

Electronic Supporting Information for

High-efficiency visible-light-driven oxidation of primary C–H bonds in toluene over CsPbBr₃ perovskite supported by hierarchical TiO₂ nanoflakes

Jiayu Yi,^a Sunzai Ke,^a Suwei Lu,^a Bo Weng,^b Lijuan Shen,^a Xuhui Yang,^a Hun Xue,^a Min-

Quan Yang^{*a} and Qingrong Qian^{*a}

^a College of Environmental and Resource Sciences, College of Carbon Neutral Modern Industry, Fujian Key Laboratory of Pollution Control & Resource Reuse, Fujian Normal University, Fuzhou 350117, P. R. China

^b cMACS, Department of Microbial and Molecular Systems, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium

**To whom correspondence should be addressed*

E-mail: yangmq@fjnu.edu.cn; qrqian@fjnu.edu.cn

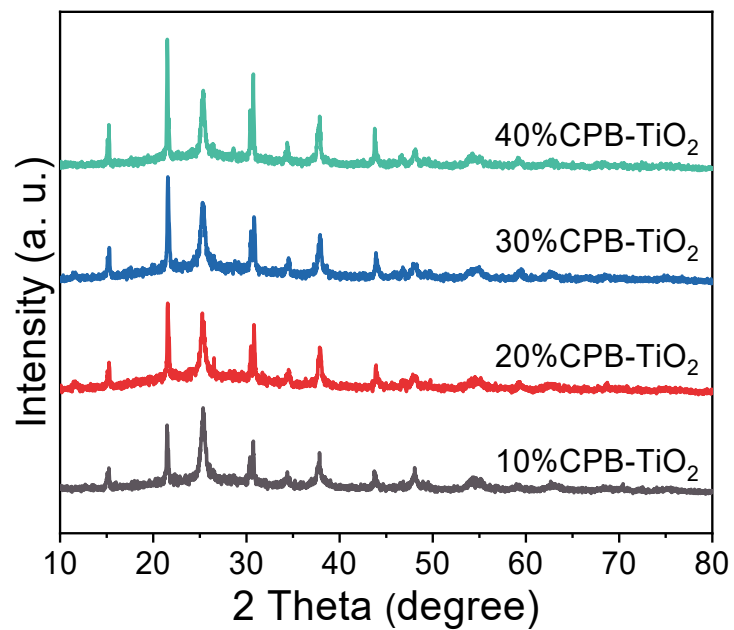


Figure S1. XRD patterns of CPB/TiO₂ composites with different weight contents of CsPbBr₃.

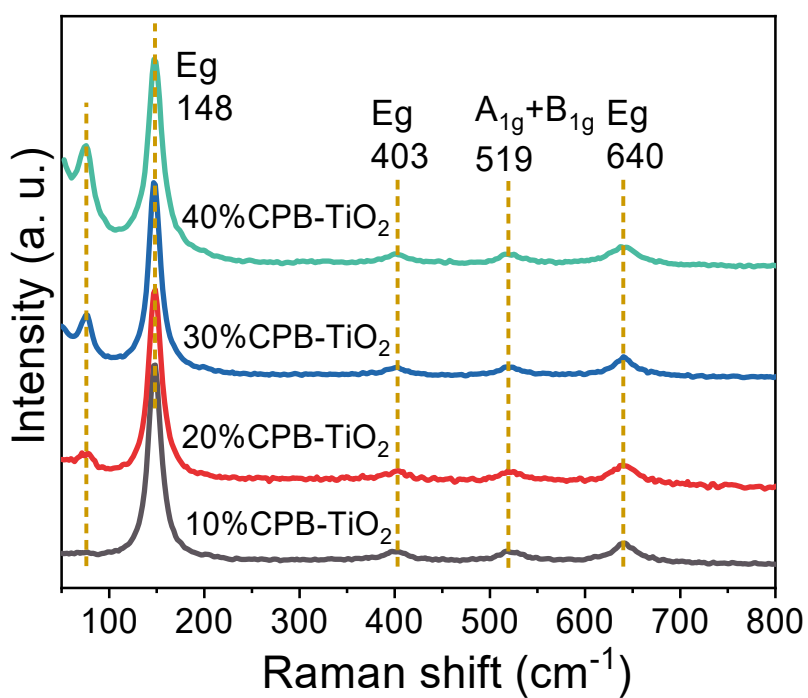


Figure S2. Raman spectra of CPB/TiO₂ composites with different weight contents of CsPbBr₃.

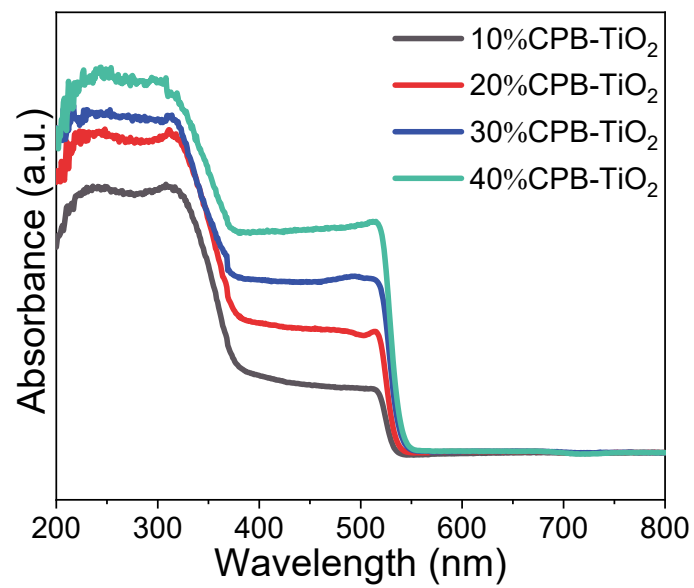


Figure S3. UV-vis diffused reflectance spectra of CPB/TiO₂ composites with different weight contents of CsPbBr₃.

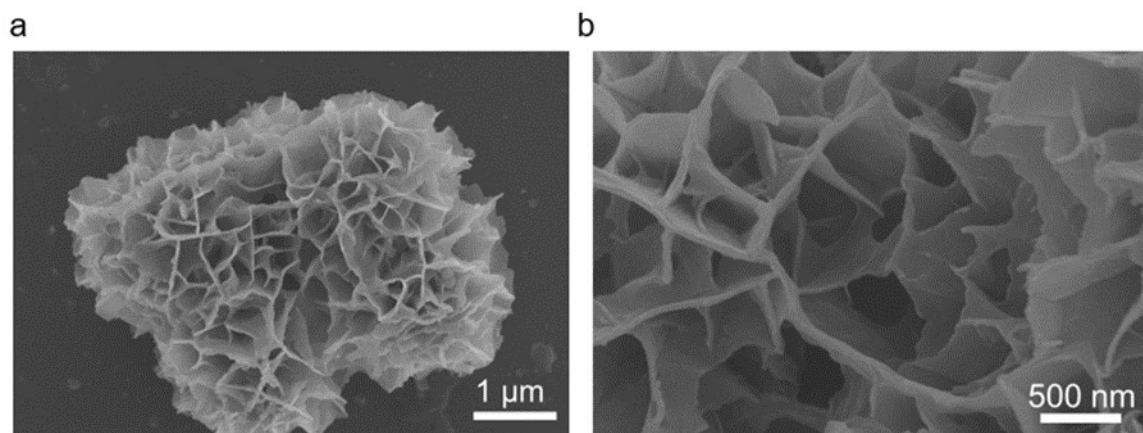


Figure S4. SEM images of blank TiO₂.

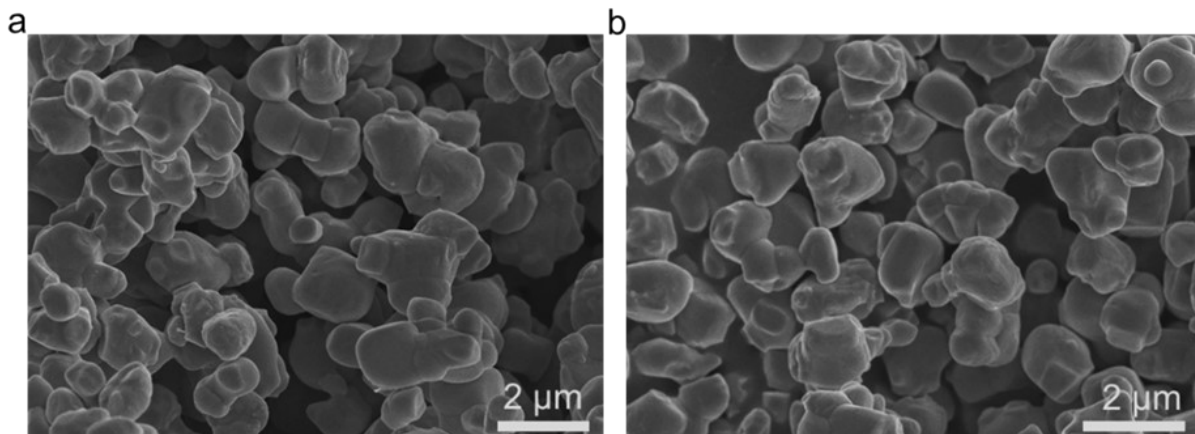


Figure S5. SEM images of blank CsPbBr₃.

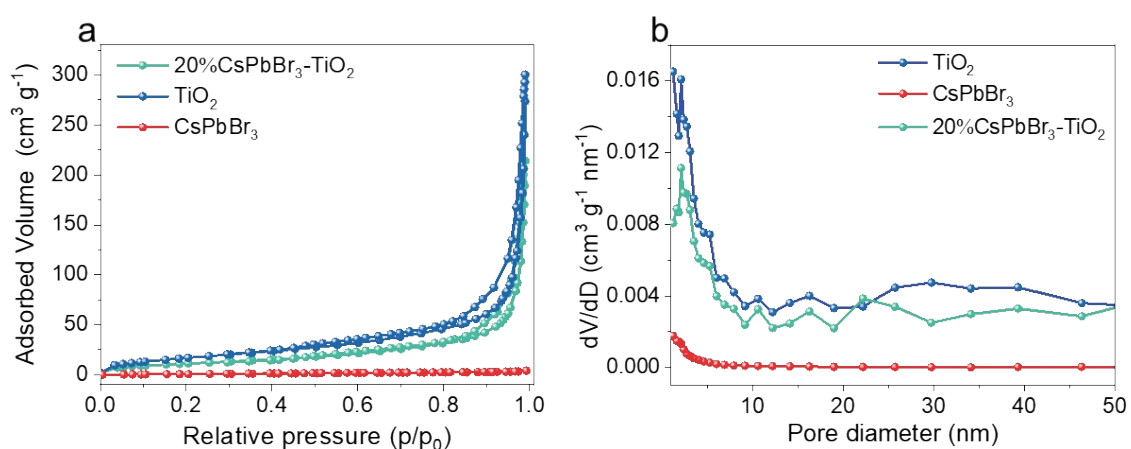


Figure S6. N₂ adsorption-desorption isotherms and the corresponding pore size distributions of blank TiO₂, CsPbBr₃ and 20% CPB/TiO₂ composite.

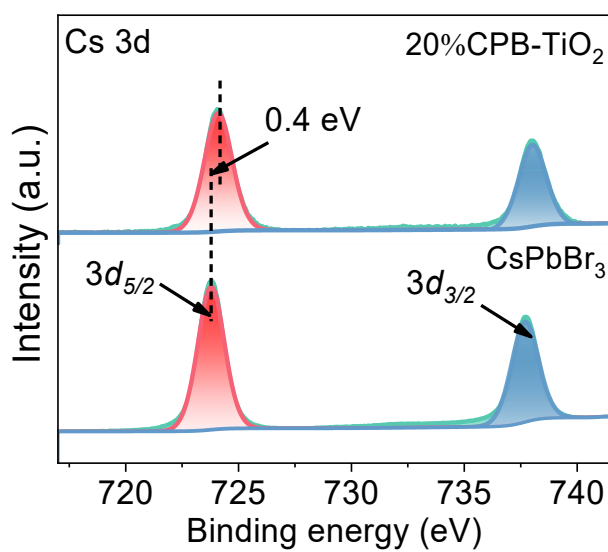


Figure S7. Cs 3d XPS spectra of CsPbBr₃ and 20%CPB/TiO₂.

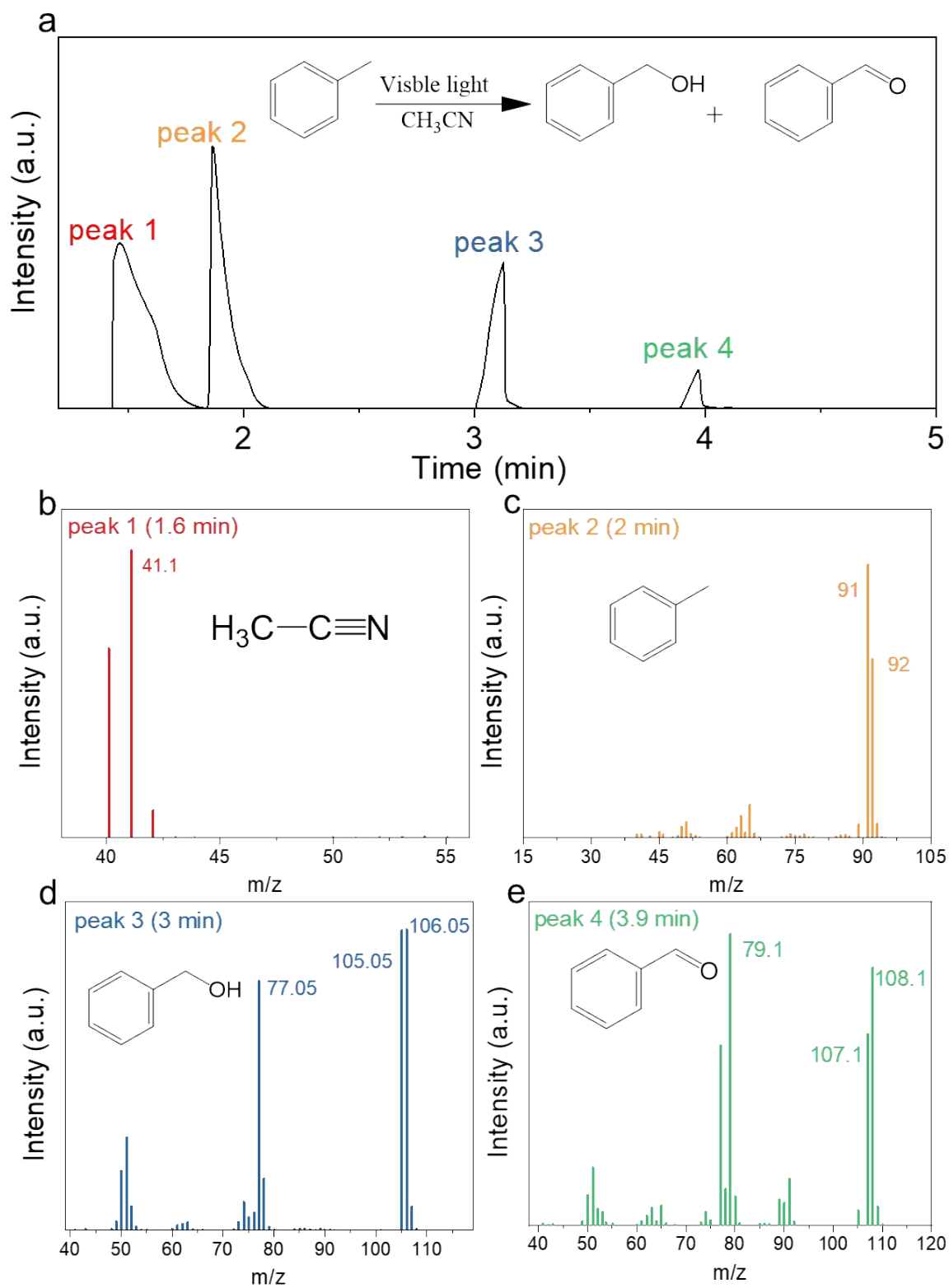


Figure S8. GC-MS spectra of the reaction solution after photocatalytic experiment.
Conditions: 1 ml toluene, 10 mg 20%CPB/TiO₂, 2 mL CH₃CN, $\lambda > 420$ nm.

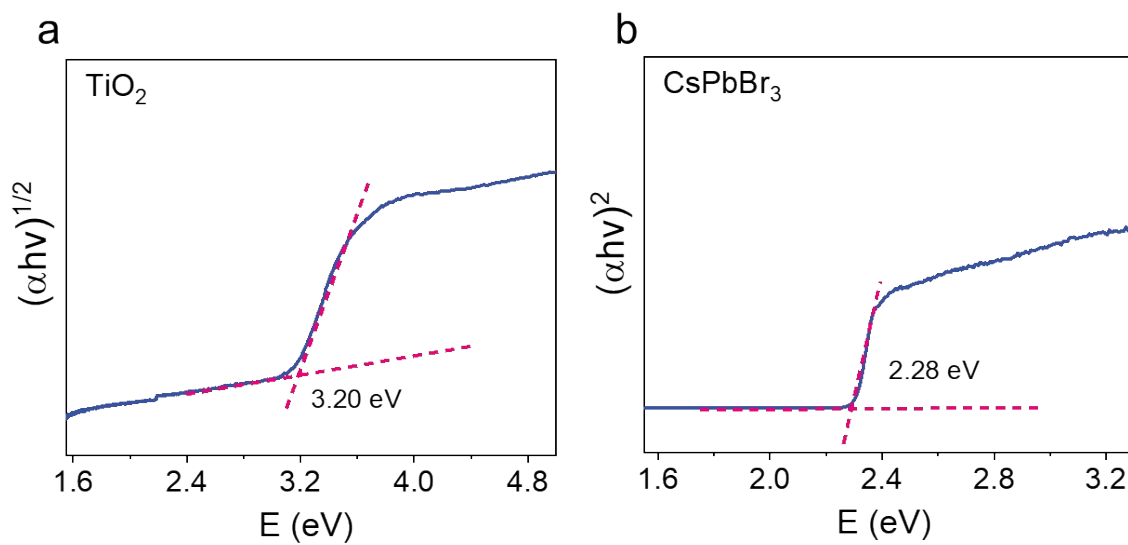


Figure S9. Band-gap values of (a) TiO₂ and (b) CsPbBr₃.

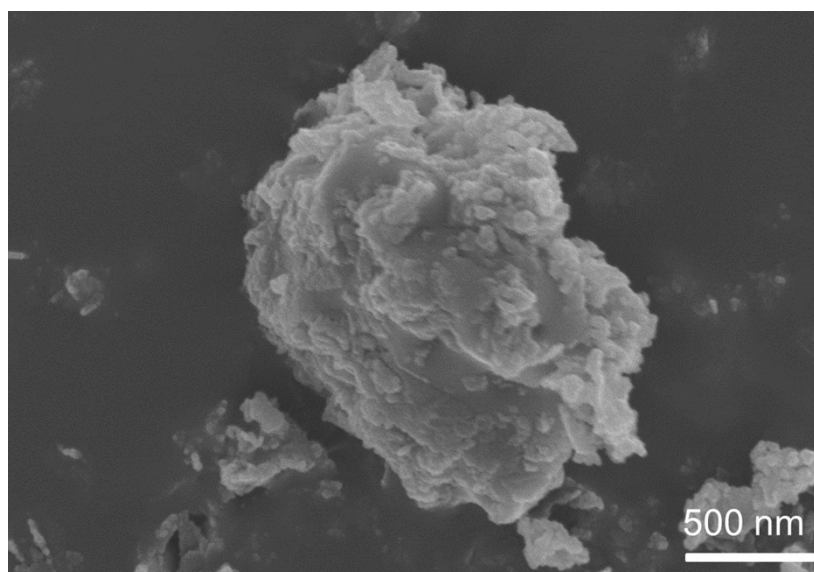


Figure S10. SEM image of collapsed TiO₂ without hierarchical structure.

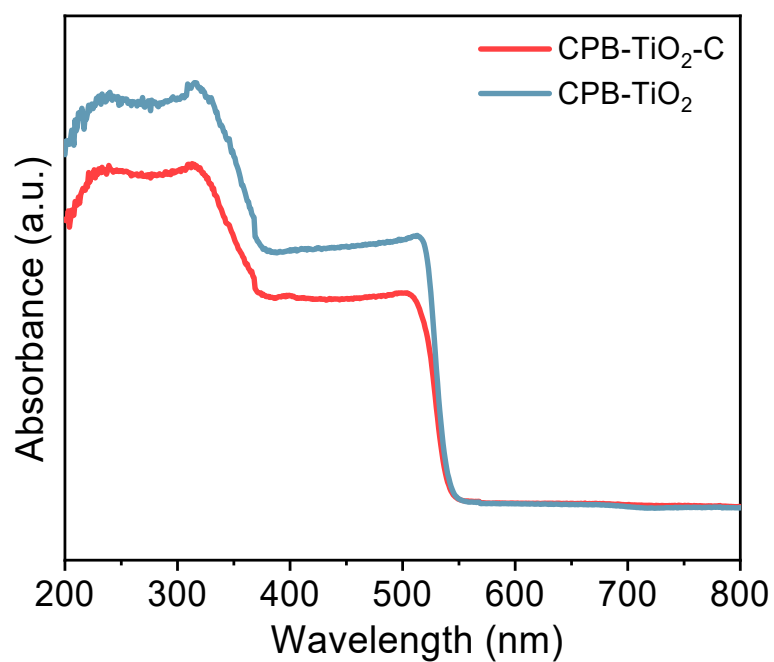


Figure S11. UV-vis diffused reflectance spectra of CPB/TiO₂ and CPB/TiO₂-C.

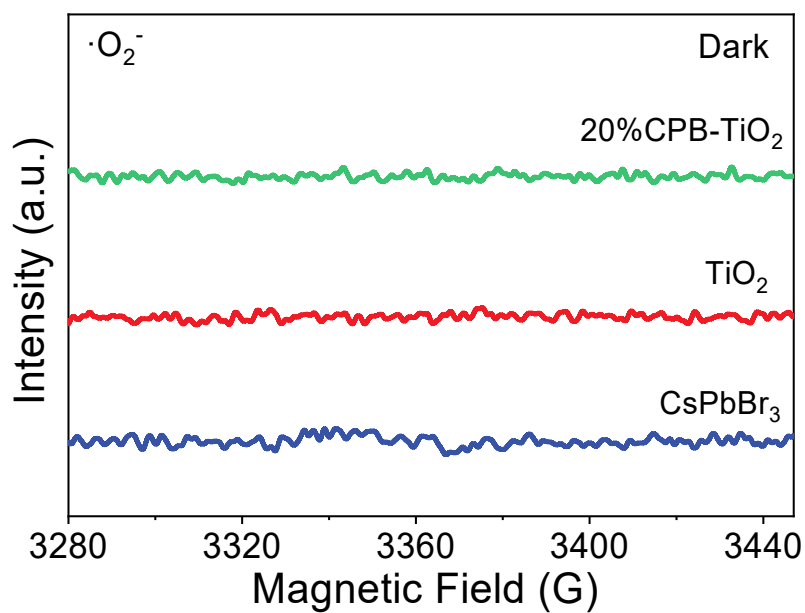


Figure S12. EPR spectra of DMPO-•O₂⁻ without light.

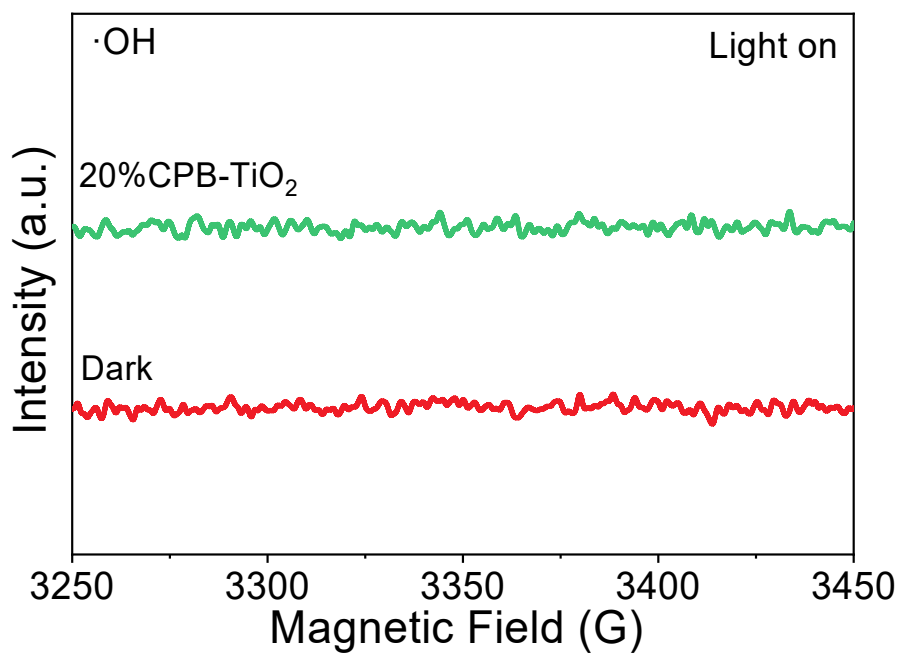


Figure S13. EPR spectra of DMPO-•OH for 20%CPB/TiO₂ in the presence of light and without light.

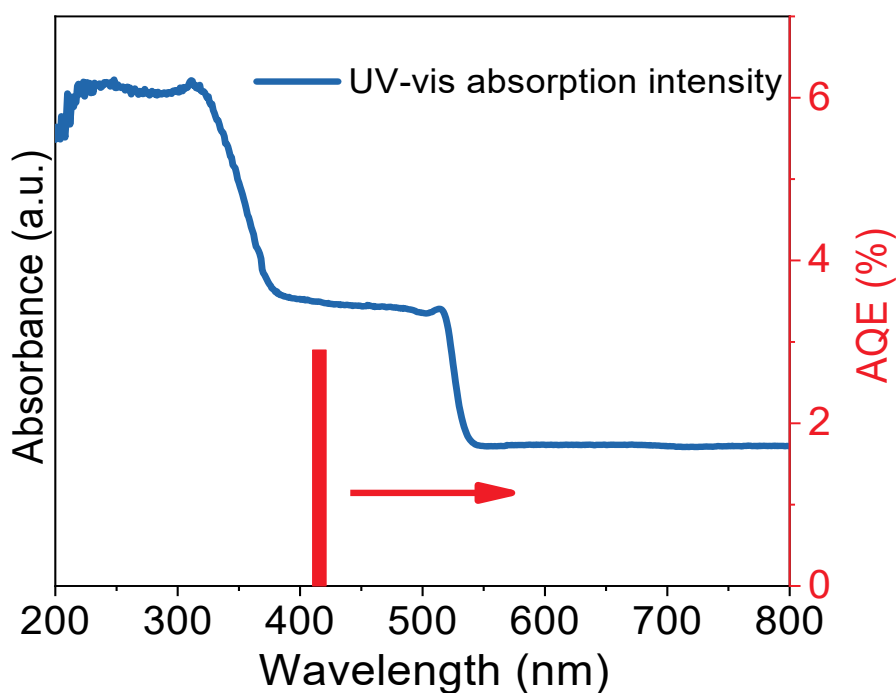


Figure S14. The apparent quantum efficiency measured at 420 ± 5 nm of 20%CsPbBr₃/TiO₂ composite.

Note: The number of incident photons (N) is calculated by equation 1. The corresponding AQE is calculated to be 2.9% according to equation 2.

$$N = \frac{E\lambda}{hc} = \frac{I \times A \times t \times \lambda}{h \times c} \quad (\text{Equation 1})$$

$$AQE = \frac{\text{Number of transformed toluene}}{\text{Number of incident photos}} = \frac{M \times N_A}{N} \quad (\text{Equation 2})$$

Where I is the light intensity (420.38 W m^{-2}), A is the irradiation area of catalyst solution ($1.77 \times 10^{-4} \text{ m}^2$), t is light incident time (2 h), λ is the wavenumber of incident light, h is Planck constant, c is lightspeed, M represents the amount of transformed toluene ($54.4 \text{ } \mu\text{mol}$), N_A represents Avogadro's constant.

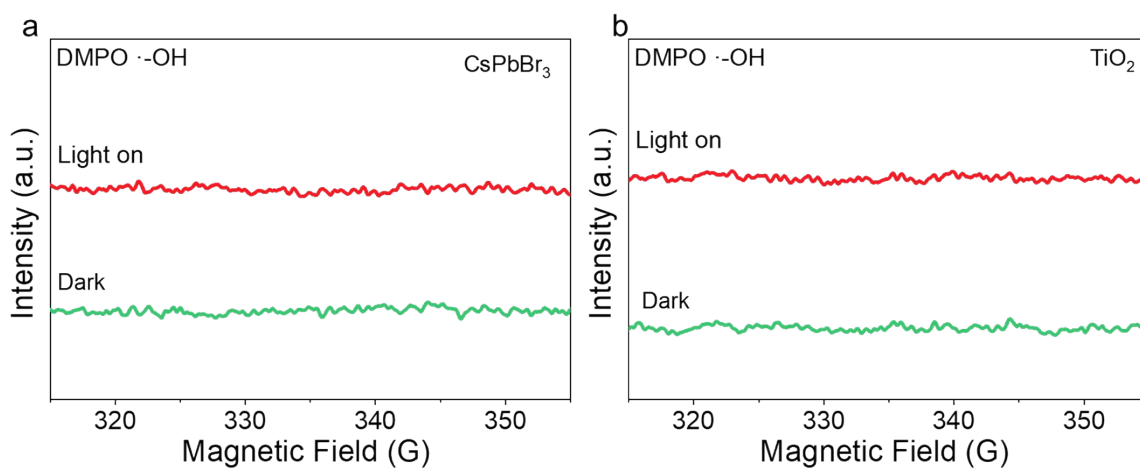


Figure S15. EPR spectra of DMPO-•OH for (a) CsPbBr₃ and (b) TiO₂ in the presence of light and without light.

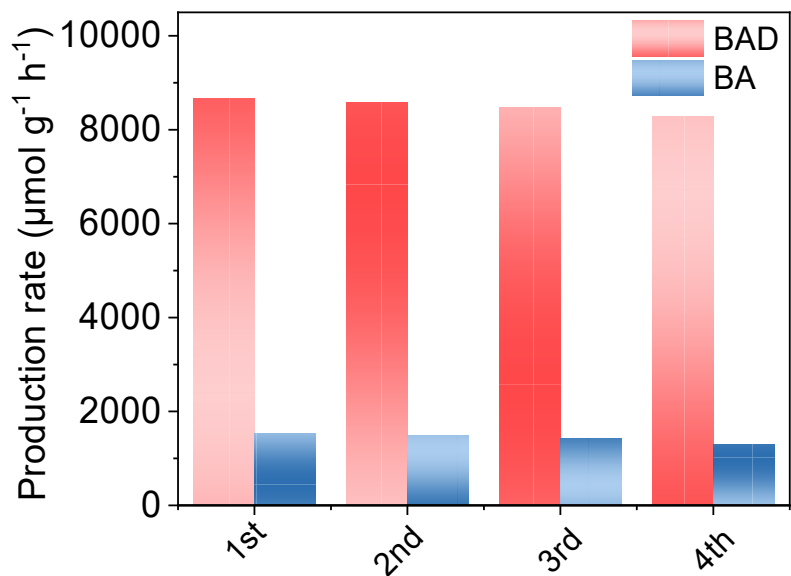


Figure S16. Cycle test of the 20%CsPbBr₃/TiO₂ under visible light.

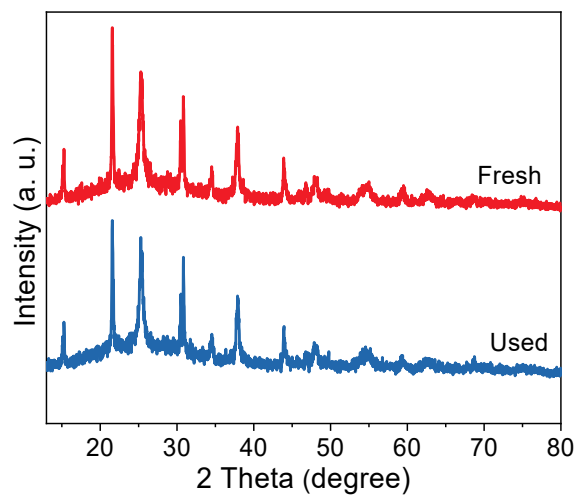


Figure S17. XRD patterns of the used and fresh 20%CsPbBr₃/TiO₂ composite..

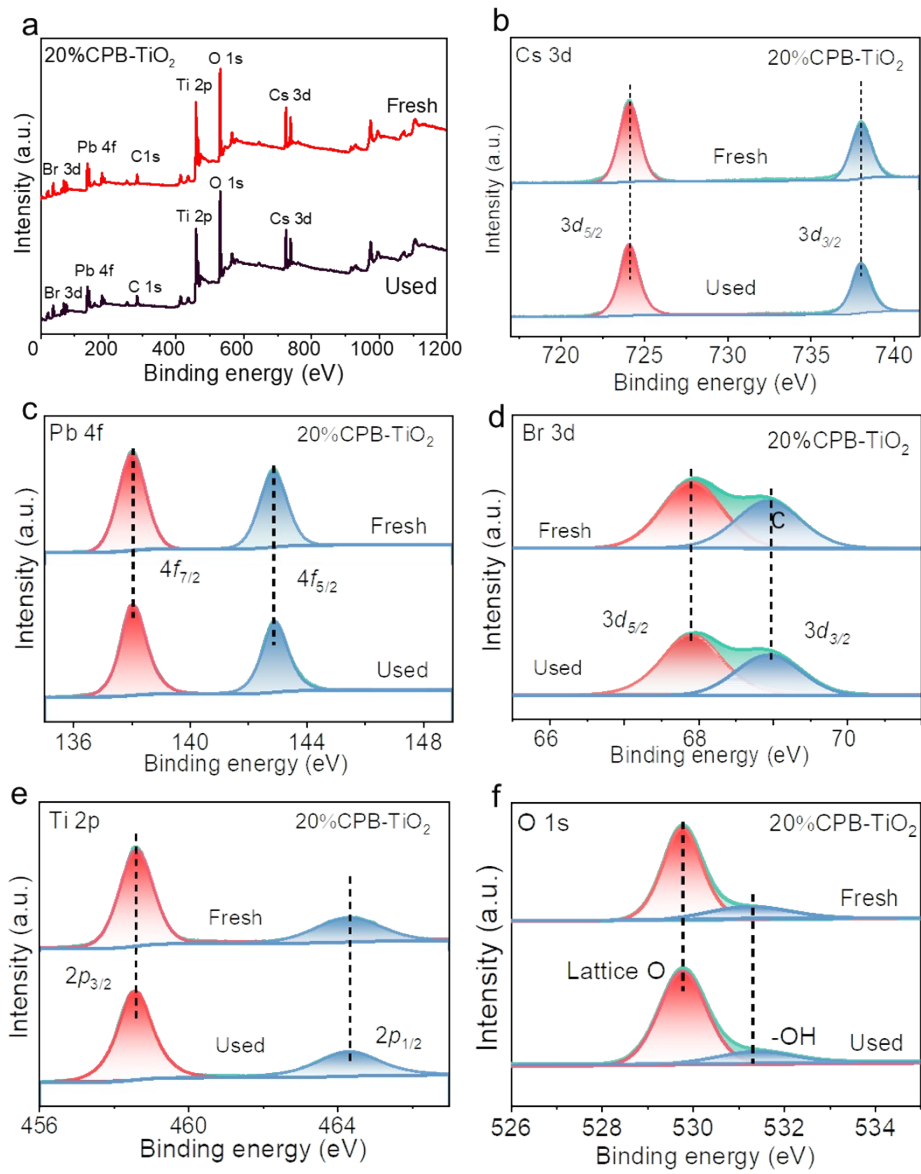


Figure 18. XPS analysis for the used and fresh 20%CsPbBr₃/TiO₂ composite.

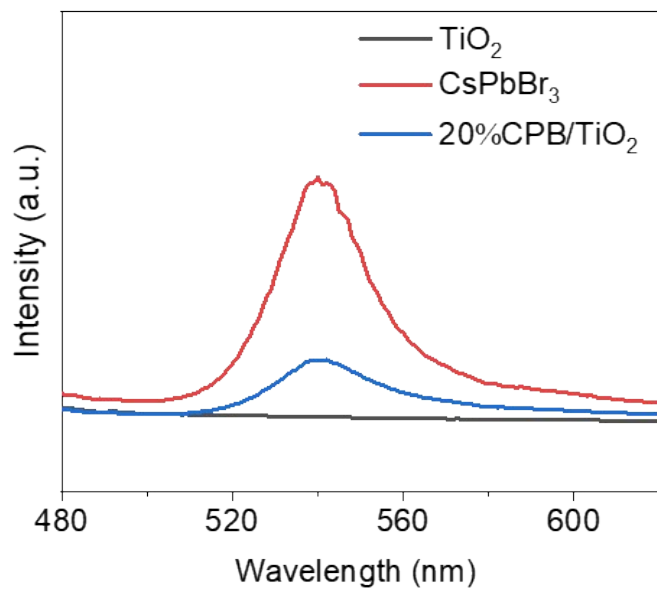


Figure S19. The PL spectra of CsPbBr₃, TiO₂ and 20%CsPbBr₃/TiO₂.

Table S1. Summary of surface area and pore volume of the TiO₂, CsPbBr₃ and CPB/TiO₂ composites.

Samples	Surface area (m² g⁻¹)	Pore volume (cm³ g⁻¹)
TiO ₂	66.467	0.455
CsPbBr ₃	3.196	0.006
20% CPB/TiO ₂	41.882	0.317

Table S2. Comparison on photocatalytic activity for selective toluene oxidation over the photocatalysts prepared in the present work and reported in the literature.

Photocatalyst	Reaction condition	Rate ($\mu\text{mol}/(\text{g h})$)	Ref.
CsPbBr ₃ /TiO ₂	$\lambda \geq 420$ nm, sample (15 mg), toluene (1 mL), O ₂ (0.1 MPa), reaction time (5 h)	10200	This work
TiO ₂ /Bi ₂ MoO ₆	$\lambda \geq 400$ nm, sample (50 mg), toluene (10 mmol), O ₂ (3 mL/min), reaction time (3 h)	1069	[1]
CdS@C ₃ N ₄	$\lambda > 400$ nm, sample (100 mg), toluene (10 mmol), O ₂ (3 mL/min), reaction time (3 h)	500	[2]
CdS	$\lambda > 420$ nm, sample (8 mg), toluene (0.1 mmol), O ₂ (0.1 MPa), reaction time (10 h)	413	[3]
BiOBr/TiO ₂	$\lambda > 420$ nm, sample (20 mg), toluene (9.4 mmol), O ₂ (0.1 MPa), reaction time (4 h)	1169	[4]
Bi ₂ WO _{6-x} /BiOCl	$\lambda > 400$ nm, sample (50 mg), toluene (10 mmol), O ₂ (1 atm), reaction time (2 h)	5162	[5]
CdIn ₂ S ₄ -CdS	$\lambda > 420$ nm, sample (10 mg), toluene (47.2 μmol), O ₂ , reaction time (6 h)	645	[6]
Fe-Bi ₂ WO ₆	$\lambda > 420$ nm, sample (20 mg), toluene (10 mmol), O ₂ (1 mL/min), reaction time (5 h)	1347	[7]
Cl-BiOBr/TiO ₂	$\lambda > 420$ nm, sample (20 mg), toluene (1 mL), O ₂ , reaction time (4 h)	2121	[4]
Cs ₃ Bi ₂ Br ₉ /g-C ₃ N ₄	$\lambda > 400$ nm, sample (10 mg), toluene (5 mL), O ₂ (0.1 MPa), reaction time (0.17 h)	8347	[8]
Cs ₃ Bi ₂ Br ₉ /P25	Full-spectrum, sample (10 mg), toluene (5 ml), O ₂ , reaction time (4 h)	10651	[9]
NiO _x /FAPbBr ₃ /TiO ₂	AM 1.5 G, sample (10 mg), toluene (2.5 ml), O ₂ , reaction time (4 h)	4419	[10]
FAPbBr ₃ /TiO ₂	AM 1.5 G, sample (10 mg), toluene (2.5 ml), O ₂ , reaction time (4 h)	2859	[10]

Reference

1. L.-N. Song, F. Ding, Y.-K. Yang, D. Ding, L. Chen, C.-T. Au and S.-F. Yin, *ACS Sustain. Chem. Eng.*, 2018, **6**, 17044-17050.
2. P. Chen, F. Liu, H. Ding, S. Chen, L. Chen, Y.-J. Li, C.-T. Au and S.-F. Yin, *Appl. Catal., B*, 2019, **252**, 33-40.
3. Y. Zhang, N. Zhang, Z.-R. Tang and Y.-J. Xu, *Chem. Sci.*, 2012, **3**.
4. R. Yuan, S. Fan, H. Zhou, Z. Ding, S. Lin, Z. Li, Z. Zhang, C. Xu, L. Wu, X. Wang and X. Fu, *Angew. Chem. Int. Ed. Engl.*, 2013, **52**, 1035-1039.
5. X. Cao, Z. Chen, R. Lin, W.-C. Cheong, S. Liu, J. Zhang, Q. Peng, C. Chen, T. Han, X. Tong, Y. Wang, R. Shen, W. Zhu, D. Wang and Y. Li, *Nat. Catal.*, 2018, **1**, 704-710.
6. Y.-X. Tan, Z.-M. Chai, B.-H. Wang, S. Tian, X.-X. Deng, Z.-J. Bai, L. Chen, S. Shen, J.-K. Guo, M.-Q. Cai, C.-T. Au and S.-F. Yin, *ACS Catal.*, 2021, **11**, 2492-2503.
7. X.-X. Deng, S. Tian, Z.-M. Chai, Z.-J. Bai, Y.-X. Tan, L. Chen, J.-K. Guo, S. Shen, M.-Q. Cai, C.-T. Au and S.-F. Yin, *Ind. Eng. Chem. Res.*, 2020, **59**, 13528-13538.
8. Z.-J. Bai, Y. Mao, B.-H. Wang, L. Chen, S. Tian, B. Hu, Y.-J. Li, C.-T. Au and S.-F. Yin, *Nano Res.*, 2023, **16**, 6104-6112.
9. Z. Cui, Q. Zhang, H. Fu, Q. Liu, X. Liu, Y. Wu, P. Gao, Z. Wang, Z. Zheng, H. Cheng, Y. Liu, Y. Dai, B. Huang and P. Wang, *Appl. Catal., B*, 2023, **333**, 122812.
10. H. Huang, H. Yuan, J. Zhao, G. Solís-Fernández, C. Zhou, J. W. Seo, J. Hendrix, E. Debroye, J. A. Steele, J. Hofkens, J. Long and M. B. J. Roelofs, *ACS Energy Lett.*, 2018, **4**, 203-208.