

Supplementary Materials

Explainable deep learning elucidated orbital–spin synergy in multi-field-responsive Pt-BiFeO₃ for efficient photocatalytic H₂ production

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Supplementary Text

Materials

All chemicals were of analytical grade and used without further purification. Bismuth nitrate pentahydrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, iron(III) nitrate nonahydrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, platinum(IV) nitrate solution $\text{Pt}(\text{NO}_3)_4$, citric acid $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, ethylene glycol $\text{C}_2\text{H}_6\text{O}_2$, and nitric acid HNO_3 were used for the synthesis of pristine and Pt-doped BiFeO_3 photocatalysts. Methanol and deionized water were employed as the reaction media for photocatalytic hydrogen evolution. The chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd.. The spin-trapping agent 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was provided by Shanghai Macklin Biochemical Co., Ltd..

Experimental synthesis of pristine and Pt-doped BiFeO_3

Pristine BiFeO_3 and Pt-doped BiFeO_3 photocatalysts were prepared using a modified citrate-assisted sol–gel method. Stoichiometric amounts of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in a mixed solvent containing deionized water and ethylene glycol, with a small amount of dilute HNO_3 added to facilitate dissolution of the Bi precursor. Platinum(IV) nitrate solution was subsequently introduced according to the designed Pt/Fe molar ratio, followed by the addition of citric acid as a chelating agent. The molar ratio of citric acid to total metal ions was set to 1:1. The resulting solution was continuously stirred at 80 °C for 2 h to promote homogeneous mixing and metal–citrate complexation.

The homogeneous precursor solution was further heated at 80 °C until a viscous gel was formed. The obtained gel was dried at 120 °C for 12 h and subsequently subjected to thermal pretreatment at 300 °C for 2 h to facilitate the decomposition of organic constituents. The resulting precursor was ground into powder and calcined in air at 600 °C for 2 h to obtain crystalline BiFeO_3 -based photocatalysts. The Pt precursor amount was adjusted to obtain nominal precursor Pt/Fe molar ratios of 0%, 5%, 10%, and 15%, and the corresponding samples were denoted as BFO, 5Pt-BFO, 10Pt-BFO, and 15Pt-BFO, respectively. Here, 5, 10, and 15 represent the nominal precursor Pt/Fe molar ratios rather than the actual Pt substitution fractions in the final products. Pristine BiFeO_3 was synthesized using the identical procedure without introducing Pt precursor and was used as the reference sample. Unless otherwise specified, Pt- BiFeO_3 refers to the optimized 10Pt-BFO sample.

Characterization

The crystal structures of the obtained samples were characterized by X-ray diffraction (XRD), and Rietveld refinement was performed to analyze lattice parameters and structural distortion induced by Pt substitution. The morphology and elemental distribution were examined by transmission electron microscopy (TEM) and scanning transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (STEM–EDS) elemental mapping. X-ray photoelectron spectroscopy (XPS) was employed to investigate the chemical states of Bi, Fe, Pt, and O species. The actual bulk Pt/Fe molar ratios of the Pt-concentration series were quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES). UV–Vis diffuse

reflectance spectra were further analyzed using Tauc plots to evaluate the evolution of the optical band gap with Pt concentration.

Synchrotron Pt L₃-edge X-ray absorption fine structure (XAFS) spectra were collected for BiFe(Pt)O₃ together with PtO₂ and Pt foil references. The X-ray absorption near-edge structure (XANES) spectra were used to evaluate the Pt-centered electronic state, whereas Fourier transform extended X-ray absorption fine structure (FT-EXAFS) and R-space fitting were employed to analyze the local coordination environment of Pt. Synchrotron Fe L_{2,3}-edge and Pt L_{2,3}-edge X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements were further performed on pristine BiFeO₃ and BiFe(Pt)O₃. The averaged XAS spectra were obtained from the circular-polarization-resolved absorption signals, and the XMCD spectra were extracted from the difference between the corresponding left- and right-circularly polarized XAS signals. These measurements were used to directly probe the element-specific spin polarization and atomic-scale spin redistribution induced by Pt substitution.

Photocatalytic hydrogen evolution

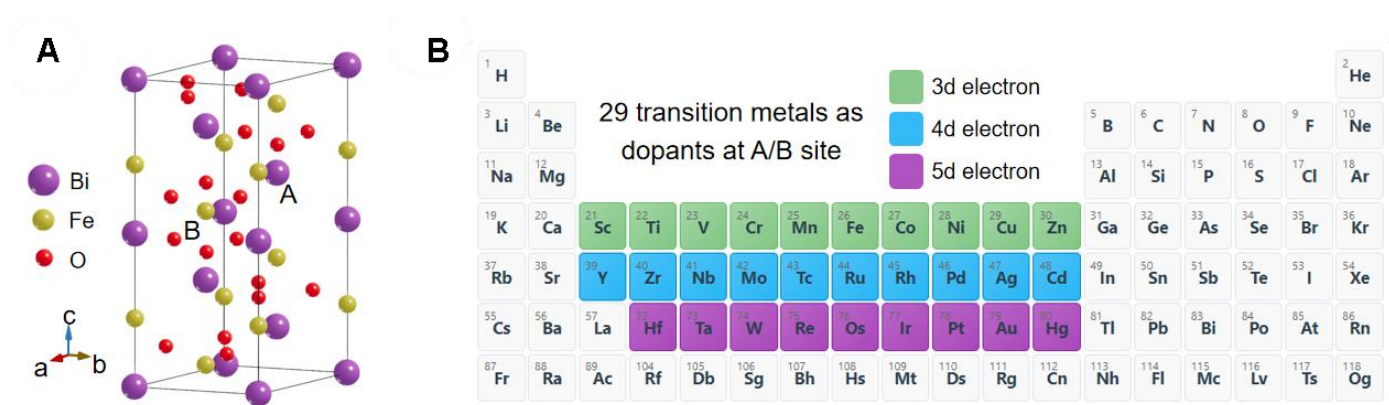
The photocatalytic hydrogen evolution performance was evaluated using a sealed quartz reactor under simulated solar irradiation (XES-40S3-TT-200, PerfectLight, China). The photocatalyst was degassed before illumination to remove dissolved gases and establish adsorption–desorption equilibrium between the catalyst surface and the reaction medium. A certain amount of photocatalyst was dispersed in deionized water or an H₂O/MeOH solution. During irradiation, the generated hydrogen was periodically collected and quantified by gas chromatography. The hydrogen evolution rate was calculated based on the amount of hydrogen generated per unit catalyst mass and irradiation time.

Various external-field conditions were employed to investigate the multi-field-responsive photocatalytic performance. Magnetic-field experiments were conducted by positioning permanent magnets around the reactor to provide a static magnetic field of approximately 0.30 T, calibrated using a Gaussmeter (Lake Shore, United States). Mechanical vibration was introduced using an ultrasonic bath operating at 40 kHz and a rated power of 120 W (KQ-300DE, Kunshan Ultrasonic, China). Ferroelectric polarization was introduced by applying a DC electric field of 2 kV mm⁻¹ at 80 °C for 10 min to pressed catalyst pellets using a high-voltage power supply (610E, Trek, United States). The prepoled pellets were subsequently ground into powders and dispersed for photocatalytic testing. Individual or combined magnetic, mechanical, and polarization fields were applied to examine their effects on photocatalytic hydrogen evolution.

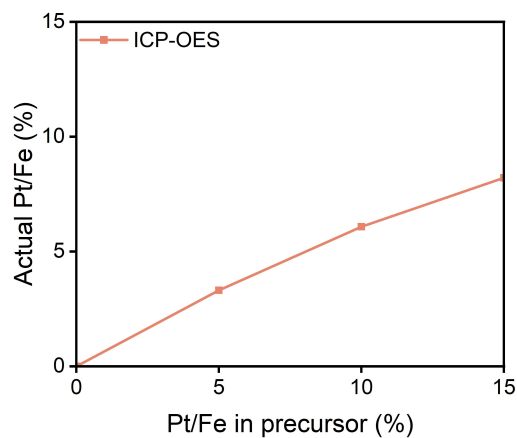
Apparent quantum yield (AQY) measurements were conducted at 420 nm, and the AQY was calculated according to the ratio of the number of electrons involved in hydrogen evolution to the number of incident photons. Photocatalytic cycling tests were performed and the evolved hydrogen was quantified after each cycle to evaluate operational stability. To determine the optimal Pt concentration, BFO, 5Pt-BFO, 10Pt-BFO, and 15Pt-BFO were comparatively evaluated under light irradiation (L) and coupled light irradiation and magnetic field (L + M) using identical photocatalytic conditions. The concentration-dependent magnetic-field response was evaluated from the relative change in the H₂ evolution rate upon application of

the magnetic field. The photoelectrochemical properties were measured to clarify the charge-transfer behavior. Transient photocurrent responses, electrochemical impedance spectroscopy (EIS), and photoluminescence (PL) measurements were conducted to evaluate photogenerated carrier separation efficiency, migration kinetics, and recombination dynamics.

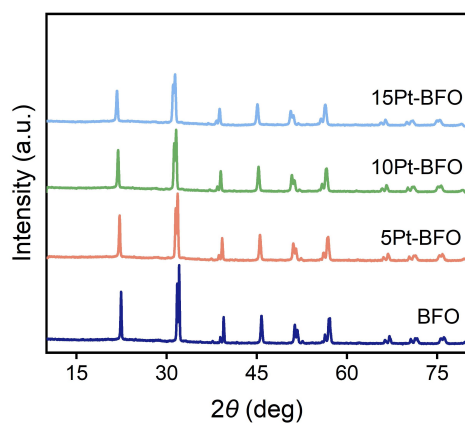
Supplementary Figures



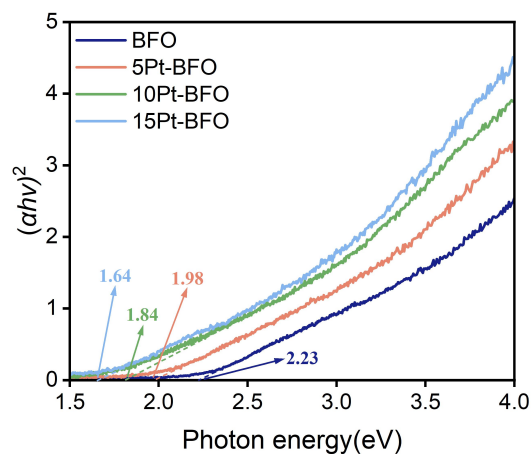
Supplementary Figure 1. (A) Crystal structure of pristine BiFeO₃. (B) Transition metals used in metal-doped BiFeO₃ supercells.



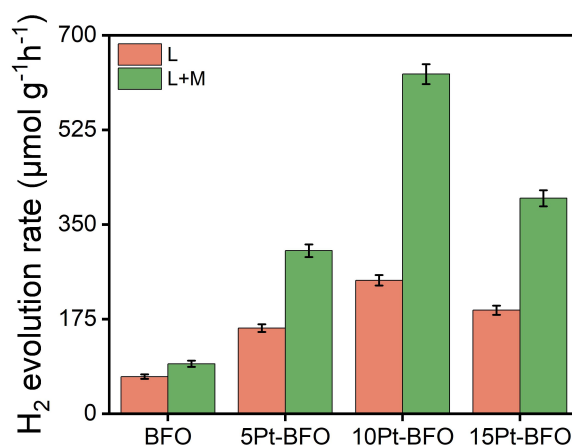
Supplementary Figure 2. Nominal precursor Pt/Fe molar ratios and the actual bulk Pt/Fe ratios determined by ICP-OES for BFO, 5Pt-BFO, 10Pt-BFO, and 15Pt-BFO.



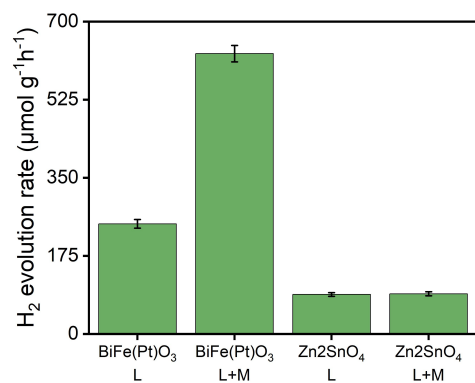
Supplementary Figure 3. XRD patterns of BFO, 5Pt-BFO, 10Pt-BFO, and 15Pt-BFO.



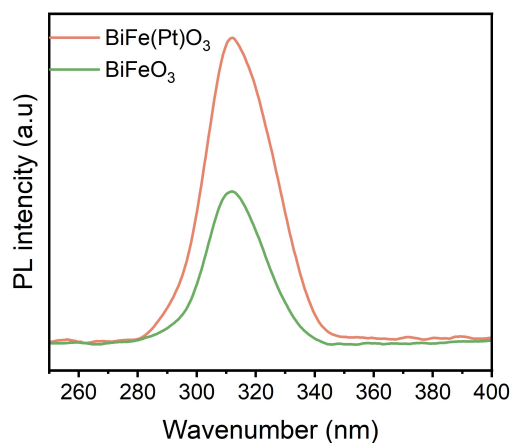
Supplementary Figure 4. Tauc plots of BFO, 5Pt-BFO, 10Pt-BFO, and 15Pt-BFO for evaluating the band gaps of the BiFe(Pt)O₃ series.



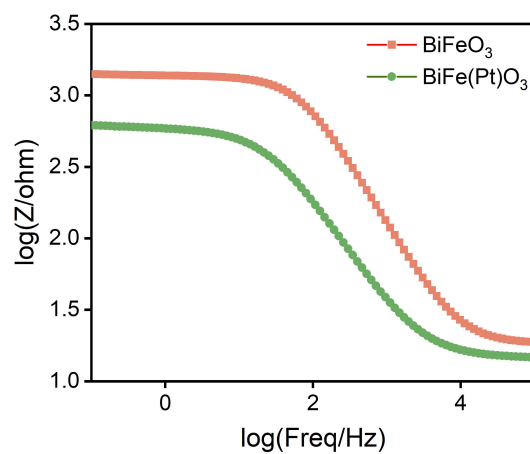
Supplementary Figure 5. H₂ evolution rates of BFO, 5Pt-BFO, 10Pt-BFO, and 15Pt-BFO under light irradiation (L) and under coupled light irradiation and magnetic field (L + M).



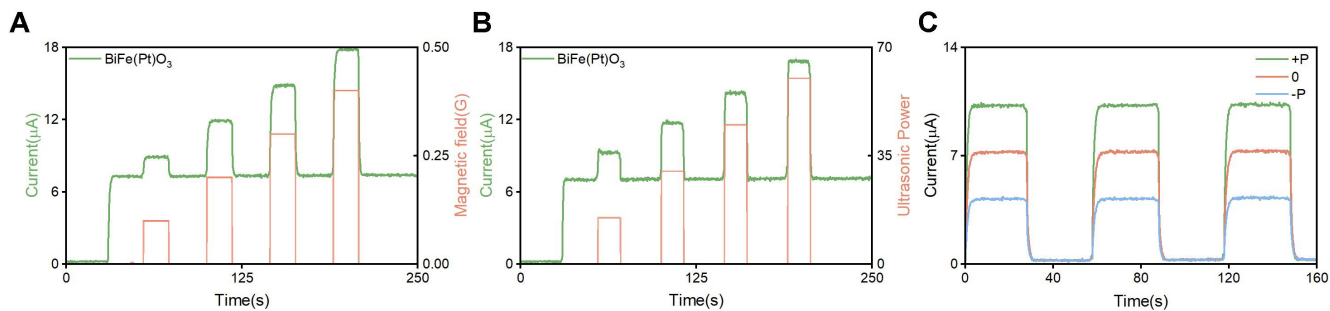
Supplementary Figure 6. Comparison of the H₂ evolution rates of BiFe(Pt)O₃ and the non-magnetic photocatalyst Zn₂SnO₄ under light irradiation (L) and under coupled light irradiation and magnetic field (L + M).



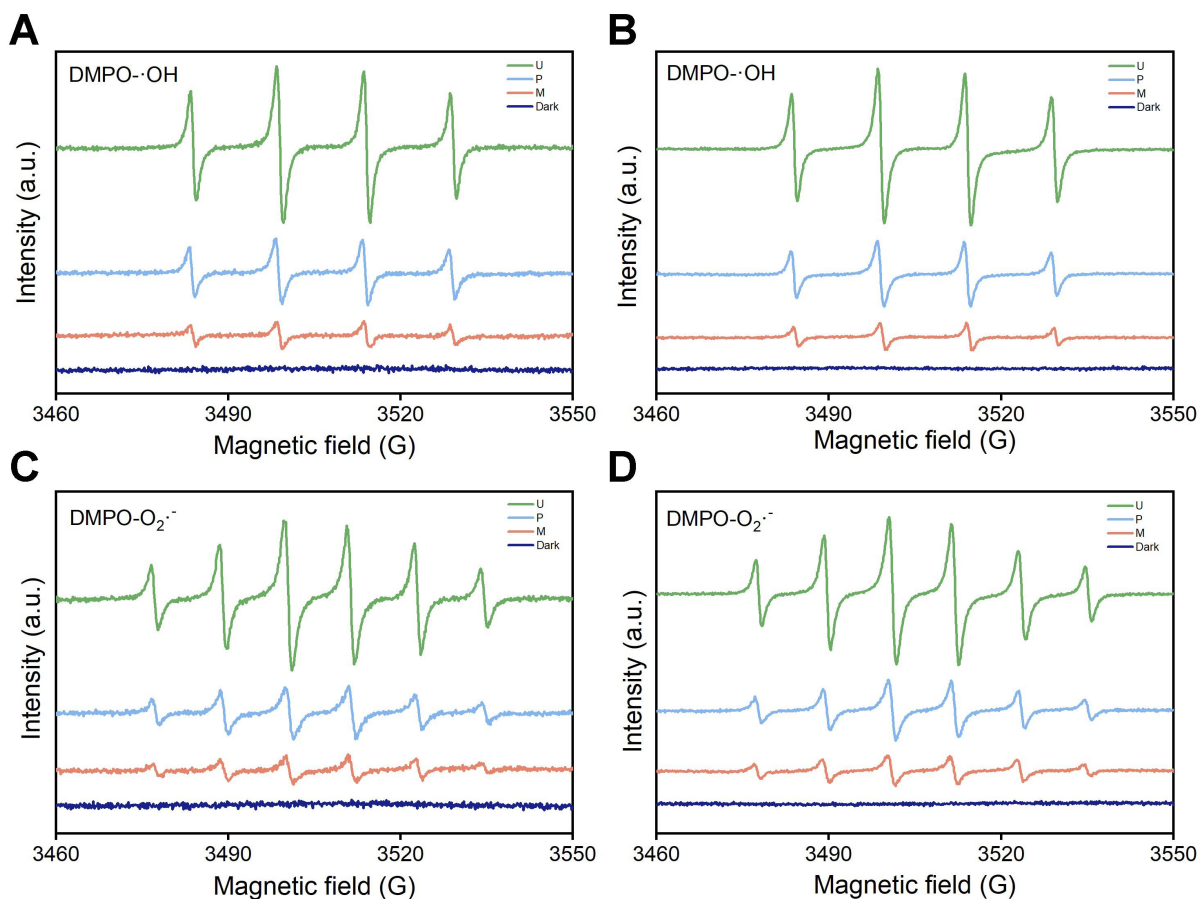
Supplementary Figure 7. Photoluminescence (PL) spectra of pristine BiFeO₃ and Pt-modified BiFeO₃ photocatalysts.



Supplementary Figure 8. Bode phase plots of pristine BiFeO₃ and Pt-modified BiFeO₃ photocatalysts.



Supplementary Figure 9. Dark transient photocurrent responses of pristine BiFeO₃ under different external-field conditions: (A) Transient photocurrent responses under different magnetic field strengths; (B) Transient photocurrent responses under different ultrasonic powers; (C) Transient photocurrent responses under different ferroelectric polarization states (prepoled, unpoled, and reverse-poled).



Supplementary Figure 10. Electron spin resonance (ESR) spectra of reactive oxygen species generated by pristine BiFeO₃ and BiFe(Pt)O₃ under different external-field conditions: (A) DMPO-•OH spectra of BiFeO₃ under dark, magnetic field (M), electric polarization (P), and ultrasonic vibration (U) conditions; (B) DMPO-•OH spectra of BiFe(Pt)O₃ under dark, M, P, and U conditions; (C) DMPO-•O₂⁻ spectra of BiFeO₃ under dark, M, P, and U conditions; (D) DMPO-•O₂⁻ spectra of BiFe(Pt)O₃ under dark, M, P, and U conditions.

Supplementary Tables

Supplementary Table 1. Raw DFT-calculated physical properties of all 29 dopants corresponding to the normalized screening results in Table 1

Supercell	Band gap*	Piezoelectric tensor*	Spin polarization	Dielectric constant	Average extinction coefficient	Refractive index	Reflectance	Absorption coefficient*
Bi(Sc)FeO ₃	2.556	-0.077	0.264	3.656	6.915	2.388	0.225	7.243
BiFe(Sc)O ₃	2.415	-0.135	0.318	7.685	6.760	2.772	0.243	7.289
Bi(Ti)FeO ₃	2.025	-0.064	0.383	34.187	7.066	5.847	0.501	8.035
BiFe(Ti)O ₃	2.358	-0.239	1.000	4.151	7.041	2.528	0.242	8.612
Bi(V)FeO ₃	2.342	0.524	0.211	11.828	6.936	3.439	0.302	7.112
BiFe(V)O ₃	2.359	-0.110	0.170	11.905	7.319	3.450	0.303	7.250
Bi(Cr)FeO ₃	2.148	0.126	0.428	4.719	6.870	2.258	0.214	7.313
BiFe(Cr)O ₃	2.586	-0.141	0.291	14.945	7.060	3.866	0.347	7.838
Bi(Mn)FeO ₃	2.593	-0.031	0.952	25.259	6.752	5.026	0.446	7.413
BiFe(Mn)O ₃	2.216	-0.693	0.072	13.458	6.679	3.668	0.327	6.419
Bi(Fe)FeO ₃	2.214	-0.095	0.292	3.667	6.935	2.368	0.242	7.633
BiFe(Fe)O ₃	2.267	-0.082	0.065	3.964	6.993	2.487	0.256	8.081
Bi(Co)FeO ₃	2.393	0.130	0.058	6.469	7.408	2.544	0.206	8.032
BiFe(Co)O ₃	1.904	0.075	0.094	24.811	7.457	4.981	0.443	8.339
Bi(Ni)FeO ₃	1.108	-0.115	0.070	7.744	7.947	2.790	0.225	4.371
BiFe(Ni)O ₃	2.588	0.009	0.502	16.406	7.376	4.050	0.365	8.319
Bi(Cu)FeO ₃	1.547	0.030	0.371	16.525	6.408	4.065	0.366	7.801
BiFe(Cu)O ₃	1.846	-0.210	0.036	21.580	7.553	4.645	0.417	7.823
Bi(Zn)FeO ₃	2.177	-0.094	0.268	4.300	6.871	2.537	0.252	8.612
BiFe(Zn)O ₃	2.101	-0.251	0.571	17.726	7.467	4.210	0.380	8.574
Bi(Y)FeO ₃	2.298	-0.173	0.148	4.581	6.452	2.487	0.275	7.738
BiFe(Y)O ₃	2.509	-0.073	0.334	3.899	6.893	2.449	0.266	7.859
Bi(Zr)FeO ₃	2.183	-0.127	0.309	3.842	6.938	2.357	0.228	7.544
BiFe(Zr)O ₃	2.223	-0.163	0.012	4.047	7.010	2.485	0.245	8.017
Bi(Nb)FeO ₃	1.568	-0.106	0.270	16.881	8.347	4.109	0.370	8.208
BiFe(Nb)O ₃	1.196	-0.154	0.166	4.031	7.648	2.397	0.256	8.814
Bi(Mo)FeO ₃	2.526	0.067	0.409	3.682	6.879	2.374	0.232	7.424
BiFe(Mo)O ₃	2.475	-0.489	0.269	11.777	7.145	3.432	0.301	8.626
Bi(Tc)FeO ₃	2.796	-0.043	0.937	6.713	6.792	2.591	0.214	6.749
BiFe(Tc)O ₃	1.878	-0.317	0.982	16.416	7.404	4.052	0.365	8.525
Bi(Ru)FeO ₃	2.007	-0.420	0.800	6.566	6.646	2.562	0.228	8.115
BiFe(Ru)O ₃	1.447	-0.166	0.742	6.347	7.283	2.519	0.235	7.952
Bi(Rh)FeO ₃	1.327	-0.068	0.568	5.209	6.807	2.282	0.198	6.939
BiFe(Rh)O ₃	2.867	-0.020	0.966	6.657	7.615	2.580	0.229	8.106
Bi(Pd)FeO ₃	1.861	0.243	0.380	16.928	7.388	4.114	0.371	7.497
BiFe(Pd)O ₃	1.395	-0.200	0.145	30.090	7.295	5.485	0.478	7.233
Bi(Ag)FeO ₃	2.084	0.064	0.182	9.743	6.791	3.121	0.265	6.912
BiFe(Ag)O ₃	0.899	0.242	0.733	14.395	7.218	3.794	0.340	7.474
Bi(Cd)FeO ₃	2.215	0.886	0.337	5.974	6.948	2.444	0.237	7.237
BiFe(Cd)O ₃	2.554	-0.137	0.666	5.995	6.720	2.449	0.234	7.723
Bi(Hf)FeO ₃	1.686	0.064	0.566	3.809	7.123	2.349	0.256	8.122

BiFe(Hf)O ₃	2.472	-0.179	0.621	4.219	7.000	2.291	0.250	7.704
Bi(Ta)FeO ₃	1.799	-0.172	0.574	12.411	6.923	3.523	0.311	8.198
BiFe(Ta)O ₃	1.701	-0.182	0.542	4.120	6.498	2.457	0.263	8.469
Bi(W)FeO ₃	0.352	-0.066	0.843	3.708	6.932	2.359	0.242	7.974
BiFe(W)O ₃	1.957	-0.053	0.094	6.856	6.986	2.672	0.267	7.479
Bi(Re)FeO ₃	2.211	-0.060	0.731	9.038	6.780	3.006	0.251	7.472
BiFe(Re)O ₃	1.873	-0.037	0.273	15.924	6.999	3.990	0.359	7.762
Bi(Os)FeO ₃	2.118	-0.281	0.842	12.426	6.562	3.525	0.311	9.374
BiFe(Os)O ₃	1.107	-0.170	0.579	9.623	6.916	3.102	0.263	8.505
Bi(Ir)FeO ₃	2.258	0.098	0.992	4.276	6.952	2.310	0.211	7.195
BiFe(Ir)O ₃	1.581	-0.020	0.429	6.756	7.178	2.599	0.236	7.779
Bi(Pt)FeO ₃	2.219	-0.037	0.136	8.496	6.550	2.915	0.239	7.535
BiFe(Pt)O ₃	1.839	0.323	1.000	18.014	7.146	4.244	0.383	7.887
Bi(Au)FeO ₃	1.735	-0.167	0.228	20.405	6.499	4.517	0.406	7.075
BiFe(Au)O ₃	2.055	-0.115	0.318	7.682	7.232	2.772	0.270	9.342
Bi(Hg)FeO ₃	2.060	-0.085	0.689	3.949	6.854	2.338	0.213	7.013
BiFe(Hg)O ₃	2.528	0.080	0.428	4.485	6.848	2.369	0.261	7.837

*Unit: Band gap: eV; Piezoelectric tensor: C/m², absolute value; Absorption coefficient: 10⁵/cm.

Supplementary Table 2. Comparison of H₂ evolution rates of BiFeO₃-based photocatalysts and field-assisted photocatalytic systems

Photocatalyst	Catalytic reaction condition	H ₂ evolution rate ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	Reference
BiFeO ₃ nanosheets	Mechanical field (Piezocatalysis)	124.1	[S1]
g-C ₃ N ₄ /BiFeO ₃	UV light	160.75	[S2]
BiFeO ₃ -BaTiO ₃	UV-Vis light	328	[S3]
Co-doped BiFeO ₃ nanosheets	Mechanical field (Piezocatalysis)	321.9	[S4]
Au-decorated BiFeO ₃ octahedral	Visible light	1400	[S5]
	Light (L)	246.8 $\pm$ 9.7	This work
	L + Magnetic field (M)	628.3 $\pm$ 18.4	
	L + Polarization (P)	846.7 $\pm$ 21.9	
	L + Ultrasonic field (U)	1273.5 $\pm$ 36.2	
	L + M + P	1896.2 $\pm$ 45.7	
	L + P + U	2914.8 $\pm$ 76.5	
	L + M + U	2247.6 $\pm$ 63.1	
Pt-doped BiFeO ₃	L + M + P + U	5287.4 $\pm$ 132.6	

Supplementary Table 3. Definitions and physical meanings of key descriptors adopted as input features for SHAP interpretability

Descriptor	Definition
S-3d	Contribution of 3d/4s/4p/4d/4f/5s/5p/5d/6s/6p orbital states of the substituted dopant element
S-4s	
S-4p	
S-4d	
S-4f	
S-5s	
S-5p	
S-5d	
S-6s	
S-6p	
Total-s	
Total-p	
Total-d	Total contribution of s/p/d/f orbital states
Total-f	
Total	Total contribution of all orbital components
s%	Relative contribution ratio of s/p/d/f/5d orbital states
p%	
d%	
f%	
5d%	
S-spin up	Spin-up contribution of the substituted dopant element
S-spin down	Spin-down contribution of the substituted dopant element
S-net spin	Net spin contribution of the substituted dopant element, calculated from the difference between spin-up and spin-down contributions
Total-spin up	Total spin-up contribution of the doped BiFeO ₃ system
Total-spin down	Total spin-down contribution of the doped BiFeO ₃ system
Total-net spin	Total net spin of the doped BiFeO ₃ system, calculated from the difference between total spin-up and spin-down contributions

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