

## Supporting Information

### **In Situ Growth of Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub> on Ultrathin BiVO<sub>4</sub> Nanosheets to Fabricate Heterojunction Intimate Interfaces for Enhancing Photocatalytic Activity**

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## Materials.

Cesium bromide (CsBr, 99.9%), bismuth tribromide (BiBr<sub>3</sub>, 99%), octadecene (ODE, 90%), oleylamine (OAm, 90%), oleic acid (OA, 90%), dimethyl sulfoxide (DMSO, 99.9%), Nitric acid (HNO<sub>3</sub>) were purchased from Aladdin company. Bismuth nitrate pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>•5H<sub>2</sub>O, 99%), ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>, 99%) were obtained from Shanghai Xian Ding Biotechnology Co. Isopropanol (IPA, 99.7%), hexane (anhydrous, 98%), Ethanol (EtOH, 99.7%). All the chemicals were analytical grade (A.R.) and used without further purification.

## Synthesis of BiVO<sub>4</sub> nanosheets

BiVO<sub>4</sub> nanosheets (BiVO<sub>4</sub> NSs) were synthesized by colloidal two-phase method. First, a 25 ml three-neck flask was taken and OA (1 mL), OM (1 mL) and ODE (10 mL) were added, after which 0.242 g Bi(NO<sub>3</sub>)<sub>3</sub>•5H<sub>2</sub>O was dispersed in it under stirring and heated to 160°C under N<sub>2</sub> atmosphere until it was completely dissolved to form a transparent solution. Subsequently, the temperature was reduced to 100°C. Another 20 ml glass vial was taken and 0.116 g NH<sub>4</sub>VO<sub>3</sub> was dissolved in 12 ml of 2.4 M aqueous nitric acid solution and slowly injected into the above solution containing dissolved Bi(NO<sub>3</sub>)<sub>3</sub> and kept at 100°C for 40 min. The solution was naturally cooled to room temperature and then extracted by adding a mixture of hexane and ethanol (v/v = 1:1), the upper yellow solution was taken and centrifuged to obtain a yellow precipitate washed three times with a mixture of hexane and ethanol, and finally dried in an oven at 60° C for 12 h.

## Synthesis of Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub>

For the synthesis of ligand free Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub>, 0.36 mmol of CsBr and 0.24 mmol of BiBr<sub>3</sub> were dissolved in 4 mL of dimethyl sulfoxide (DMSO) in a molar ratio of 3:2 to form the precursor solution. Under vigorous stirring, 1 mL of Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub> precursor solution was added dropwise to 50 mL of isopropanol, stirred for 3 min at room temperature and then centrifuged at 6000 rpm for 5 min. The obtained precipitate was washed twice with isopropanol and ethanol, respectively, and dried in an oven at 60°C for 12 h.

## Synthesis of the Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub>/BiVO<sub>4</sub> heterojunction

A certain amount of BiVO<sub>4</sub> NSs was added to 1 mL Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub> precursor solution (CsBr/BiBr<sub>3</sub>/DMSO) to be ultrasonically dispersed well, and the mixed Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub> precursor solution was added dropwise to 50 mL of isopropanol solution under vigorous stirring at room temperature for 3 h. Finally, the Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub>/BiVO<sub>4</sub> composites were centrifuged at 6000 rpm for 5 min, washed twice with isopropanol and ethanol, respectively, and dried under vacuum at 60°C for 6 h. After drying for 6 h, the Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub>/BiVO<sub>4</sub> composites were harvested. Specifically, different ratios of Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub>/BiVO<sub>4</sub> composites varied the amount of BiVO<sub>4</sub> NSs by fixing the amount of Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub> precursor (CsBr/BiBr<sub>3</sub>/DMSO). the weight percentages of BiVO<sub>4</sub>

relative to  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  were 3%, 5%, and 7%, respectively, and were labeled 3%  $\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{BiVO}_4$ , 5%  $\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{BiVO}_4$ , and 7%  $\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{BiVO}_4$ .

### Materials Characterization

The morphology of the prepared samples was obtained by scanning electron microscopy (SEM, Hitachi S-4800). The detailed heterojunction structures of the samples were obtained by transmission electron microscopy (TEM, TecnaiG2F20) at an accelerating voltage of 200 kV. Zeta potential was performed using Zetasizer Nano ZS (Malvern Instruments, U.K.), the samples were dispersed in ethanol solutions. The phase structure of the samples was measured by X-ray diffraction (XRD) via Bruker D8 Focus with  $\text{Cu K}\alpha$  radiation. X Ray photoelectron spectroscopy (XPS) tests were performed using Thermo Scientific K-Alpha spectrometer. The Fourier transform infrared spectroscopy (FTIR) spectra were examined on a spectrometer (Bruker ALPHA-E, Germany). The optical properties were characterized by UV-visible diffuse reflectance spectroscopy (UV-vis DRS, Shimadzu UV-3600) using  $\text{BaSO}_4$  as a reflectance standard. Steady-state photoluminescence (PL) spectra were recorded on Hitachi F-7000 spectrometer and the excitation wavelength was 420 nm. Time resolved PL measurement was performed using Edinburgh FS5 spectrofluorometer with pulsed LED. Electron Spin Resonance Spectroscopy (ESR, JES-FA200) was used to analyze reactive radicals. The detection of  $\cdot\text{O}_2^-$  was conducted in acetonitrile solution with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the spin trap.

### Photocatalytic experiments

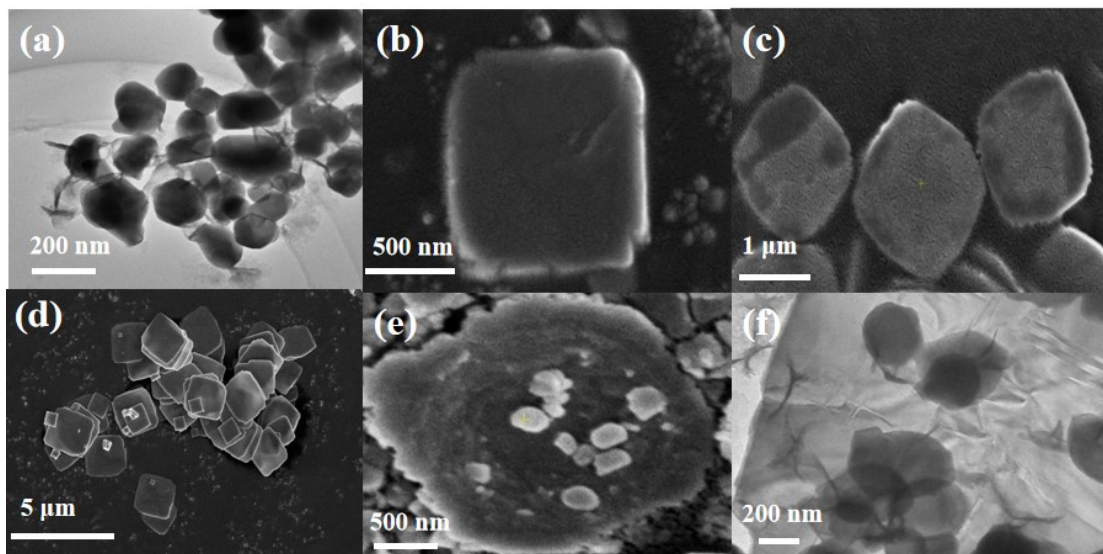
The photocatalytic degradation of Sudan III was carried out in a glass vial at room temperature under cooling water circulation. The irradiation was conducted with a 300 W Xe lamp with 400 nm cut-off filter ( Beijing Zhongjiao Jinyuan Co., Ltd.). The calibrated light intensity was  $100 \text{ mW cm}^{-2}$ . Briefly, 20 mg of photocatalyst was mixed with 20 mL of Sudan Red III ethanol solution (10 mg/L). The mixture was stirred in the dark for 30 min to reach the adsorption-desorption equilibrium. During the photocatalytic reactions, 2 mL of the suspension was transferred every 8 min and centrifuged for separation. The degradation rate of Sudan Red III was monitored by optical absorbance method using a DH-2000-BAL absorption spectrometer from the United States. For MR and MB photocatalysis, the photocatalytic degradation process was the same except for the monitor wavelength.

In order to better understand the photocatalytic degradation mechanism, active radical trapping experiments were performed under the same conditions. Isopropyl alcohol (IPA), p-benzoquinone (BQ) and ammonium oxalate ( $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ) at 0.5 mmol/L were used as hydroxyl radical ( $\cdot\text{OH}$ ), superoxide radical ( $\cdot\text{O}_2^-$ ) and hole ( $\text{h}^+$ ) trapping agents for the evaluation of the main active substances, respectively.

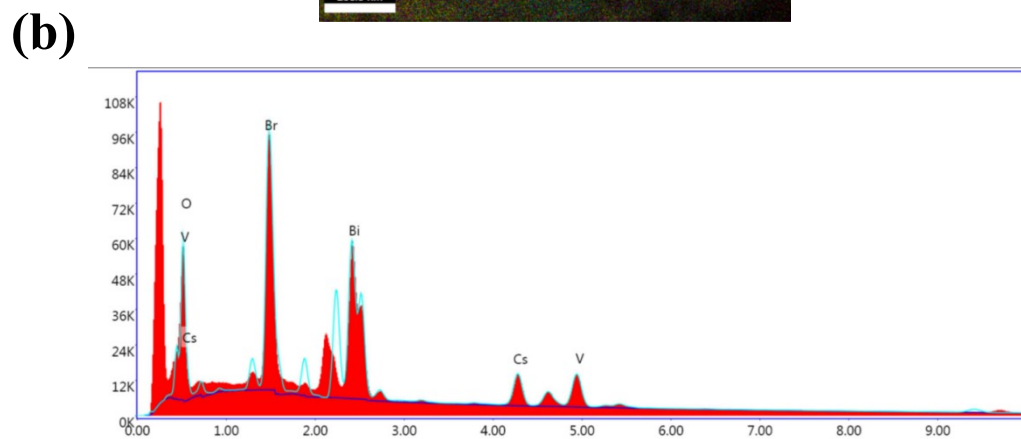
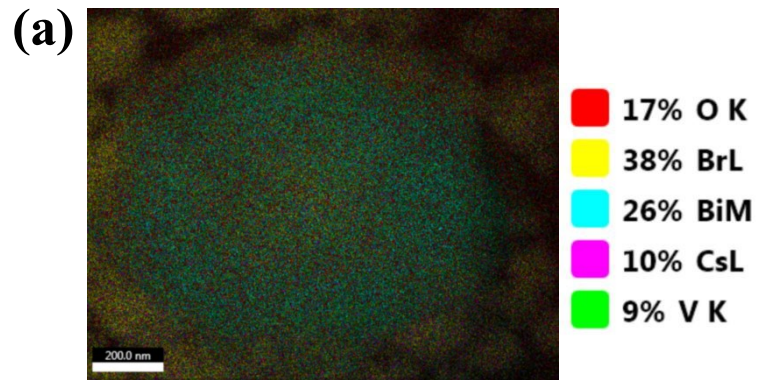
### Photoelectrochemical testing

Photoelectrochemical tests on the samples ( $\text{BiVO}_4$ ,  $\text{Cs}_3\text{Bi}_2\text{Br}_9$ ,  $\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{BiVO}_4$ )

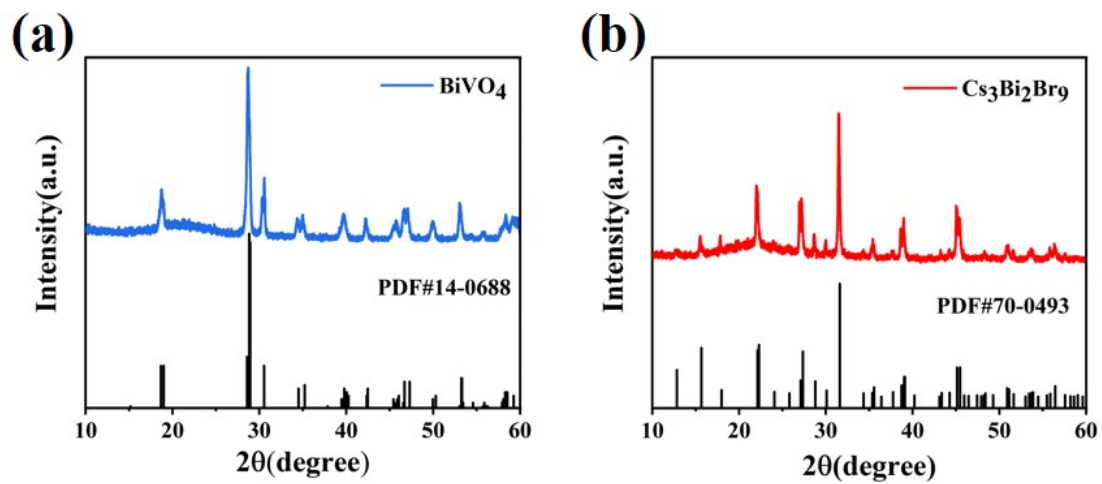
were performed on an electrochemical workstation (CHI660, Shanghai Chenhua, China) with a conventional three-electrode system. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in Ethanol solution was used as the electrolyte. For the preparation of the working electrode, a mixture of 3 mg of catalyst, 200  $\mu$ L of isopropanol and 10  $\mu$ L of nafion solution was sonicated for 1 h. Then, the suspension was dropped onto indium tin oxide (ITO) glass and dried. The reference electrode was an Ag/AgCl electrode and the counter electrode was a Pt electrode. The impedance tests were performed at open circuit potential and in the dark. For the photocurrent studies, measurements were made at room temperature at open circuit potential using a 300 W Xe lamp (AM 1.5 G, 100 mW cm<sup>-2</sup>) irradiation.



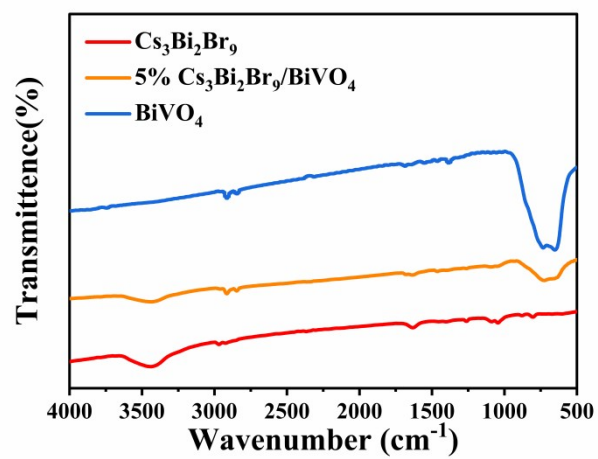
**Fig. S1.** (a) TEM of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$ . (b-d) SEM of  $\text{BiVO}_4$  NSs. (e) SEM and (f)TEM of  $\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{BiVO}_4$ .



**Fig. S2.** EDS spectroscopy of  $\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{BiVO}_4$  composites.

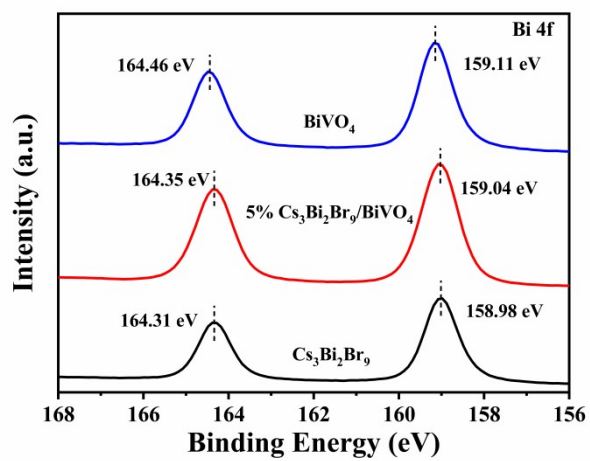


**Fig. S3.** XRD patterns of (a) Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub> and (b) BiVO<sub>4</sub> NSs.

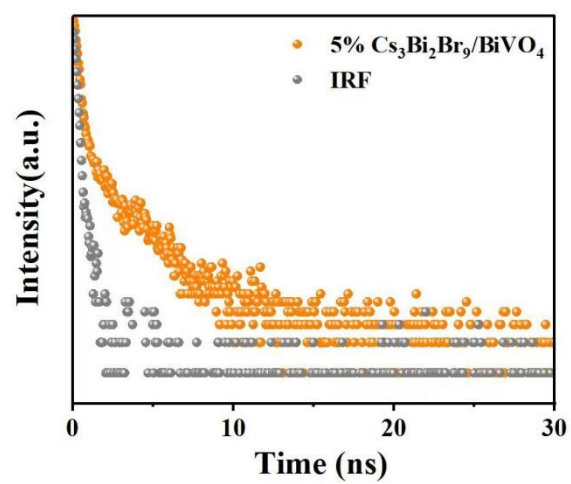


**Fig. S4.** FTIR of Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub>, BiVO<sub>4</sub> and 5% Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub>/BiVO<sub>4</sub>.

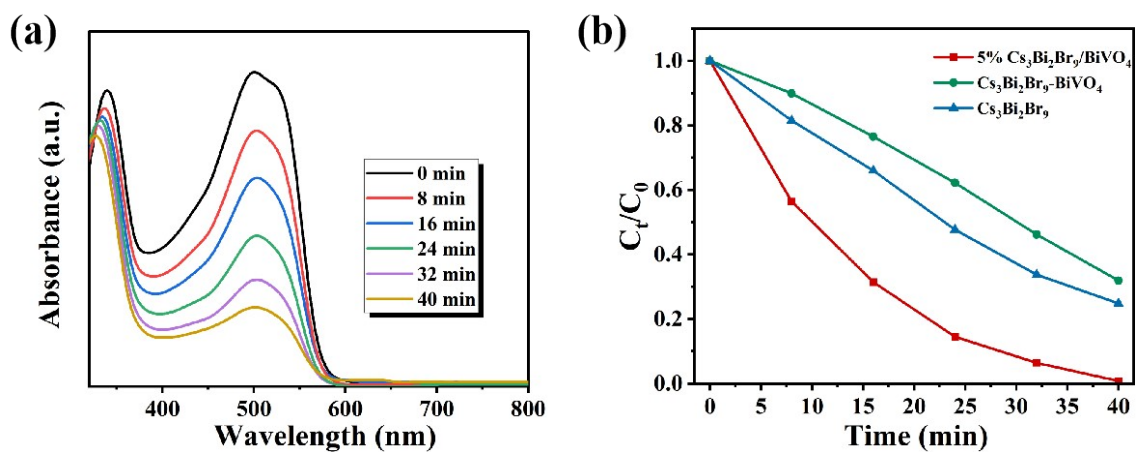




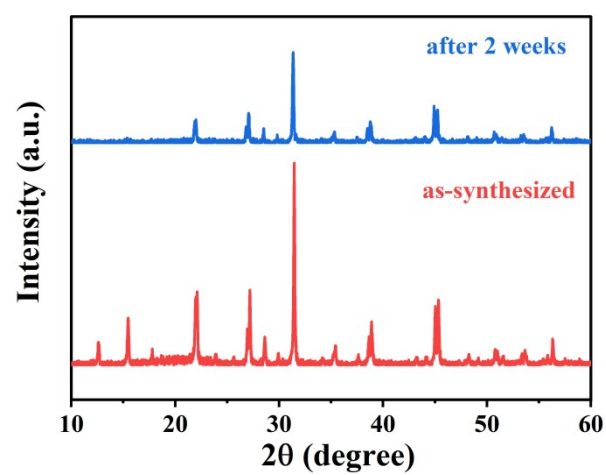
**Fig. S5.** High resolution XPS spectra of Bi 4f in Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub>, BiVO<sub>4</sub> and 5% Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub>/BiVO<sub>4</sub>.



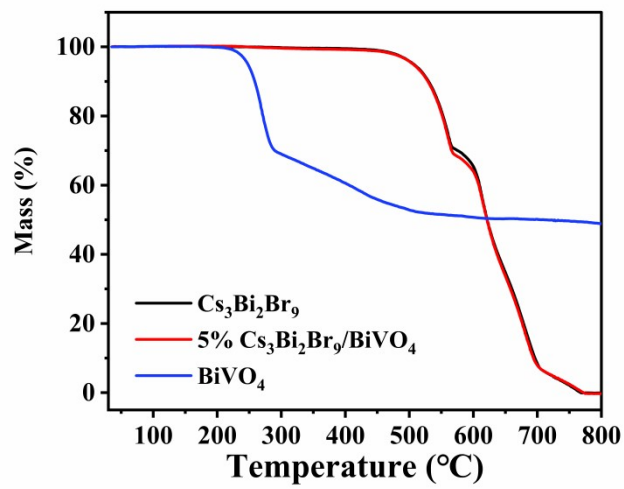
**Fig. S6.** The TRPL decay curves and IRF of the Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub>/BiVO<sub>4</sub> composites



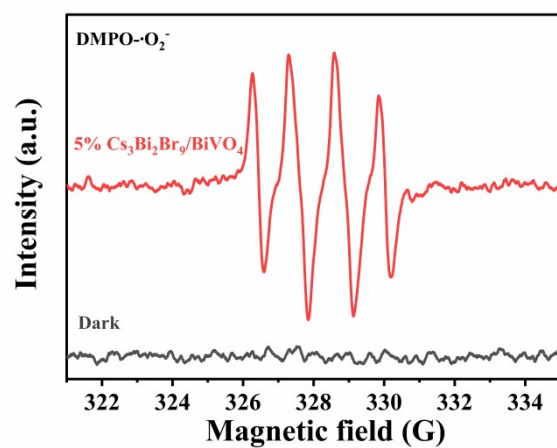
**Fig. S7.** (a) Ultraviolet/Visible spectra of Sudan Red III in the presence of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  at different irradiation times. The inset shows the change of solution color with time. (b) Comparison of  $C_t/C_0$  with time for the photocatalytic degradation of Sudan Red III by mechanically ground mixed  $\text{Cs}_3\text{Bi}_2\text{Br}_9\text{-BiVO}_4$  and prepared 5%  $\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{BiVO}_4$  heterojunction.



**Fig. S8.** XRD patterns of 5%  $\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{BiVO}_4$  after storage for two weeks under ambient conditions.



**Fig. S9.** TG of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$ ,  $\text{BiVO}_4$  and 5%  $\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{BiVO}_4$  composites.



**Fig. S10.** ESR spectra of 5% Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub>/BiVO<sub>4</sub> in dark and light conditions.

**Table S1.** A summary of the photodegradation performances of various perovskite-based photocatalysts.

Photocatalysts	Contaminants	Concentrations (mg/L)	Time (min)	Degradation (%)	ref.
CsPbBr <sub>3</sub>	MO	10	100	89	1
Cs <sub>2</sub> AgBiBr <sub>6</sub>	RhB	100	120	98	2
CsPbX <sub>3</sub> /CN	6-APA	10	120	83.3	3
CsPbBr <sub>3</sub> /BiOCl	RhB	2.27	60	99.9	4
CsPbBr <sub>3</sub> -MoS <sub>2</sub> -GO	Sudan III	10	100	99.9	5
CsPbBrCl <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Eosin B	5.8	120	94	6
CsPb(Br <sub>1-x</sub> Cl <sub>x</sub> ) <sub>3</sub> -Au	Sudan III	1	360	71	7
PEA <sub>2</sub> SnBr <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	MB	3.19	40	99.9	8
Cs <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub>	RhB	20	100	100	9
	MB			99.3	
Cs <sub>3</sub> Bi <sub>2-x</sub> Sb <sub>x</sub> Br <sub>9</sub>	RhB	1.35	150	96	10
Cs <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub> /BiVO <sub>4</sub>	Sudan III	10	40	99.2	This work

**Table S2.** The fitted PL decay parameters of Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub>, BiVO<sub>4</sub> and 5% Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub>/BiVO<sub>4</sub>.

Samples	$\tau_1$	$\tau_2$	A <sub>1</sub>	A <sub>2</sub>	$\tau_{\text{ave}}$ (ns)
Cs <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub>	0.261	4.563	3165	63.55	1.38
BiVO <sub>4</sub>	0.190	2.821	1372	85.32	1.45
5% Cs <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub> /BiVO <sub>4</sub>	0.275	3.351	3519	107.2	1.11



## References

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