

Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2019

Beyond CoO_x: A versatile amorphous cobalt species as efficient cocatalyst for visible-light-driven photocatalytic water oxidation

Hongyuan Zhang,^{‡a} Changfa Guo,^{‡a} Jiabin Ren,^a Jiqiang Ning,^b Yijun Zhong,^a Ziyang Zhang^b and Yong Hu^{*a}

^aKey Laboratory of the Ministry of Education for Advanced Catalysis Materials, Department of Chemistry, Zhejiang Normal University, Jinhua 321004, China. E-mail: yonghu@zjnu.edu.cn; yonghuzjnu@163.com

^bVacuum Interconnected Nanotech Workstation, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China.

[‡]These authors contributed equally to this work.

Experimental

All the chemicals were purchased from Sinopharm Chemical Reagent Corp (Shanghai, China) and were used without further purification.

Synthesis of flower-like Bi_2WO_6 nanosheets

Bi_2WO_6 was synthesized according to our previous work,¹ 0.364 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.8 g of PVP were dispersed in 20 mL ethylene glycol with ultrasonication and then stirred for 15 min. Afterwards, 20 mL of aqueous solution containing 0.248 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ were added to the above solution slowly and stirred for 20 min. The resulting solution was sealed in a 50 mL PTFE-lined stainless-steel autoclave, and then heated to 180 °C and maintained for 5 h. The final product was collected by centrifugation, washed with ethanol and distilled water for several times, and dried at 60 °C for 4 h.

Preparation of $\text{Bi}_2\text{WO}_6/\text{a-Co-E}$ nanocomposites

A certain amounts of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) were dissolved in 2 mL of distilled water, and the molar ratio of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and EDTA-2Na was controlled 1:1. The as-obtained 100 mg of Bi_2WO_6 powder was added to mortar for fully grinding and then dispersed in the above solution. The mixture was stirred for 5 min and dried at 60 °C until the water was completely evaporated to obtain pink product. The resulting sample was calcined at a certain temperature (250 °C, 300 °C and 350 °C) in air for 120 min with a heating rate of 2.5 °C min⁻¹ to gain different $\text{Bi}_2\text{WO}_6/\text{a-Co-E}$ nanocomposites.

The loading amount of a-Co-E on Bi_2WO_6 was adjusted by changing the amounts of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and EDTA-2Na. Samples with different weight ratios of Bi_2WO_6 to a-Co-E (0.5%, 1.5%, 3.0%, 5.0%) were labelled as $\text{Bi}_2\text{WO}_6/\text{a-Co-E-0.5\%}$,

Bi₂WO₆/a-Co-E-1.5%, Bi₂WO₆/a-Co-E-3.0%, Bi₂WO₆/a-Co-E-5.0%, respectively.

The Bi₂WO₆/a-Co-E in this manuscript generally refers to the sample of the best photocatalytic performance, that is, the sample with 3.0% a-Co-E loading and calcined at 300 °C in air.

For comparison, the bulk a-Co-E was prepared in terms of Bi₂WO₆/a-Co-E except for adding Bi₂WO₆. Bi₂WO₆/a-E was prepared by calcining the mixture of EDTA-2Na and Bi₂WO₆ with the absence of cobalt salts. The mechanical mixture of Bi₂WO₆ and a-Co-E with 3 wt% content was also obtained.

Preparation of Bi₂WO₆/CoO_x nanocomposites

The synthesis process of Bi₂WO₆/CoO_x is similar to that of Bi₂WO₆/a-Co-E, and the mass ratio of Bi₂WO₆ to CoO_x was only adjusted by changing the contents of Co(NO₃)₂·6H₂O.

Preparation of BiFeO₃/a-Co-E nanocomposites

The BiFeO₃ nanofibers were synthesized according to our previous work.² 0.3 mmol of Bi(NO₃)₃·5H₂O, 0.3 mmol of ferric acetylacetonate and 0.25 g of PAN (Mw≈150000) were dissolved in 5 mL N, N-dimethylformamide and kept stirring for overnight. The precursor sol was placed into a 5 mL syringe attached to a needle, and the voltages applied to the tip and collector were 15 and -2 kV, respectively. The distance between the needle tip and the collector was controlled to be 14 cm and the feeding rate was set to 0.3 mL h⁻¹. The resulting precursor was first calcined at 120 °C for 120 min, and then calcined in air at 550 °C for 120 min with a heating rate of 5 °C min⁻¹. After cooled to room temperature, the as-obtained product was collected and washed with ethanol for several times. BiFeO₃/CoO_x and BiFeO₃/a-Co-E were

prepared using the same method as that of $\text{Bi}_2\text{WO}_6/\text{CoO}_x$ and $\text{Bi}_2\text{WO}_6/\text{a-Co-E}$ by using BiFeO_3 to replace Bi_2WO_6 , respectively.

Preparation of $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{a-Co-E}$ nanocomposites

1.21 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 2.02 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 50 mL acetone getting a homogeneous solution. Then, 150 mL of distilled water were added under vigorous stirring and the pH was adjusted to 10 using concentrated ammonia. After filtering and rinsing with distilled water, the red co-precipitate was dispersed in 40 mL aqueous solution containing 5 M of NaOH and 2 g of sodium dodecyl benzene sulfonate. The resulting solution was sealed in Teflon-liner autoclave and kept at 180 °C for 48 hours. The final products were washed with distilled water and alcohol several times, and then dried at 80 °C for overnight. $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{a-Co-E}$ and $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{CoO}_x$ were prepared with the same method as that of $\text{Bi}_2\text{WO}_6/\text{a-Co-E}$ and $\text{Bi}_2\text{WO}_6/\text{CoO}_x$ by using $\text{Bi}_2\text{Fe}_4\text{O}_9$ to replace Bi_2WO_6 , respectively.

Preparation of $\text{SiO}_2/\text{a-Co-E}$ nanocomposites

The SiO_2 spheres were prepared according to the previous literature.² Tetraethyl orthosilicate (TEOS) was hydrolyzed in an ethanol medium with the addition of deionized water and ammonia. Typically, 10 mL of TEOS and 40 mL of NH_4OH were mixed with 100 mL of absolute ethanol with continuous stirring for 8 h at room temperature, resulting in the formation of a white SiO_2 colloidal suspension. The silica particles were centrifugally separated and washed several times by ethanol and deionized water and dried at 60 °C for usage. $\text{SiO}_2/\text{a-Co-E}$ with 3 wt% loading was prepared using the same method as that of $\text{Bi}_2\text{WO}_6/\text{a-Co-E}$ by using SiO_2 to replace Bi_2WO_6 .

Characterizations

X-ray diffraction (XRD) patterns of as-prepared samples were obtained by a Philips PW3040/60 X-ray diffractometer utilizing Cu K α radiation at a scanning rate of 0.06 deg s⁻¹. The microstructure and morphology were analyzed via a Hitachi S-4800 field emission scanning electron microanalyzer (FE-SEM) with an acceleration voltage of 15 kV. The transmission electron microscopy (TEM) observation was performed on JEM-2100F field-emission TEM. X-ray photoelectron spectroscopy (XPS) analysis were conducted on an electron spectrometer (ESCALAB 250Xi). UV-vis diffuse reflectance spectra were recorded on a Thermo Nicolet Evolution 500 UV-vis spectrophotometer and the spectral range is from 200 to 800 nm. The content of elements in the as-prepared sample was determined by inductive coupled plasma atomic emission spectrometer (ICP-AES, Leeman Prodigy). The photoluminescence (PL) spectrum was measured on an FLS 920 fluorescence spectrophotometer with an excitation wavelength of 325 nm.

Photoelectrochemical measurements

Photocurrent measurements were performed on a CHI840C electrochemical workstation (Chenhua Instrument, China) with a standard three-electrode system. The working electrode, counter electrode and reference electrode were ITO precoated by photocatalyst (coated area: 1 cm²), Pt wire and Hg/Hg²⁺ (saturated KCl) respectively. 0.1 M Na₂SO₄ aqueous solution was used as the electrolyte. A Xe lamp with a cut-on filter ($\lambda > 420$ nm) was employed as the visible light source. 5 mg of certain test sample was add to 50 μ L of ethanol and 10 μ L of Nafion solution (5 wt%) under sonication, then 15 μ L of mixture ink was pipetted on the surface of an ITO glass to obtain 1 \times 1 cm² coating films. The electrochemical impedance spectroscopy (EIS)

measurements were conducted on the Zennium E station, the three-electrode system with $K_3 [Fe(CN)_6]$ (5 mM) and KCl (1 M) aqueous solution, using an ac voltage of 10 mV and the frequency was in the range of 0.1 to 100 Hz.

Photocatalytic O_2 evolution experiments

Photocatalytic O_2 production was tested on Labsolar-III AG system under visible light irradiation using ultraviolet filtered 300W xenon lamp with a 420 nm cut-off filter (MicroSolar300, Perfect Light) as light source ($\lambda > 420$ nm). Typically, 40 mg of photocatalyst were dispersed in aqueous solution (50 mL) consisting of 200 mg of NaOH and 238.1 mg of $Na_2S_2O_8$. The obtained suspension was vacuumed for 30 min to remove air with argon and the reactor was cooled by a continuous flow of 25 °C water. The amount of generated O_2 was measured by an online gas chromatography (Agilent Technologies GC-7890B, TCD, Ar carrier). The apparent quantum efficiency (AQE) was calculated using the following equation (1):

$$AQE = \frac{N_e}{N_p} = \frac{4 \times N_{O_2}}{N_p} = \frac{4 \times N_{O_2}}{\frac{I \times A \times t}{h \times \nu}} \times 100\% \quad (1)$$

Here, N_e , N_p , and N_{O_2} are the number of reacted electrons, incident photons and generated O_2 , respectively; I is the light intensity; A is the irradiation area; t is the irradiation time; h is the Planck constant; and ν is the incident light frequency.

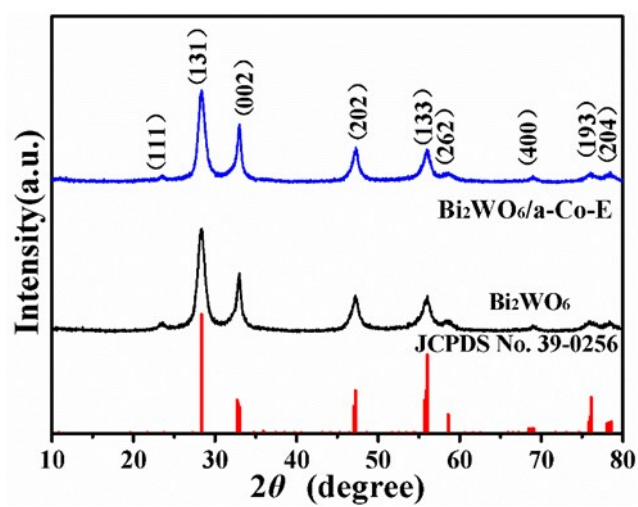


Fig. S1 XRD patterns of the as-prepared Bi_2WO_6 and $\text{Bi}_2\text{WO}_6/\text{a-Co-E}$ samples.

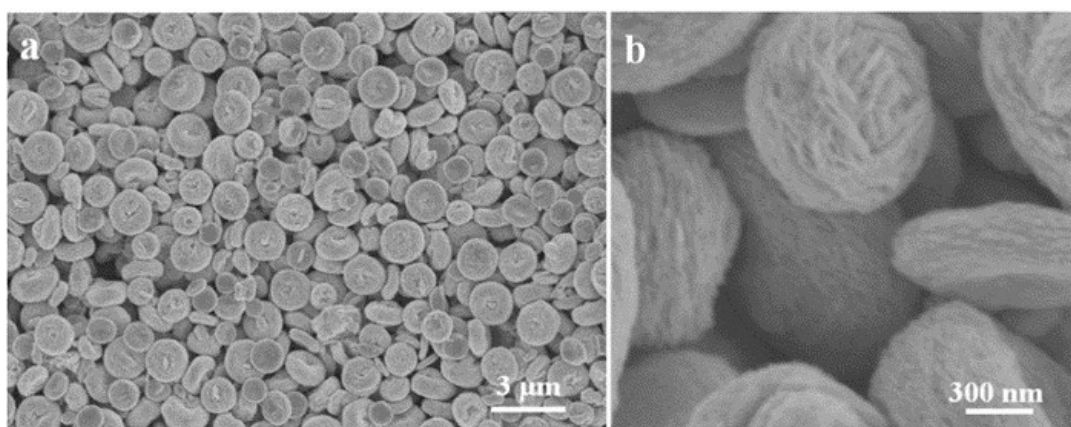


Fig. S2 (a) Low-resolution and (b) high-resolution SEM images of as-prepared Bi_2WO_6 microstructures.

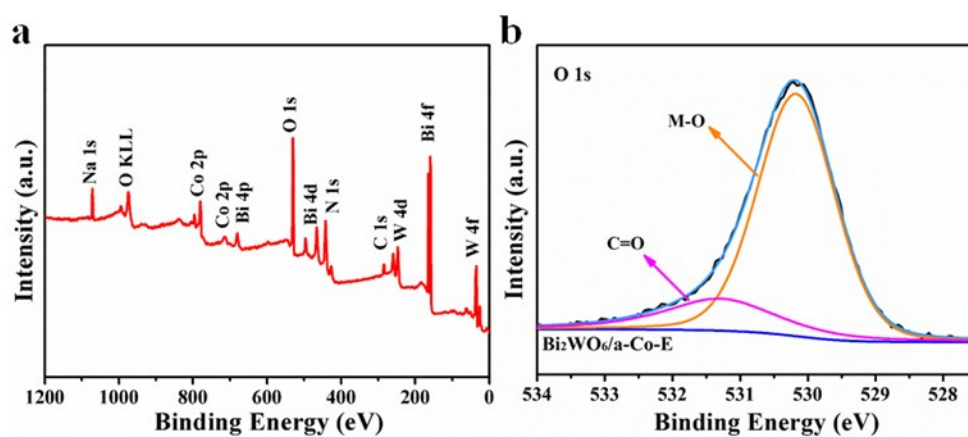


Fig. S3 XPS spectra of the as-prepared Bi₂WO₆/a-Co-E: (a) Survey spectrum, (b) high-resolution spectrum of O1s.

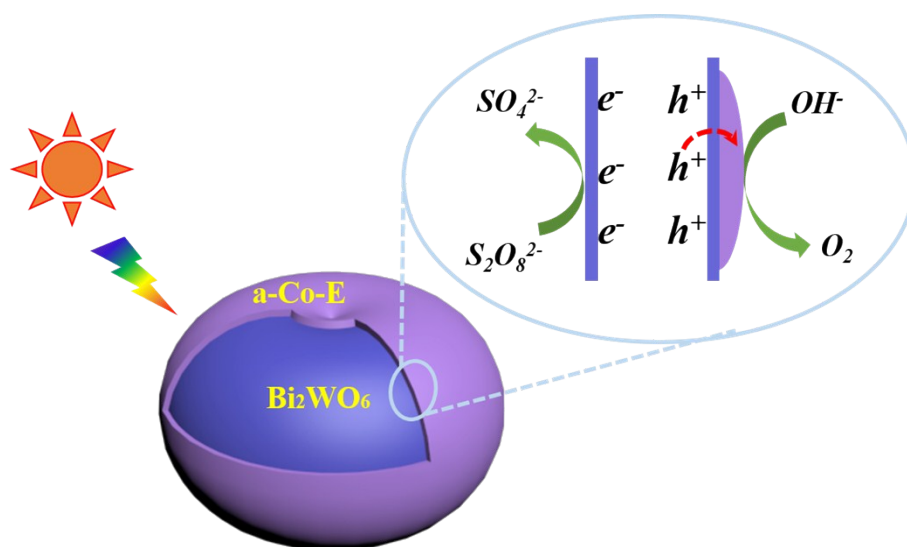


Fig. S4 Schematic illustration of the photocatalytic mechanism of Bi₂WO₆/a-Co-E for water oxidation under visible-light irradiation.

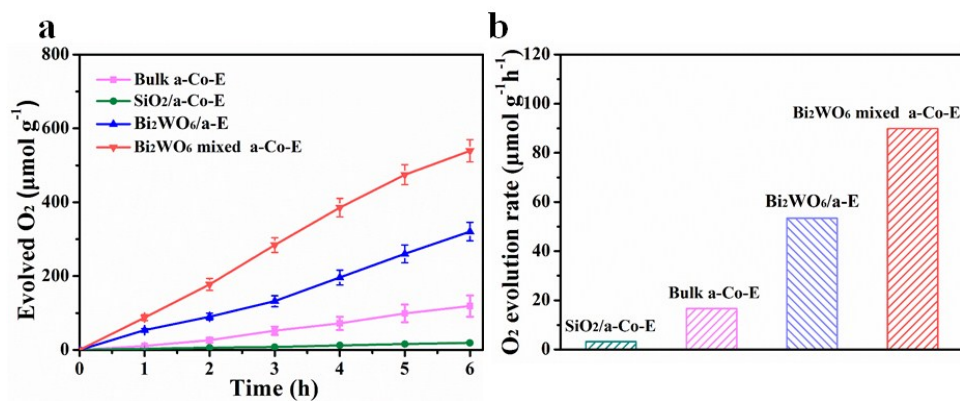


Fig. S5 (a) Typical time course of O₂ evolution and (b) average O₂ evolution rate over a-Co-E anchored SiO₂, bulk a-Co-E, Bi₂WO₆/a-E and the mixture of a-Co-E and Bi₂WO₆.

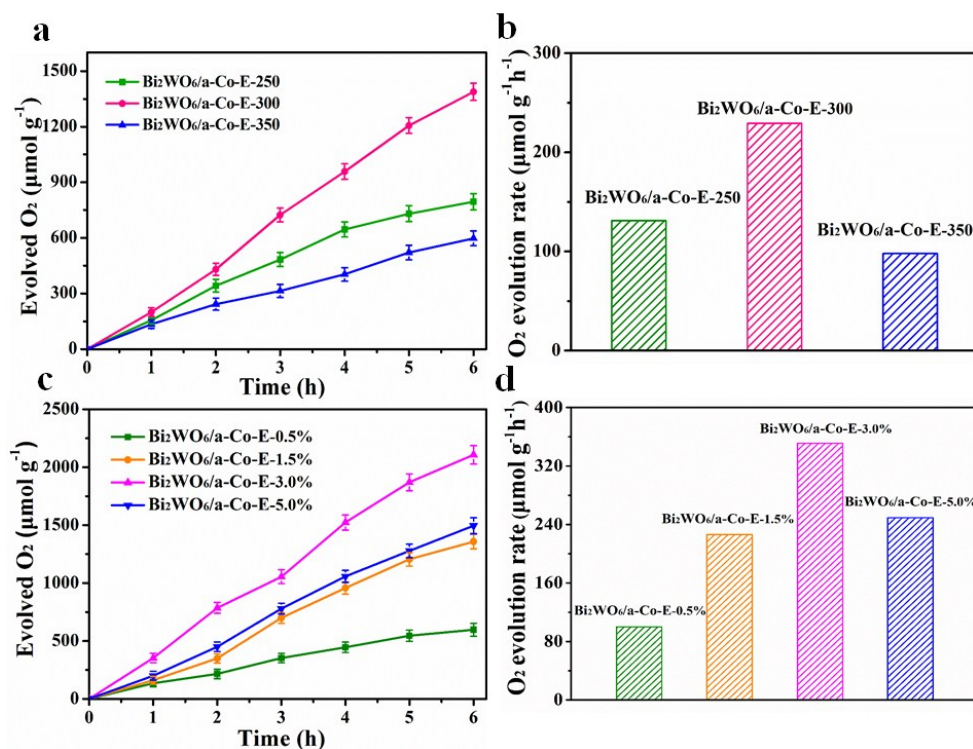


Fig. S6 Typical time course of O₂ evolution catalysed by the different Bi₂WO₆/a-Co-E samples (a and c) and the corresponding average O₂ production rate in 6 h (b and d).

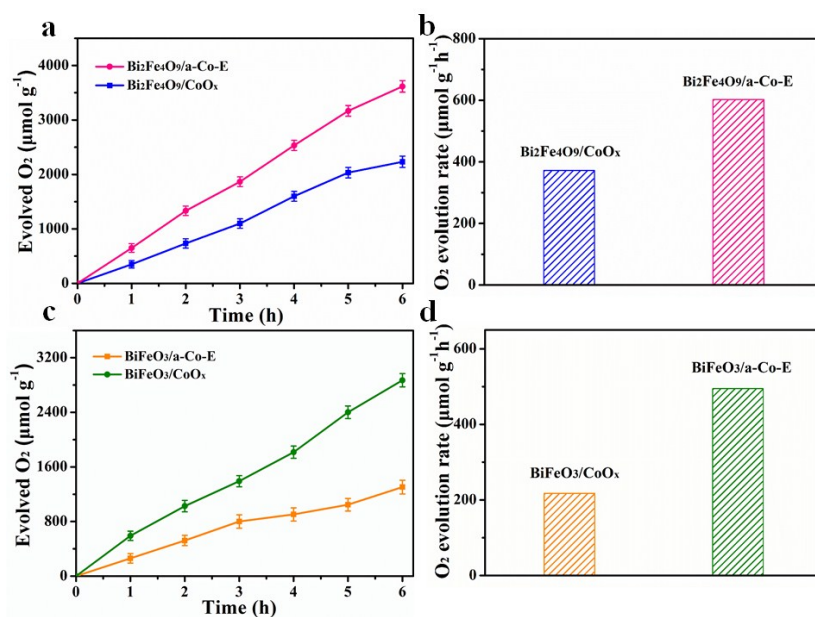


Fig. S7 Typical time course of O_2 evolution catalysed by the (a) $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{a-Co-E}$ and (b) $\text{BiFeO}_3/\text{a-Co-E}$ nanocomposites, respectively.

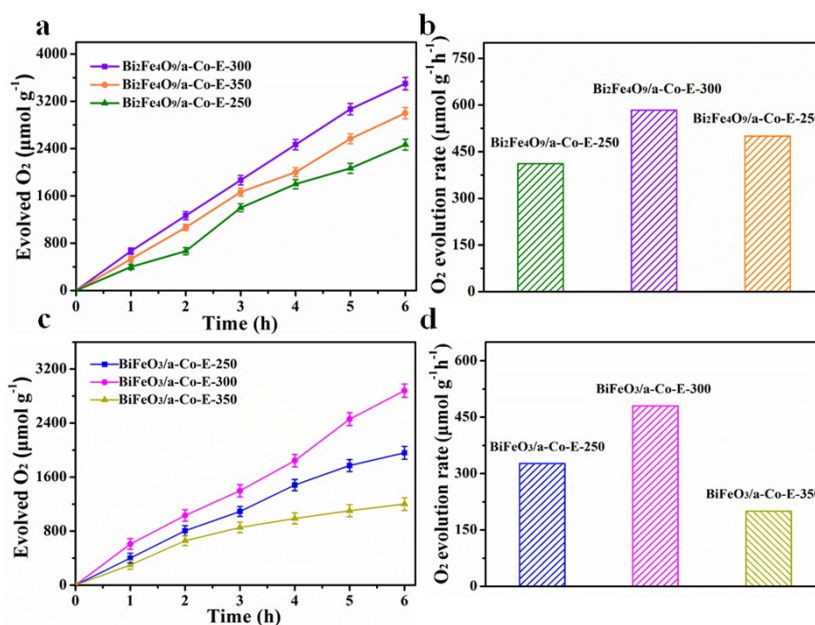


Fig. S8 (a and c) Typical time course of O_2 evolution catalysed by $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{a-Co-E}$ and $\text{BiFeO}_3/\text{a-Co-E}$ produced at the different temperatures and (b and d) the corresponding average O_2 production rate in 6 h.

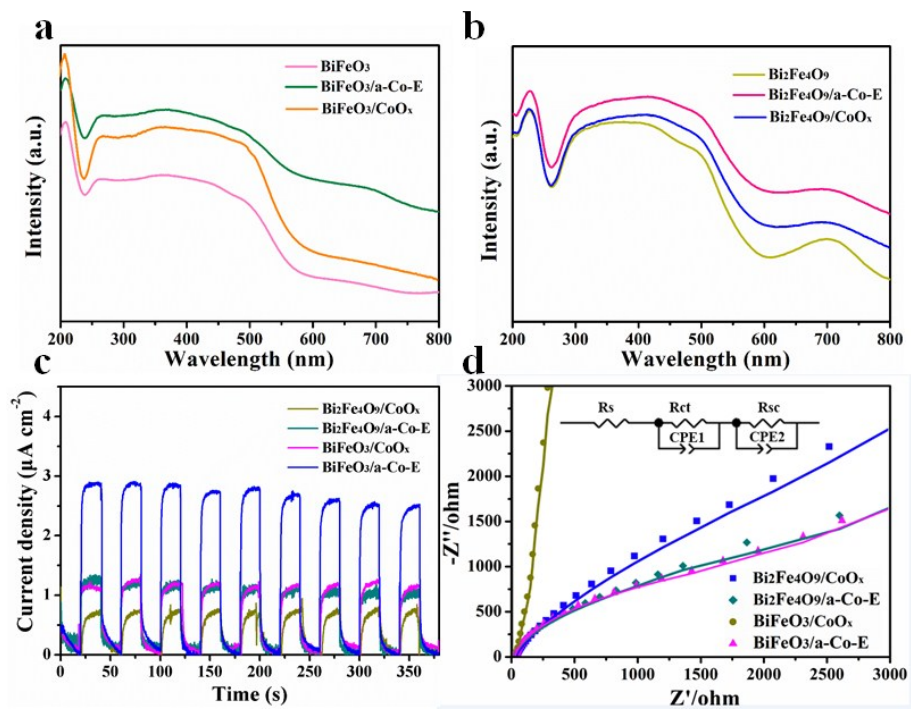


Fig. S9 (a and b) UV-vis DRS spectra, (c) Photocurrent responses, and (d) EIS of the as-prepared Bi₂Fe₄O₉/a-Co-E, Bi₂Fe₄O₉/CoO_x, BiFeO₃/a-Co-E, and BiFeO₃/CoO_x photocatalysts.

Table S1 Values of elements in equivalent circuit resulted from fitting the EIS data.

	Bi₂WO₆/ CoOx	Bi₂WO₆/ a-Co-E	BiFeO₃/ CoOx	BiFeO₃/a- Co-E	Bi₂Fe₄O₉/ CoOx	Bi₂Fe₄O₉/ a-Co-E
R _s	19.48	11.7	19.7	17.05	27.7	14.43
R _{ct}	2992	2165	40390	1002	2807	806
R _{sc}	9086	6750	53764	4616	32750	4782
CPE1-T	2.4637E-5	2.999E-7	2.2184E-5	5.2863E-7	2.9997E-5	3.6231E-7
CPE1-P	0.92152	0.77916	0.898	0.85699	0.87011	0.77916
CPE2-T	7.0126E-5	1.3787E-5	3.016E-3	2.2662E-3	9.8649E-5	1.3787E-5
CPE2-P	0.91166	0.63043	0.74646	0.74581	0.817464	0.63043

Table S2 The selected results for photocatalytic O₂ evolution rate in recent literature

Samples	cocatalyst	Sacrificial agents	Lights source	O ₂ evolution rates ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	References
Bi ₂ Fe ₄ O ₉	a-Co-E			602.7	
	CoOx			372.2	
Bi ₂ WO ₆	a-Co-E	Na ₂ S ₂ O ₈	300W Xe lamps	352.3	This work
	CoOx		($\lambda \geq 420\text{nm}$)	91.2	
BiFeO ₃	a-Co-E			494.9	
	CoOx			217.4	
3D Bi ₂ Mo _x W _{1-x} O ₆ PBMs	5% Co ₃ O ₄	Na ₂ S ₂ O ₈	300W Xe lamps ($\lambda \geq 420\text{nm}$)	147.2	1
MoO _x /Bi ₂ WO ₆	MoOx	Ce(SO ₄) ₂	Hg lamps	288	4
			Xe lamps	53	
SCL-Bi ₂ WO ₆	none	AgNO ₃	300W Xe lamps ($\lambda \geq 400\text{nm}$)	84.4	5
BWO/PDI composite	none	AgNO ₃	500W Xe lamps ($\lambda \geq 420\text{nm}$)	~7.6	6
BiVO ₄ nanoparticles	none	AgNO ₃	300W Xe lamps ($\lambda \geq 420\text{nm}$)	~54	7
BiFeO ₃ nanowires	Au	FeCl ₃	300W Xe lamps ($\lambda \geq 380\text{nm}$)	50	8

References:

- 1 A. Etogo, R. Liu, J. Ren, L. Qi, C. Zheng, J. Ning, Y. Zhong and Y. Hu, *J. Mater. Chem. A*, 2016, **4** 13242.
- 2 D. Wang, T. Hisatomi, T. Takata, C. Pan, M. Katayama, J. Kubota, and Kazunari Domen, *Angew. Chem. Int. Ed.*, 2013, **52**, 11252.
- 3 J. Ren, D. Zhao, H. Liu, Y. Zhong, J. Ning, Z. Zhang, C. Zheng and Y. Hu, *J. Alloys Compd.*, 2018, **766**, 274.
- 4 A. Dittmer, J. Menze, B. Mei, J. Strunk, H.S. Luftman, R. Gutkowski, I.E. Wachs, W. Schuhmann and M. Muhler, *J. Phys. Chem. C*, 2016, **120**, 18191.
- 5 C. Li, G. Chen, J. Sun, J. Rao, Z. Han, Y. Hu and Y. Zhou, *ACS Appl. Mater. Interfaces*, 2015, **7**, 25716.
- 6 K. Zhang, J. Wang, W. Jiang, W. Yao, H. Yang and Y. Zhu, *Appl. Catal. B*, 2018, **232**, 175.
- 7 Y. K. Kho, W. Y. Teoh, A. Iwase, L. Mädler, A. Kudo and R. Amal, *ACS Appl. Mater. Interf.*, 2011, **3**, 1997.
- 8 S. Li, J. Zhang, M. G. Kibria, Z. Mi, M. Chaker, D. Ma, R. Nechache and F. Rosei, *Chem. Commun.*, 2013, **49**, 5856.