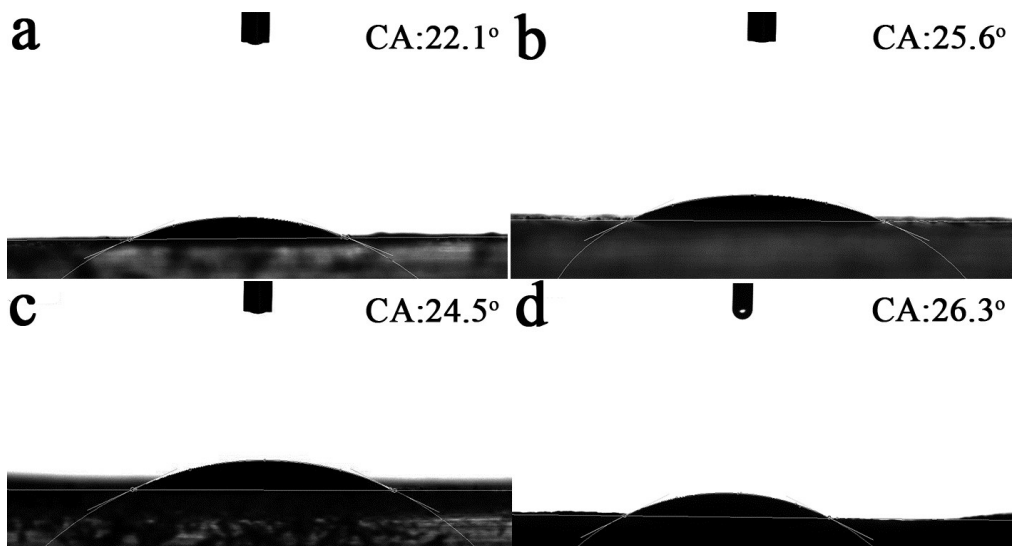


Fig. S16. Static water contact angles of $\text{Bi}_5\text{O}_7\text{I}$ (a), CdS (b), $\text{Bi}_5\text{O}_7\text{I}/\text{Ag}$ (c), and $\text{Bi}_5\text{O}_7\text{I}/\text{Ag}/\text{CdS}$ (4), respectively.

Table S1. The specific surface areas, pore sizes of the as-prepared samples.

Catalyst	Surface area (m ² /g)	Pore size (nm)
Bi ₅ O ₇ I	5.26	21.31
CdS	50.06	6.54
Bi ₅ O ₇ I/Ag	10.69	20.84
Bi ₅ O ₇ I/Ag/CdS(2)	12.14	20.03
Bi ₅ O ₇ I/Ag/CdS(4)	13.93	18.55
Bi ₅ O ₇ I/Ag/CdS(6)	15.08	17.45
Bi ₅ O ₇ I/Ag/CdS(8)	21.33	17.15

Table S2. The degradation rates of different Bi₅O₇I-based photocatalysts.

Photocatalysts	pollutant	Degradation rate	ref
Bi/GO/Bi ₅ O ₇ I	levofloxacin	95.2%	1
Bi ₅ O ₇ I/g-C ₃ N ₄	Bisphenol A	95%	1
CODs/Bi ₅ O ₇ I	Bisphenol A	94.2%	3
AgI/Bi ₅ O ₇ I	tetracycline	93.81%	4
BiOCl _{0.5} I _{0.5} /Bi ₅ O ₇ I	methyl orange	90%	5
Ag/AgBr/Bi ₅ O ₇ I	RhB	98%	6
Bi ₄ O ₅ I ₂ /Bi ₅ O ₇ I	propylparaben	92.8%	7
SrTiO ₃ /Bi ₅ O ₇ I	RhB	89.6%	8
This Work	Bisphenol A	98.2%	

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