

Supporting Information

Spatial Construction of Pd and MnO_x on Facet-engineered BiVO₄ Photocatalyst for Efficient Removal of Glyphosate Pesticide

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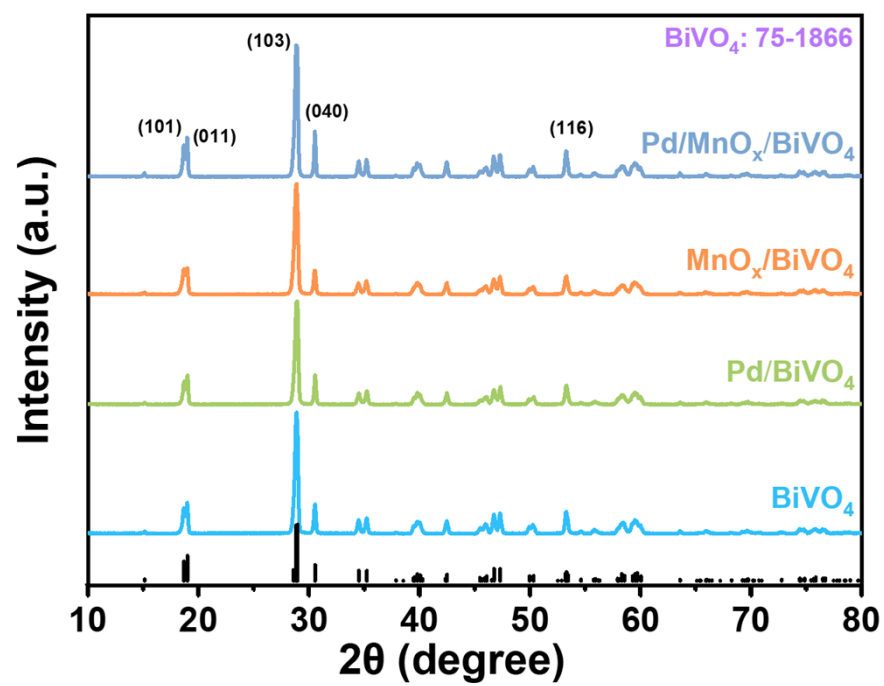


Fig. S1. XRD patterns of decahedron BiVO₄ crystals and BiVO₄ with different cocatalysts.

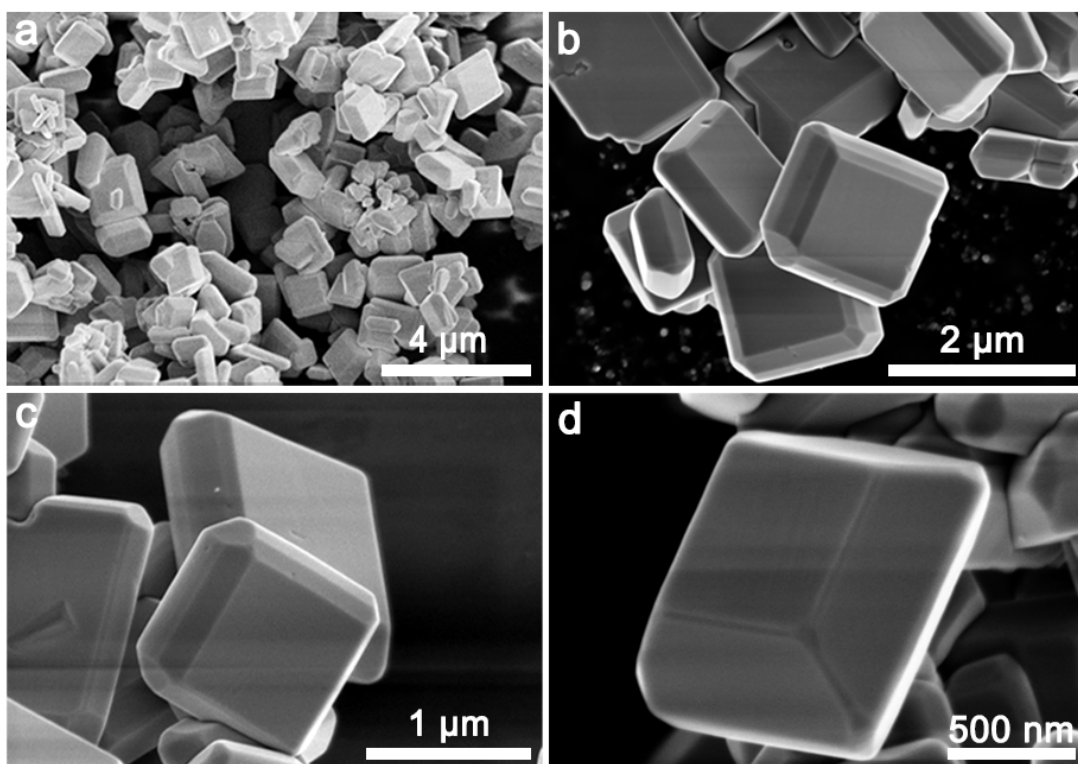


Fig. S2. SEM images of BiVO₄ nanoparticles.

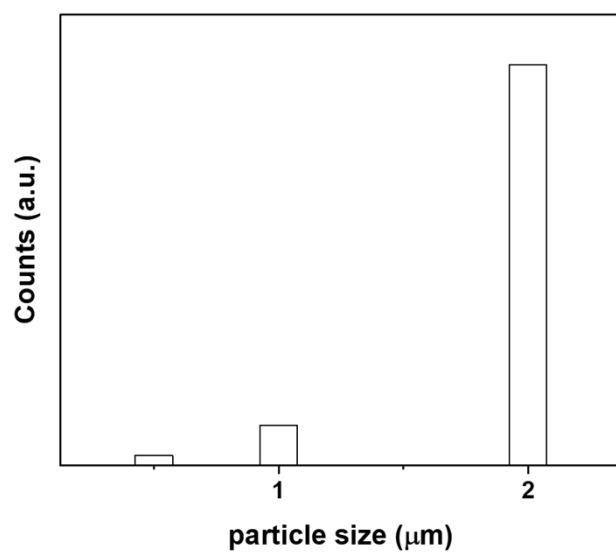


Fig. S3. The particle size distribution of BiVO₄ particles.

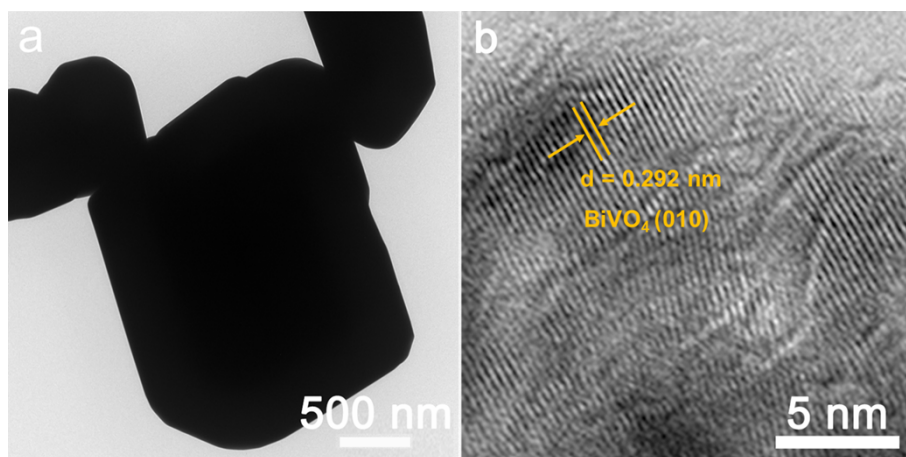


Fig. S4. TEM and HRTEM images of BiVO_4 nanoparticle.

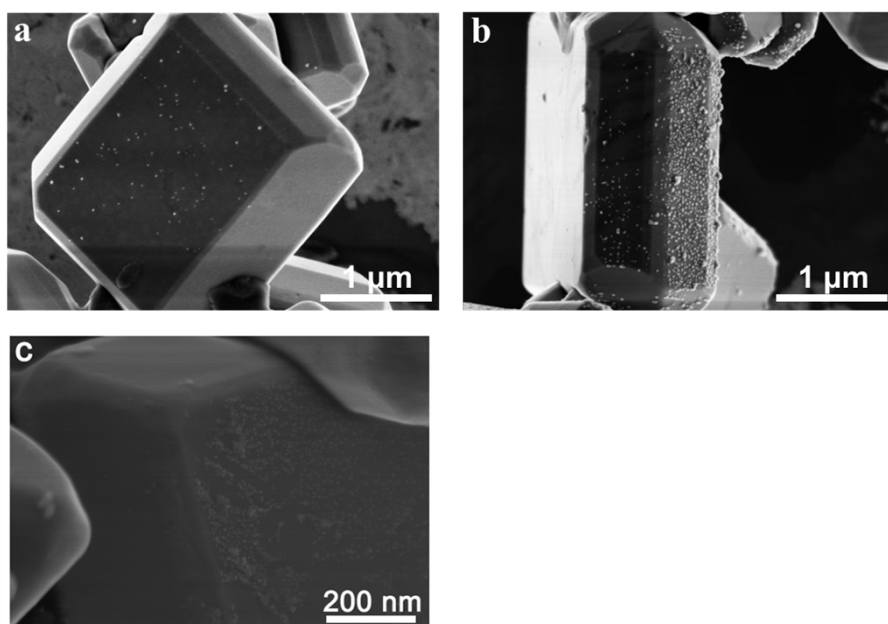


Fig. S5. SEM images of BiVO₄ samples with deposition of (a) Au, (b) Ag, (c) Pd.

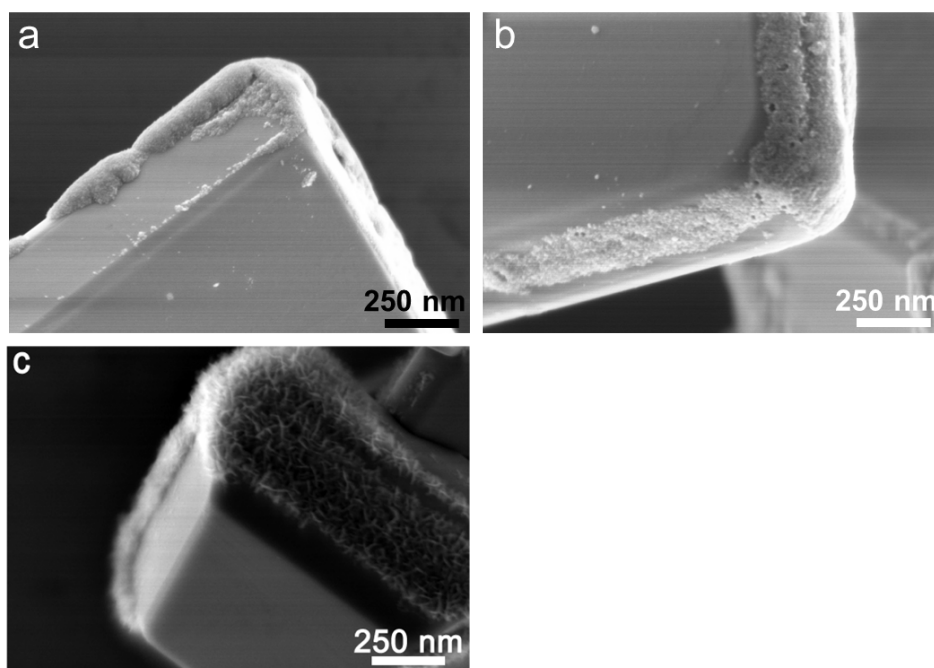


Fig. S6. SEM images of BiVO₄ samples with oxide deposition of (a) CoO_x, (b) NiO_x, (c) MnO_x.

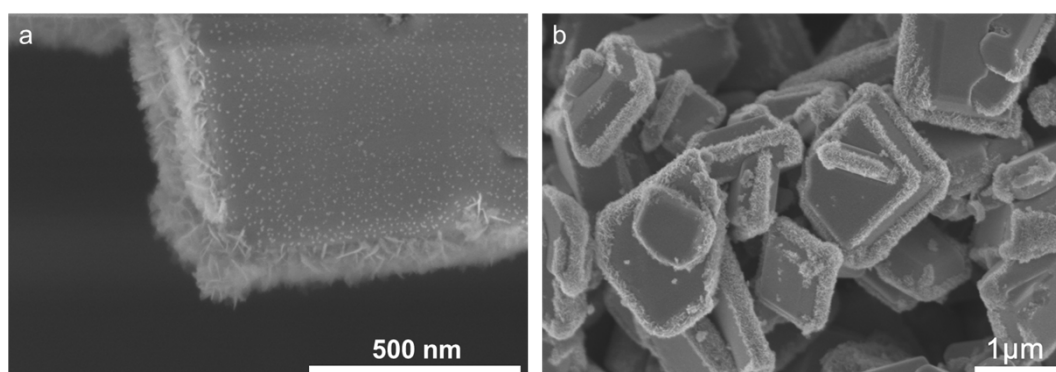


Fig. S7. SEM images of BiVO_4 samples with selective deposition of dual cocatalysts.

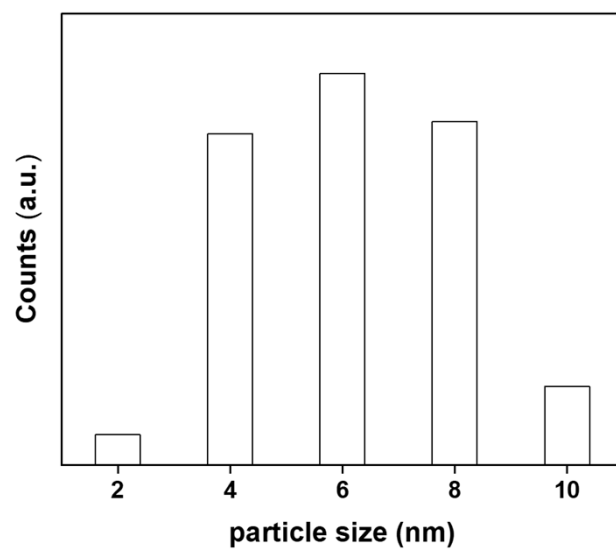


Fig. S8. The particle size distribution of Pd nanoparticles on Pd/MnO_x/BiVO₄.

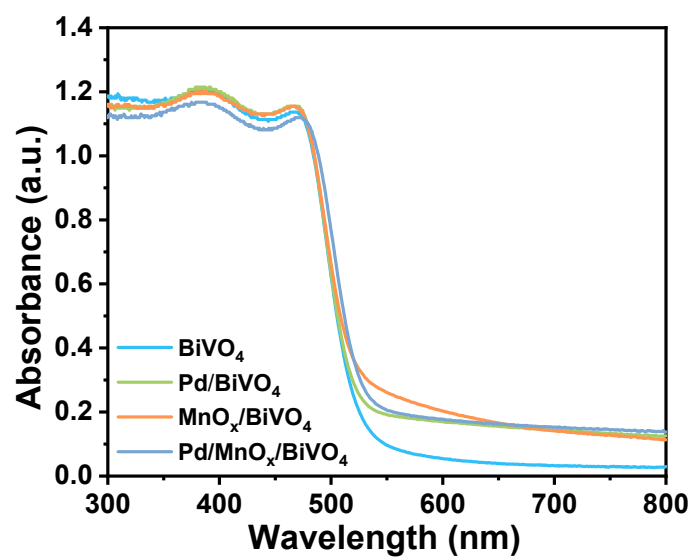


Fig. S9. UV-vis diffuse reflectance spectra of decahedron BiVO₄ crystals and BiVO₄ with different cocatalysts.

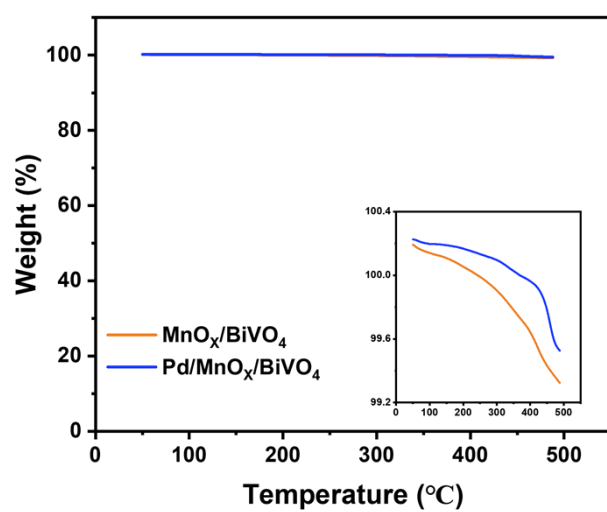


Fig. S10. Thermogravimetry curves of MnO_x/BiVO₄ and Pd/MnO_x/BiVO₄.

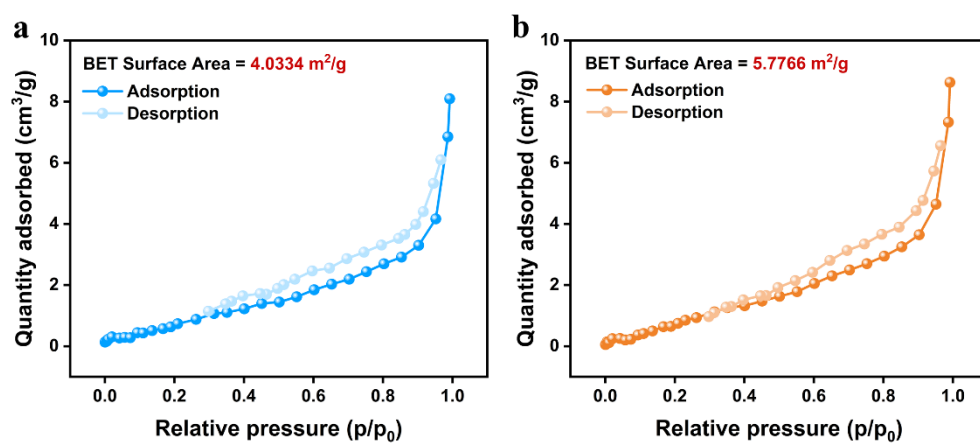


Fig. S11. BET measurement of $\text{MnO}_x/\text{BiVO}_4$ and $\text{Pd}/\text{MnO}_x/\text{BiVO}_4$.

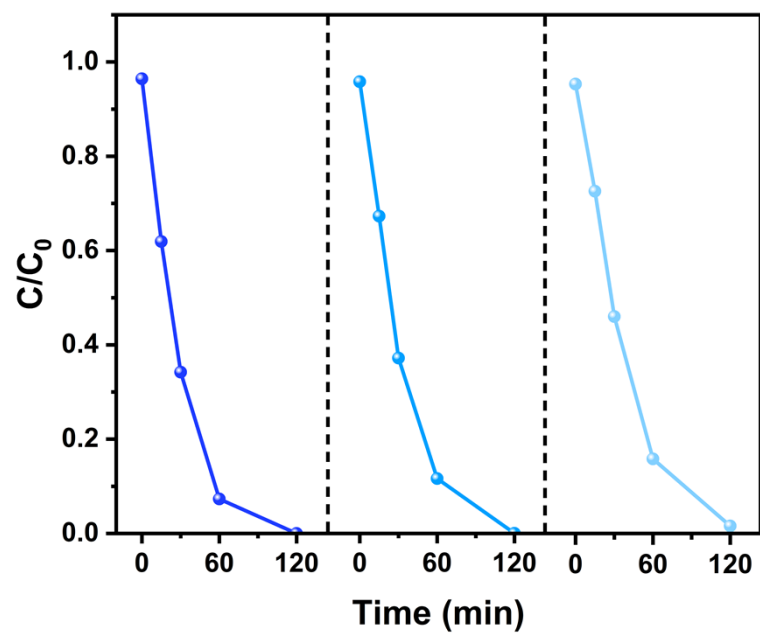


Fig. S12. The stability tests of 3 cycles for Pd/MnO_x/BiVO₄.

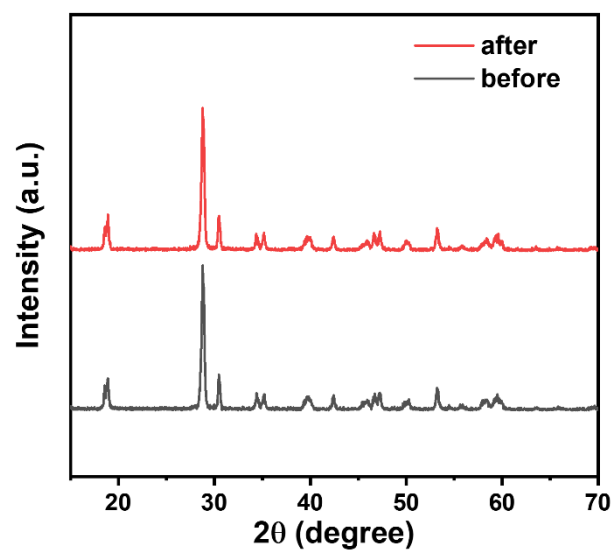


Fig. S13. XRD pattern of Pd/MnO_x/BiVO₄ photocatalyst before and after degradation.

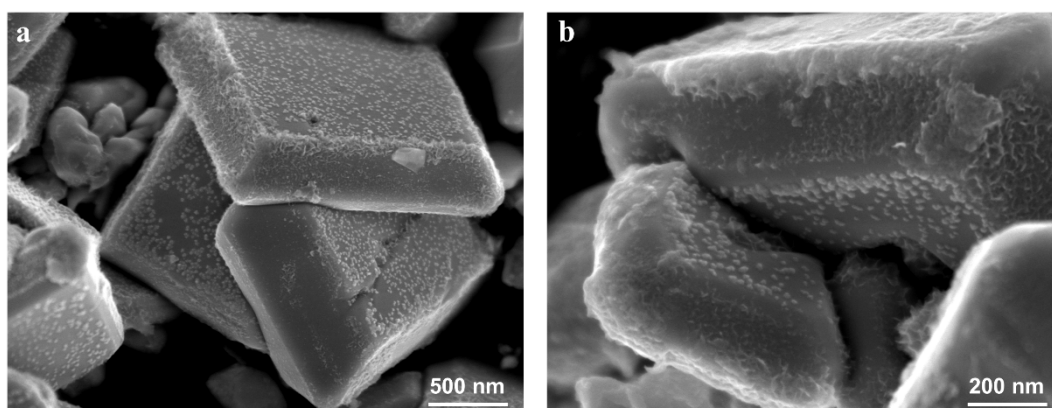


Fig. S14. SEM images of Pd/MnO_x/BiVO₄ photocatalyst after degradation.

Table S1. The concentration of Pd and Mn elements in the reaction solution

Element	Sample	Concentrations (ppm)
Pd	Before reaction	0
	After reaction	0.238
Mn	Before reaction	0
	After reaction	0.317

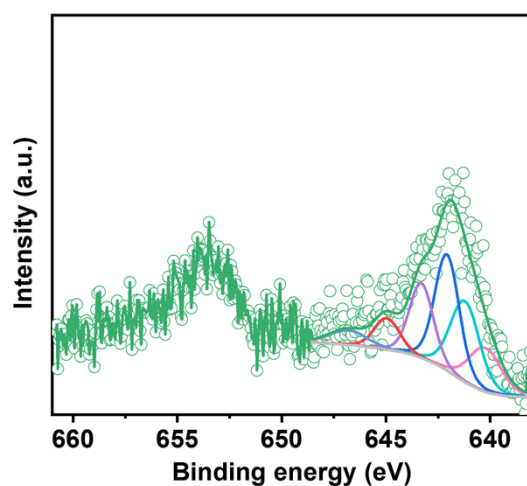


Fig. S15. Corresponding XPS fine spectra of $\text{MnO}_x/\text{BiVO}_4$ of Mn 2p.

Table S2. The summarized fitting parameters of Mn $2p_{3/2}$

Sample	Element	$2p_{3/2}$ Position (eV)	Area ratio (%)
$\text{MnO}_x/\text{BiVO}_4$ -before	Mn^{3+}	640.25	14.61
		641.21	24.08
		643.30	18.31
	Mn^{4+}	642.07	29.23
		644.95	8.14
		646.81	5.63
$\text{MnO}_x/\text{BiVO}_4$ -after	Mn^{3+}	640.22	10.24
		641.12	22.21
		643.19	19.11
	Mn^{4+}	642.19	32.40
		644.15	8.32
		646.05	7.71

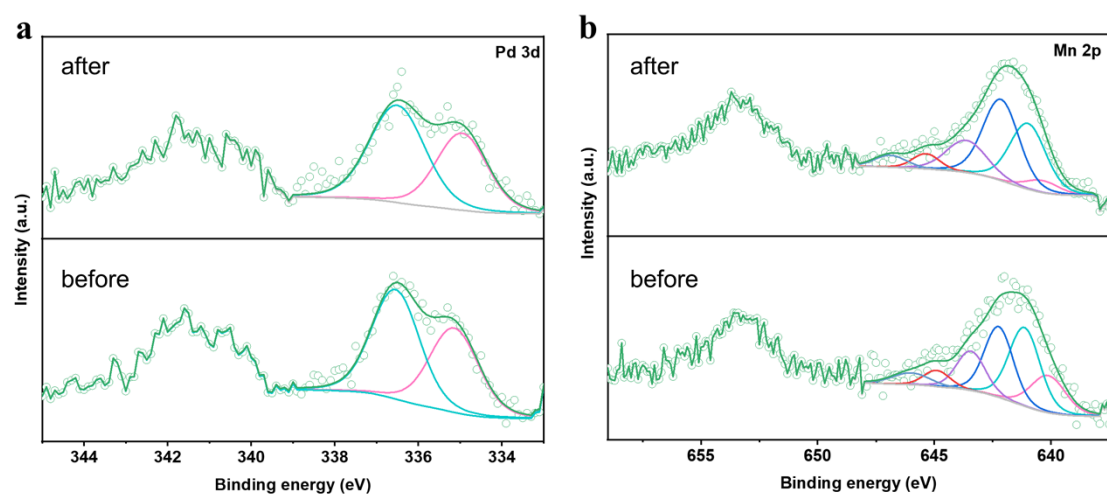


Fig. S16. Corresponding XPS fine spectra of Pd/MnO_x/BiVO₄: (a) Pd 3d and (b) Mn 2p.

Table S3. The summarized fitting parameters of Pd 3d_{5/2}

Sample		Element	3d _{5/2} Position (eV)	Area ratio (%)
Pd/MnO _x /BiVO ₄ -before		Pd	335.14	44.13
		Pd ²⁺	336.54	55.87
Pd/MnO _x /BiVO ₄ -after		Pd	335.16	42.21
		Pd ²⁺	336.50	57.79

Table S4. The summarized fitting parameters of Mn 2p_{3/2}

Sample	Element	2p _{3/2} Position (eV)	Area ratio (%)
Pd/MnO _x /BiVO ₄ -before	Mn ³⁺	640.12	16.66
		641.13	31.43
		643.43	14.54
	Mn ⁴⁺	642.24	26.24
		644.89	5.42
		646.00	5.70
Pd/MnO _x /BiVO ₄ -after	Mn ³⁺	640.37	5.28
		640.99	30.45
		643.62	16.64
	Mn ⁴⁺	642.14	37.48
		645.35	5.27
		646.88	4.88

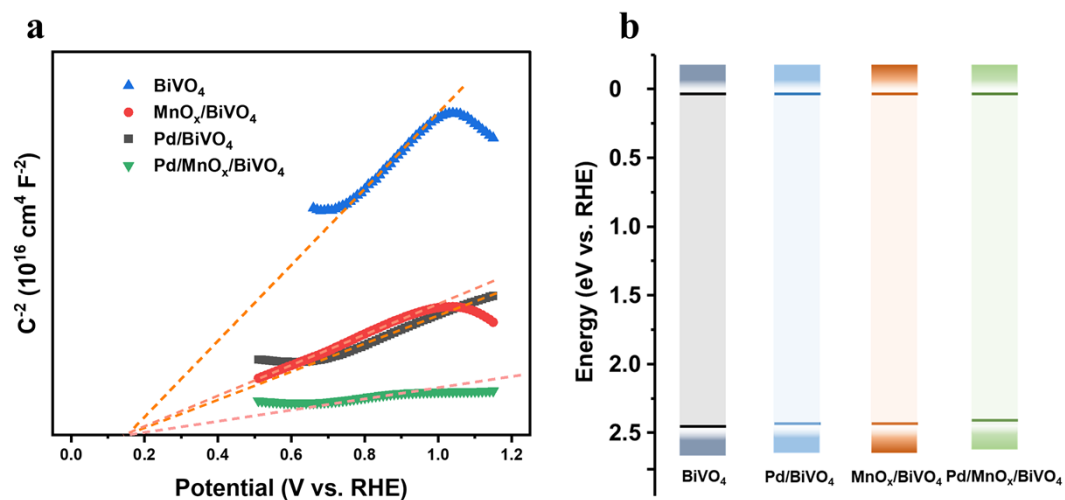


Fig. S17. (a) Mott-Schottky (M-S) measurement for various BiVO_4 samples (electrolyte solution: 0.5 M Na_2SO_4). (b) The scheme of band alignment for different BiVO_4 samples.

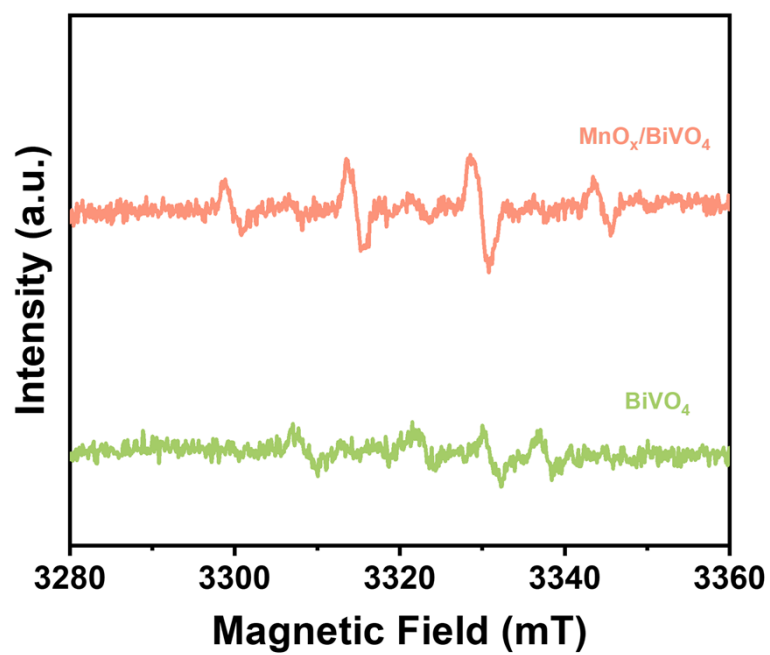


Fig. S18. EPR spectra of DMPO-•OH for BiVO₄ and MnO_x/BiVO₄ after visible-light irradiation for 1 min.

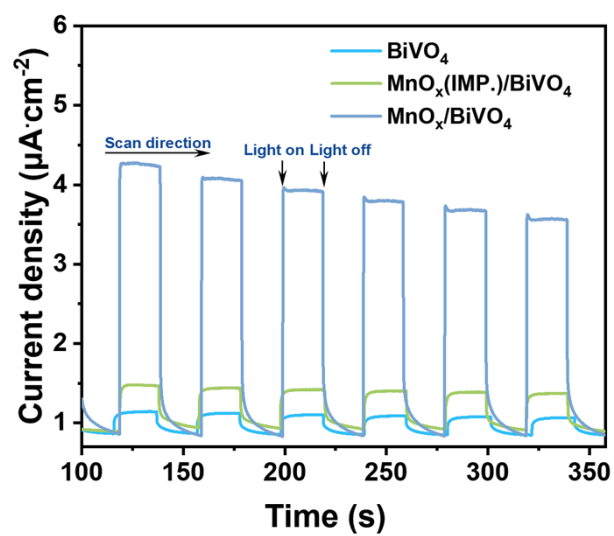


Fig. S19. Photocurrent response curves for BiVO_4 , $\text{MnO}_x(\text{imp})/\text{BiVO}_4$ and $\text{MnO}_x/\text{BiVO}_4$ under chopped illumination (electrolyte solution: 0.5 M Na_2SO_4).

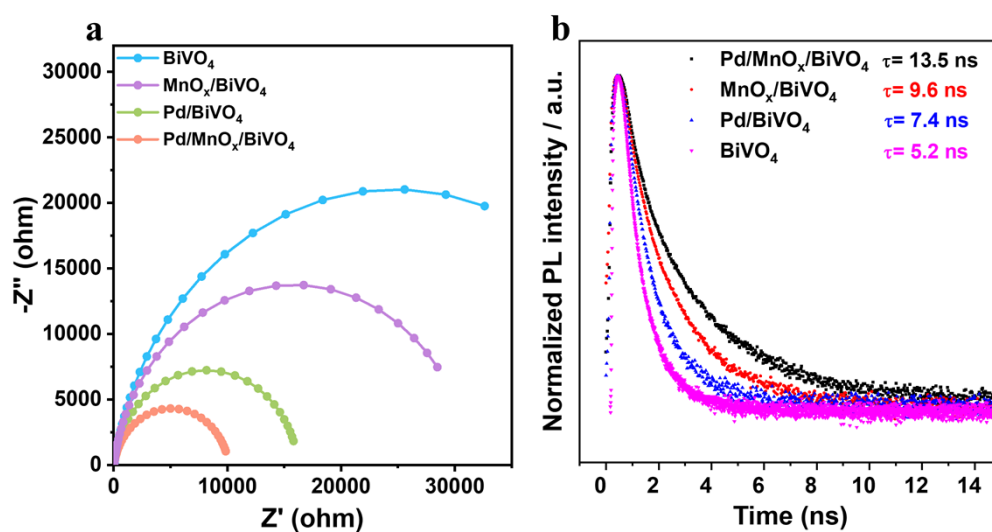


Fig. S20. (a) Photocurrent response curves for various BiVO_4 samples (electrolyte solution: 0.5 M Na_2SO_4). (b) PL decay curves for various BiVO_4 samples.

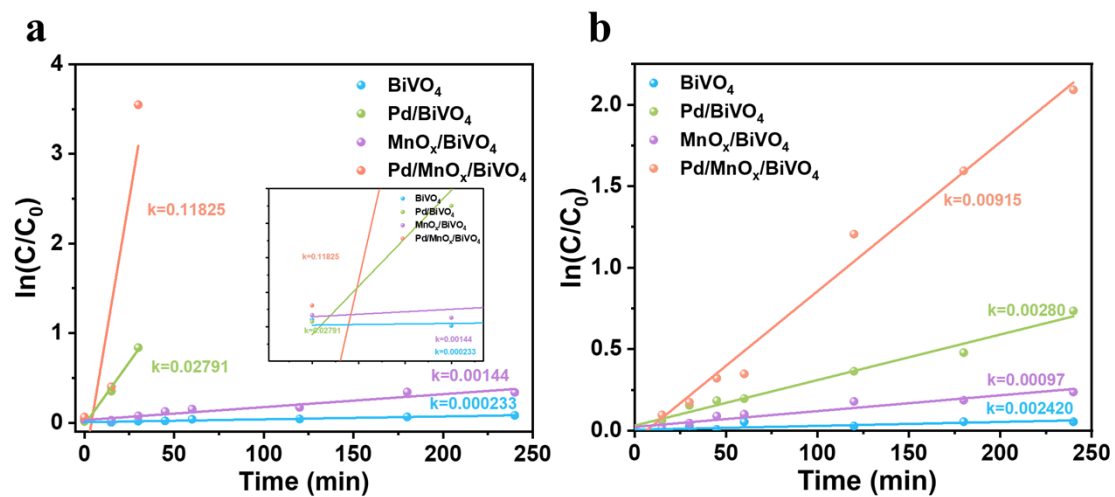


Fig. S21. Kinetic analysis of glyphosate degradation by different BiVO_4 samples under continuous gas stream of (a) O_2 and (b) N_2 .

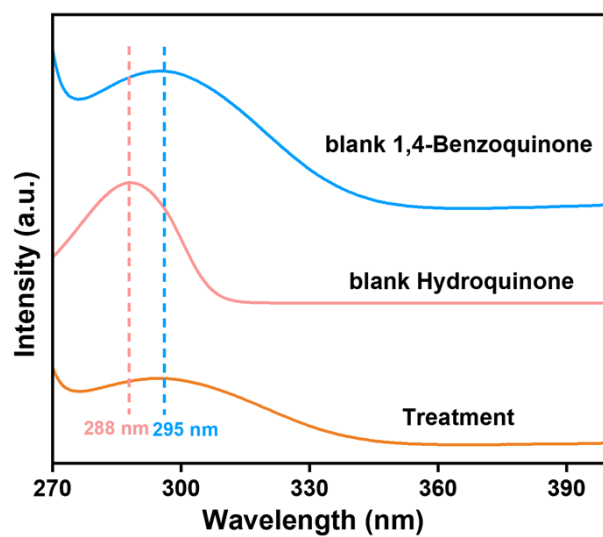


Fig. S22. Reduction experiment of p-Benzoquinone under blank photocatalytic condition.

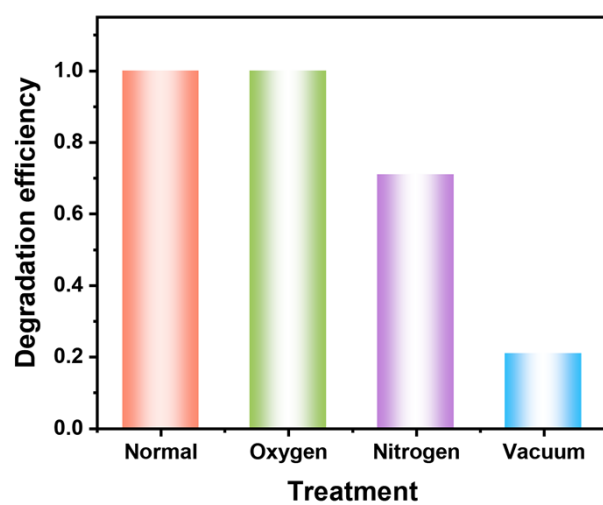


Fig. S23. Glyphosate degradation by Pd/MnO_x/BiVO₄ in different atmosphere system for 2 h.

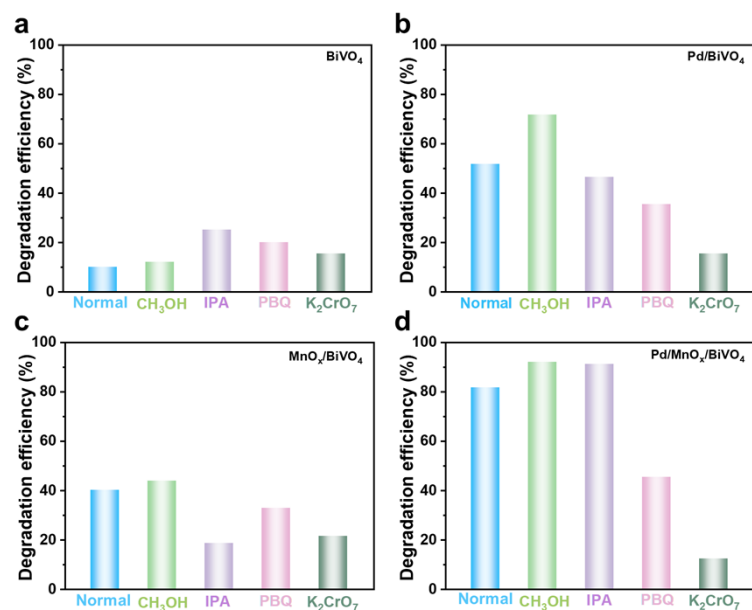


Fig. S24. Normalized degradation efficiencies of glyphosate with the addition of various scavengers by (a) BiVO_4 , (b) Pd/BiVO_4 , (c) $\text{MnO}_x/\text{BiVO}_4$, (d) $\text{Pd/MnO}_x/\text{BiVO}_4$.

Table S5 Comparison of glyphosate degradation efficiency by different photocatalysts

No.	photocatalyst	Photodegradation efficiency	Degradation time	References
1.	Pd/MnO _x /BiVO ₄	100%	120 min	This work
2.	CuO@BiVO ₄	80%	120 min	<i>Appl. Phys. A</i> 2023, 129 , 212
3.	Co(OH) ₂ -BiVO ₄ -150	78.3%	30 min	<i>J. Alloys Compd.</i> 2024, 976 , 173295.
4.	mCB-MOF-2	69%	24 h	<i>J.Am.Chem.Soc</i> 2023, 145 , 25
5.	Sc-TBAPy	100%	150 min	<i>Nat. Commun.</i> 2024, 15 , 1459
6.	TiO ₂	90%	5 h	<i>Appl. Catal., B</i> 2021, 299 , 120671.
7.	TiO ₂	100%	120 min	<i>Chem. Eng. J.</i> 2019, 360 , 1247-1254