

## Supplementary Information

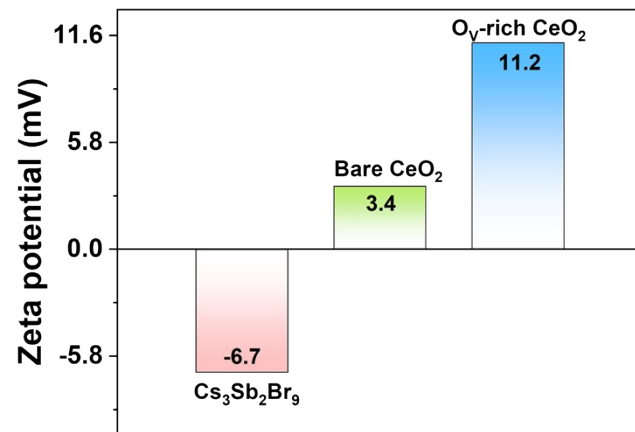
### **In situ construction of Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub>/CeO<sub>2</sub> heterojunction for efficient photooxidation of 5-hydroxymethylfurfural**

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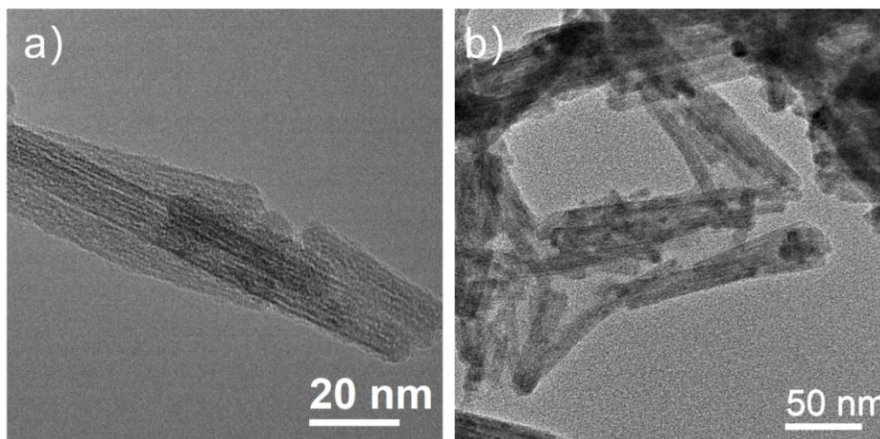
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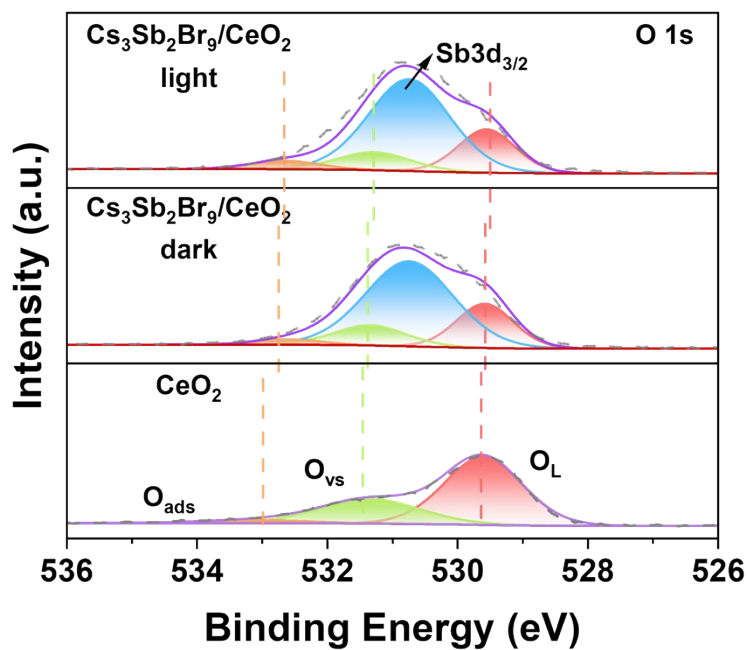
[<sup>†</sup>] These authors contributed equally to this work.



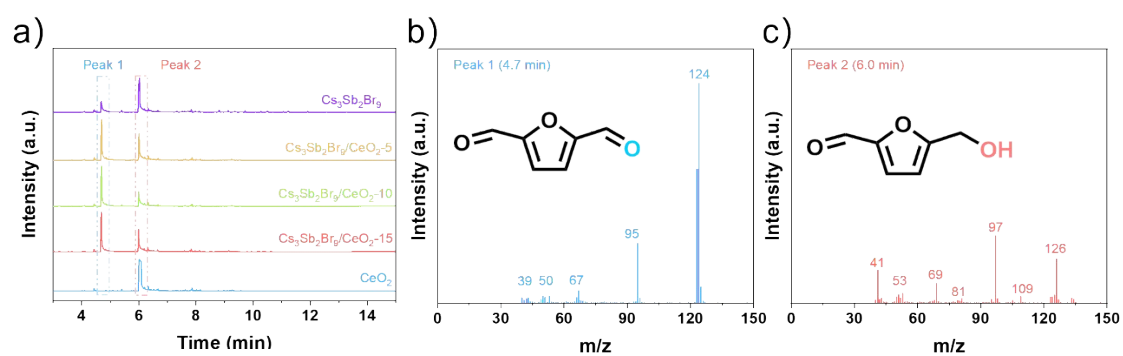
**Fig. S1.** Zeta potential of  $\text{Cs}_3\text{Sb}_2\text{Br}_9$ , Bare  $\text{CeO}_2$  and  $\text{O}_V$ -rich  $\text{CeO}_2$ .



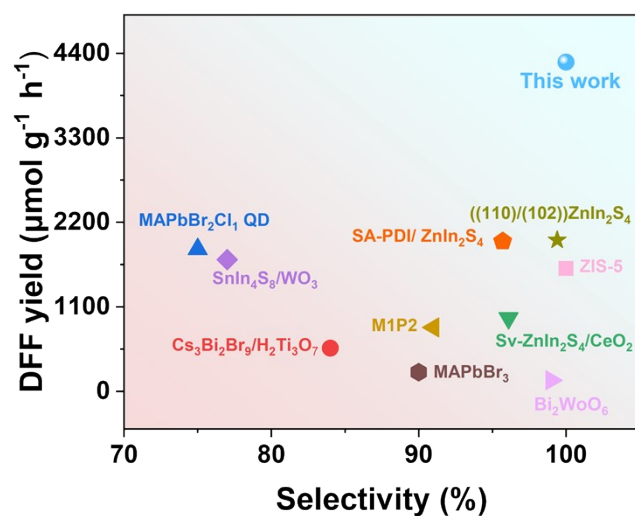
**Fig. S2.** TEM images of  $\text{CeO}_2$  (a) and  $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{CeO}_2$ -10.



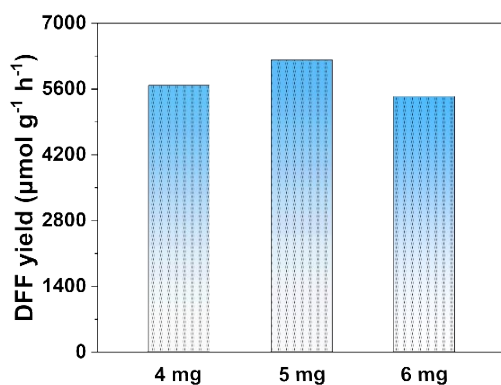
**Fig. S3.** O 1s spectra of  $\text{CeO}_2$  and  $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{CeO}_2$ -10 heterojunction.



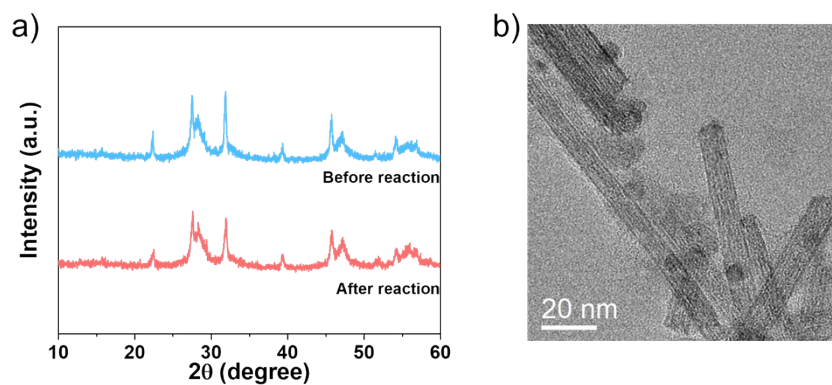
**Fig. S4.** (a) GC spectra and the corresponding MS spectra of DFF (b), HMF (c). Photocatalytic reaction conditions: 5.0 mL EtOAc, 5.0 mg cat, 20 mM HMF, 1 atm  $\text{O}_2$ , AM 1.5G 150  $\text{mW cm}^{-2}$ , 2 h illumination.



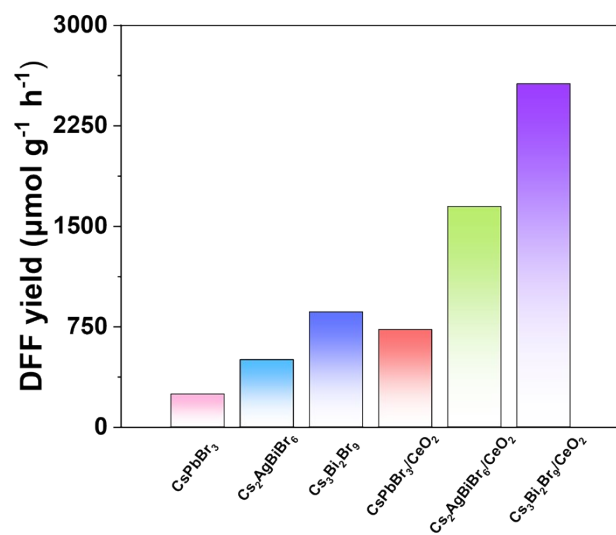
**Fig. S5.** Comparison of photocatalytic activity of Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub>/CeO<sub>2</sub> (reaction conditions: 5.0 mL EtOAc, 5.0 mg cat, 5 mM HMF, 1 atm O<sub>2</sub>, AM 1.5G 150 mW cm<sup>-2</sup>, 70 min) with literature reports.



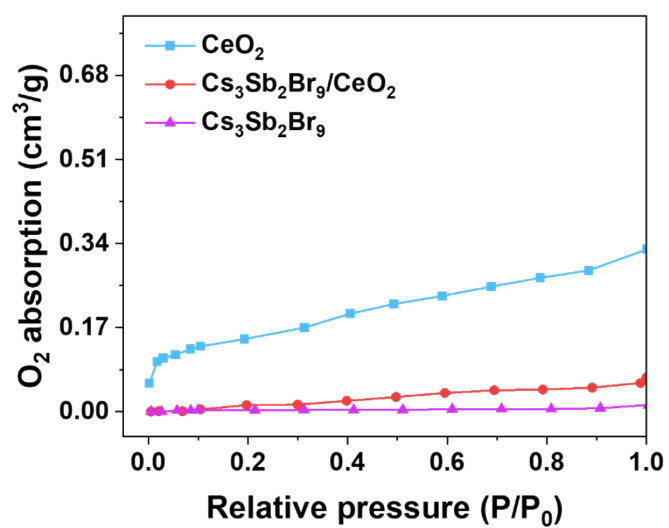
**Fig. S6.** DFF production rates under different catalyst loads (4, 5, 6 mg), identifying 5 mg as the optimal dosage. reaction conditions: 5.0 mL EtOAc, 20 mM HMF, 1 atm O<sub>2</sub>, AM 1.5G 150 mW cm<sup>-2</sup>, 2h.



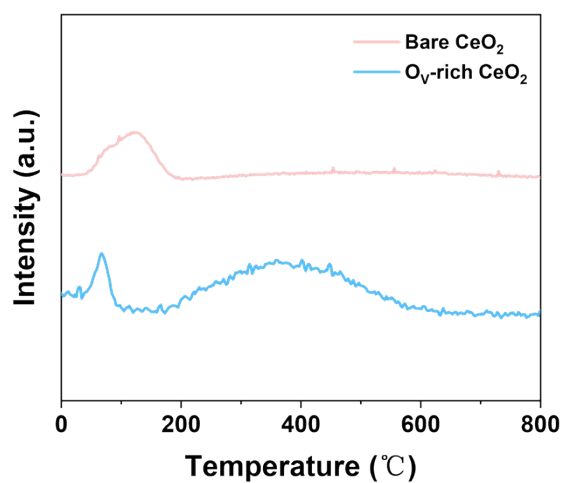
**Fig. S7.** (a) XRD patterns of  $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{CeO}_2$ -10 before and after photocatalytic reaction. (b) TEM of  $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{CeO}_2$ -10 after photocatalytic reaction (with  $\text{Na}_2\text{SO}_4$ ).



**Fig. S8.** Catalytic performance comparison of different perovskites and heterojunctions for HMF oxidation.



**Fig. S9.** O<sub>2</sub> adsorption curves of CeO<sub>2</sub>, Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> and Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub>/CeO<sub>2</sub>.



**Fig. S10.** O<sub>2</sub>-TPD curves of Bare CeO<sub>2</sub> and O<sub>V</sub>-rich CeO<sub>2</sub>.

**Table S1.** Comparison of photocatalytic HMF oxidation performances of Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub>/CeO<sub>2</sub> with previously reported photocatalytic systems (low HMF concentration, ≤ 10 mM ).

Photocatalyst	Reaction conditions	Time	HMF conv. (%)	DFF Selec. (%)	DFF Yield (μmol g <sup>-1</sup> h <sup>-1</sup> )	Ref.
Cs <sub>3</sub> Sb <sub>2</sub> Br <sub>9</sub> /CeO <sub>2</sub>	5 mg catalyst, 5 mM HMF, ethyl acetate (5 mL), AM 1.5 G, 150 mW/cm <sup>2</sup> , O <sub>2</sub>	70 min	100	100	4285.7	This work
ZIS-5	20 mg catalyst, 8 mM HMF, acetonitrile (5 mL), visible light irradiation (λ ≥ 420 nm), air, 25 °C	70 min	92	100	1600	1
Cs <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub> /H <sub>2</sub> Ti <sub>3</sub> O <sub>7</sub>	10 mg catalyst, 5 mM HMF, acetonitrile (2 mL), Blue Led (25 mW cm <sup>-2</sup> ), <467 nm, O <sub>2</sub>	1.5 h	97	84	562.7	2
MAPbBr <sub>1</sub> Cl <sub>2</sub> QD	4.5 mg catalyst, 5 mM HMF, ethyl acetate (2.5 mL), and 7.1 W blue light-emitting diodes, O <sub>2</sub>	3 h	100	75	1851.9	3
Sv-ZnIn <sub>2</sub> S <sub>4</sub> /CeO <sub>2</sub>	30 mg catalyst, 8 mM HMF, acetonitrile (5 mL), 300 W Xenon lamp (λ > 420 nm), air, 25 °C	80 min	100	96.1	952.6	4
SnIn <sub>4</sub> S <sub>8</sub> /WO <sub>3</sub>	20 mg catalyst, 10mM HMF, acetonitrile (10 mL), 300 W Xenon lamp, O <sub>2</sub>	2 h	89	77.0	1715	5
MAPbBr <sub>3</sub>	40 mg catalyst, 5 mM HMF, acetonitrile (10 mL), 450 nm blue LED light, 170 mWcm <sup>-2</sup>	10 h	100	90	112	6
((110)/(102))ZnIn <sub>2</sub> S <sub>4</sub>	20 mg catalyst, 5 mM of HMF acetonitrile (10 mL), 300 W xenon lamp, O <sub>2</sub>	1 h	91.1	99.4	1970	7
SA-PDI/ZnIn <sub>2</sub> S <sub>4</sub>	20 mg catalyst, 2 mM HMF, acetonitrile (10 mL), 300 W xenon lamp, O <sub>2</sub>	1 h	97.3	95.7	1952	8
M1P2	100 mg catalyst, 6.3 mM HMF, acetonitrile (15 mL), 25 °C, air, 405 nm	40 min	61	91	832	9
Bi <sub>2</sub> WO <sub>6</sub>	20 mg catalyst, 10 mM HMF, acetonitrile (5 mL), 300 W xenon light, (λ > 420 nm)	10 h	58.3	99	145	10

**Table S2.** Comparison of photocatalytic HMF oxidation performances of Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub>/CeO<sub>2</sub> with previously reported photocatalytic systems (high HMF concentration ).

Photocatalyst	Reaction conditions	Time	HMF conv. (%)	DFF Selec. (%)	DFF Yield ( $\mu\text{mol g}^{-1} \text{h}^{-1}$ )	Ref.
Cs <sub>3</sub> Sb <sub>2</sub> Br <sub>9</sub> /CeO <sub>2</sub>	5 mg catalyst, 20 mM HMF, ethyl acetate (5 mL), AM 1.5 G, 150 mW/cm <sup>2</sup> , O <sub>2</sub>	2 h	64	100	6226.1	This work
P-Cd <sub>0.5</sub> Zn <sub>0.5</sub> S	1 mg catalyst, 16 mM HMF, pure water (5 mL), White LED light sources (30 × 3 W)	6 h	40	65	2600	11
CC/ZnIn <sub>2</sub> S <sub>4</sub>	20 mg catalyst, 20 mM HMF, acetonitrile (20 mL), xenon lamp 400~780 nm, air	4 h	21.8	100	745	12
ZIS/CuO-180	25 mg catalyst, 20 mM HMF, H <sub>2</sub> O (10 mL), O <sub>2</sub> , 445 nm	3 h	45	85.8	2666.7	13
Cd <sub>0.7</sub> Zn <sub>0.3</sub> S/NiSe	10 mg catalyst, 33 mM HMF, acetonitrile (3 mL), 300 W Xe lamp (780 nm $\geq$ $\lambda$ $\geq$ 400 nm), air	11 h	/	98	1730	14

**Table S3.** PL decay parameters of the CeO<sub>2</sub> and Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub>/CeO<sub>2</sub>-10.

Sample	$\tau_1$ (ns)	A <sub>1</sub> %	$\tau_2$ (ns)	A <sub>2</sub> %	$\tau_3$ (ns)	A <sub>3</sub> %	$\tau_{\text{average}}$ (ns)
CeO <sub>2</sub>	0.987	22.23	3.543	52.78	12.07	24.99	5.11
Cs <sub>3</sub> Sb <sub>2</sub> Br <sub>9</sub> /CeO <sub>2</sub> -10	0.974	66.88	2.031	29.66	15.85	3.46	1.80

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