

Supporting Information

A stable iron-containing polyoxometalate coupled with semiconductor for efficient photocatalytic water oxidation under acidic condition

Qiyu Hu,^a Xiangyu Meng,^a Yinjuan Dong,^a Qing Han,^a Yifan Wang^a and Yong Ding^{*ab}

^a *State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China. E-mail: dingyong1@lzu.edu.cn*

^b *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China*

* To whom correspondence should be addressed.

E-mail addresses: dingyong1@lzu.edu.cn

Oxygen evolution yield (O₂ yield) calculation

The oxygen evolution yield (O₂ yield) were calculated under the following conditions: 100 mW/cm² under illumination at 420 nm; 10.0 mg BiVO₄, 10.0 mM NaIO₃, 15 mL acetate buffer (0.5 M, pH=3.0); total reaction volume is 15 mL and overall volume is ~32.5 mL; vigorous agitation using a magnetic stirrer.

Bare BiVO₄ system (reaction time is 23 h):

$$\begin{aligned} O_2 \text{ yield} &= \frac{\text{mole of detected } O_2 \text{ evolution}}{\text{mole of theoretic } O_2 \text{ evolution}} \times 100\% \\ &= \frac{4 \times \text{mole of } O_2 \text{ evolution}}{6 \times \text{mole of } NaIO_3} \times 100\% \\ &= \frac{4 \times 10.4 \mu\text{mol}}{6 \times 10 \text{ mM} \times 15 \text{ mL}} \times 100 \% \\ &= 4.6 \% \end{aligned}$$

Addition Fe11 into BiVO₄ system (reaction time is 23 h):

$$\begin{aligned} O_2 \text{ yield} &= \frac{\text{mole of detected } O_2 \text{ evolution}}{\text{mole of theoretic } O_2 \text{ evolution}} \times 100\% \\ &= \frac{4 \times \text{mole of } O_2 \text{ evolution}}{6 \times \text{mole of } NaIO_3} \times 100\% \\ &= \frac{4 \times 42.9 \mu\text{mol}}{6 \times 10 \text{ mM} \times 15 \text{ mL}} \times 100 \% \\ &= 19.1 \% \end{aligned}$$

Apparent quantum efficiency (AQE) calculation

The apparent quantum efficiency (AQE) was calculated from the ration of the number of reacted electrons during oxygen evolution (equivalent to n_{O_2}) to the number of incident photons n_p as following, where t is the irradiation time (s), S is the effective light irradiation area (m²), and Q is the photon flux of the incident light (μmol (photons) m⁻² s⁻¹).

Pure BiVO₄ system:

$$\begin{aligned}
n_p &= t \times S \times Q = 3600 \text{ s} \times (0.015 \text{ m})^2 \times \pi \times 42 \mu\text{mol m}^{-2} \text{ s}^{-1} = 106.877 \mu\text{mol} \\
AQE &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \% \\
&= \frac{4 \times n_{O_2}}{n_p} \times 100 \% \\
&= \frac{4 \times 0.73 \mu\text{mol}}{106.877 \mu\text{mol}} \times 100 \% \\
&= 2.7 \%
\end{aligned}$$

Addition Fe11 into BiVO₄ system:

$$\begin{aligned}
n_p &= t \times S \times Q = 3600 \text{ s} \times (0.015 \text{ m})^2 \times \pi \times 42 \mu\text{mol m}^{-2} \text{ s}^{-1} = 106.877 \mu\text{mol} \\
AQE &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \% \\
&= \frac{4 \times n_{O_2}}{n_p} \times 100 \% \\
&= \frac{4 \times 6.76 \mu\text{mol}}{106.877 \mu\text{mol}} \times 100 \% \\
&= 25.3 \%
\end{aligned}$$

Synthesis of Na₉[α -SbW₉O₃₃]·19.5H₂O

The Na₉[α -SbW₉O₃₃]·19.5H₂O was prepared via a reported method.¹ The salt was prepared by the reaction of Na₂WO₄·2H₂O (40 g, 121 mmol) in boiling water (80 mL) and dropwise adding of Sb₂O₃ (1.96 g, 6.72 mmol) dissolved in concentrated HCl (10 mL). The mixture was refluxed for 1 h and allowed to cool slowly. Colourless crystals of Na₉[α -SbW₉O₃₃]·19.5H₂O were formed after evaporation of one-third of the solution volume.

Synthesis of Na₂₇[Fe₁₁(H₂O)₁₄(OH)₂(W₃O₁₀)₂(α -SbW₉O₃₃)₆]·103H₂O

The Fe11 was prepared via a reported method.² 1.16 g (7.2 mmol) of FeCl₃ was dissolved in 80 mL of H₂O, and then 9.45 g (3.3 mmol) of Na₉[α -SbW₉O₃₃]·19.5H₂O was added. The pH of the solution obtained was 3.0. Then, the solution was heated to 90 °C for 1 h and filtered after cooling to room temperature. Slow evaporation of the clear filtrate at room temperature led to yellow crystals which are suitable for X-ray diffraction within 8–9 days. The synthesized Fe11 was purified by a simple recrystal process using deionized water as solution.

Synthesis of BiVO₄

The BiVO₄ was synthesized according to a previous report.³ 10 mmol of Bi(NO₃)₃·5H₂O and 10 mmol of NH₄VO₃ were dissolved in 60 mL of 2 M nitric acid solution. The above solution was

stirred until a yellow clear solution was obtained. Then the pH value of the solution was adjusted to 0.5 with ammonia solution (25-28 wt. %) under vigorous stirring, then light yellow precipitate can be obtained after stirring for about 2 h under room temperature. The obtained light yellow slurry was transferred to Teflon-lined stainless steel autoclaves with a capacity of 100 mL (about 70 mL slurry), and hydrothermally treated at 473 K in the oven for 24 h. After the autoclaves were cooled to room temperature, yellow precipitate was obtained, and then separated by centrifugation, washed with ultrapure water and dried at 353 K.

Photocatalytic water oxidation

The photocatalytic water oxidation was performed in a custom flask. BiVO₄ (10.0 mg) was dispersed in 15.0 ml 500.0 mM acetate buffer solution (pH 3) containing 10.0 mM NaIO₃ and the optimal quantities of 15.0 μM Fe^{III}. The reactor was thoroughly purged with argon before irradiation. The reaction was then started by irradiating the solution with a LED light source (100 mW/cm²; 420 nm) at ambient temperature under continuously stirring. After reaction, 0.1 mL of the gas phase sample in the reactor was detected by gas chromatography (GC) with a thermal conductivity detector equipped with a 2 m × 3 mm packed molecular sieves 5 Å column with an Ar carrier gas to determine the O₂ production at an interval of 1 h.

Materials and characterization

All the chemicals and salts used for synthesizing the catalysts were obtained from a chemical company and used without further purification. Ultrapure water (18.2 MΩ·cm) for the preparation of solutions was attained from a Molecular Lab Water Purifier. Crystalline structures were determined by X-ray diffraction (XRD) using a Rigaku D/MAX 2400 diffractometer (Japan) with Cu Kα radiation ($k = 1.5418 \text{ \AA}$) operating at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) spectra were measured by ESCALAB250xi with X-ray monochromatisation. The binding energy of each element was corrected by C 1s peak (284.6 eV) from residual carbon. The surface morphologies of the samples were characterized by scanning electron microscope (SEM, S4800) and transmission electron microscopy (TEM, Tecnai G2 TF20).

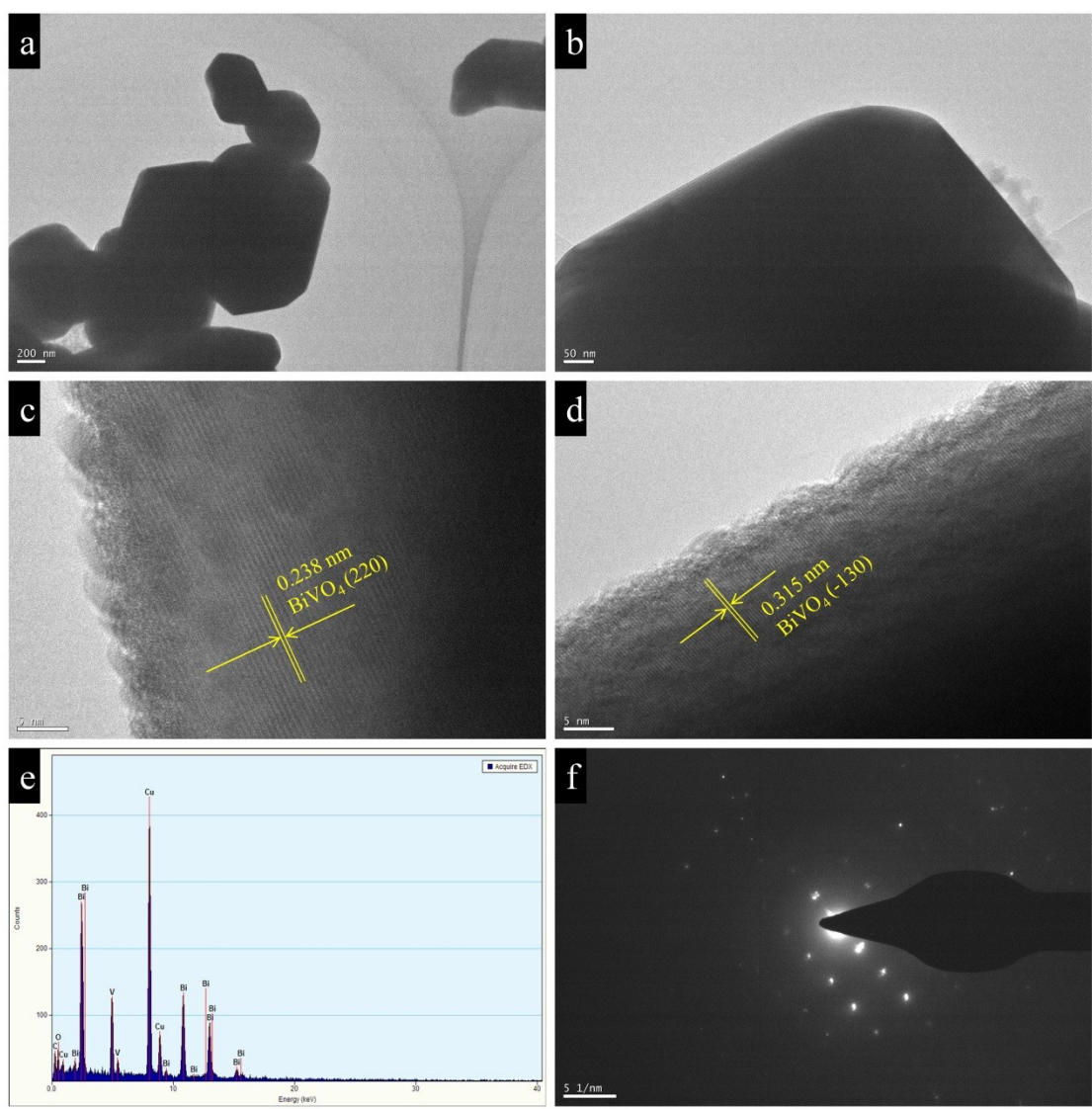


Figure S1. The TEM (a, b), HRTEM (c, d), EDX (e) images and SEAD (f) patterns of bare BiVO₄.

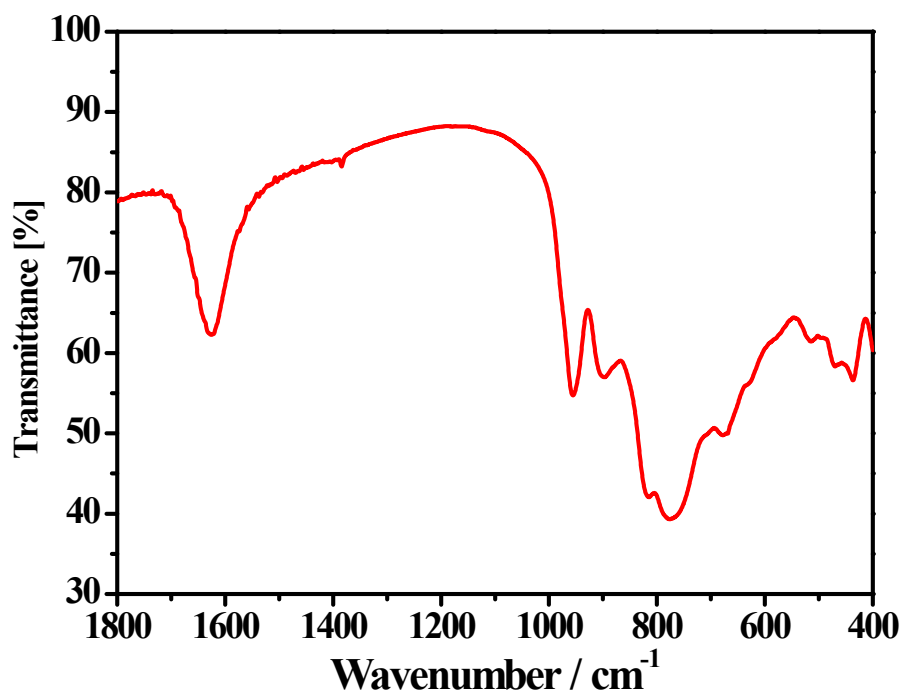


Figure S2. FT-IR spectrum of Fe11.

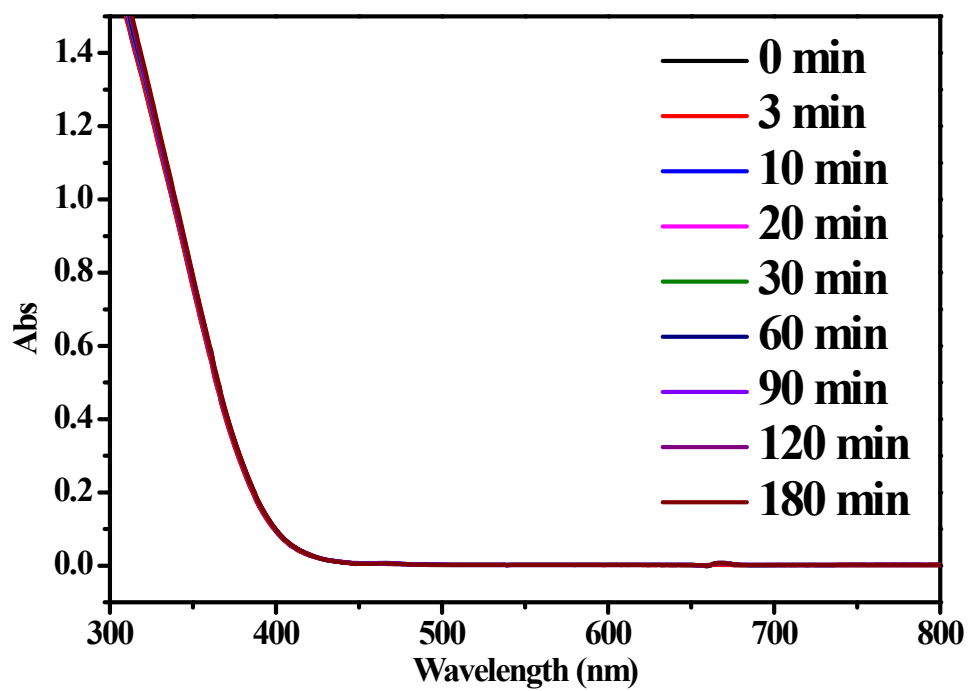


Figure S3. UV-vis absorbance spectra of 10 μM Fe11 acetate buffer solution (pH 3) with different aging time.

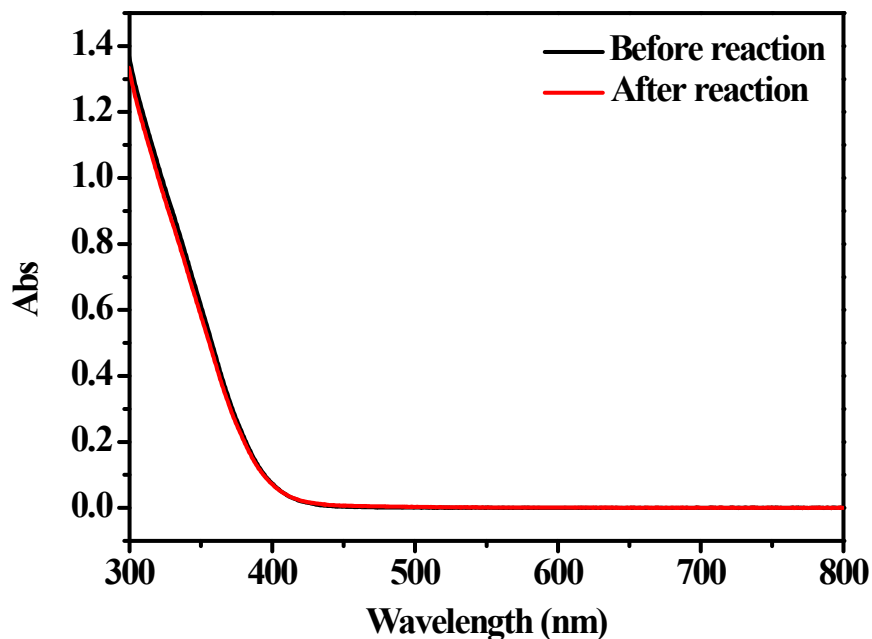


Figure S4. UV-vis absorbance spectra of 10 μM Fe11 acetate buffer solution (pH 3) before and after reaction.

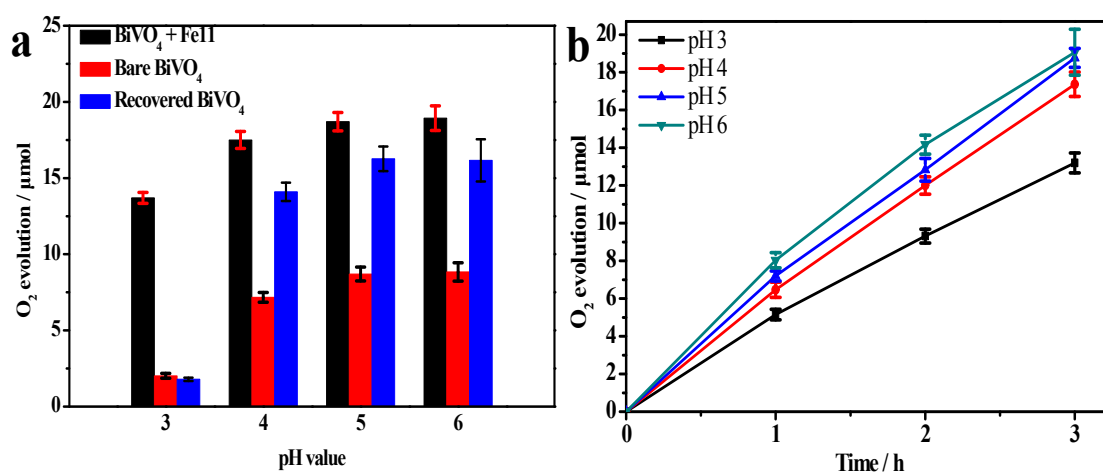


Figure S5. (a) Photocatalytic water oxidation performances of different BiVO_4 under different pH. (b) Kinetics of oxygen evolution in the BiVO_4 combined Fe11 system under different pH value. Conditions: LED lamp ($\lambda = 420 \text{ nm}$, 100 mW/cm^2); 10 μM Fe11, 10.0 mg BiVO_4 , 10.0 mM NaIO_3 , 500 mM sodium acetate buffer (pH 3); total reaction volume is 15 mL and overall volume is $\sim 32.5 \text{ mL}$; vigorous agitation using a magnetic stirrer; reaction time is 3h; room temperature.

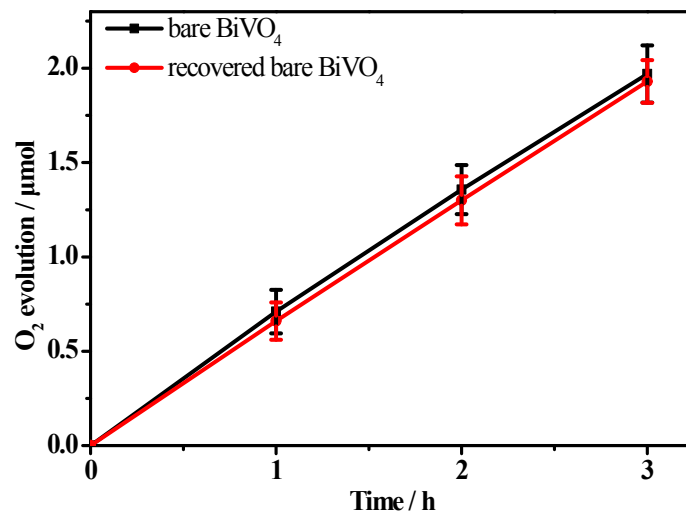


Figure S6. Kinetics of oxygen evolution in the photocatalytic system using bare BiVO₄ and recovered bare BiVO₄. Conditions: LED lamp ($\lambda = 420$ nm, 100mW/cm²); 10.0 mg BiVO₄, 10.0 mM NaIO₃, 500 mM sodium acetate buffer; total reaction volume is 15 mL and overall volume is ~32.5 mL; vigorous agitation using a magnetic stirrer; reaction time is 3h; room temperature.

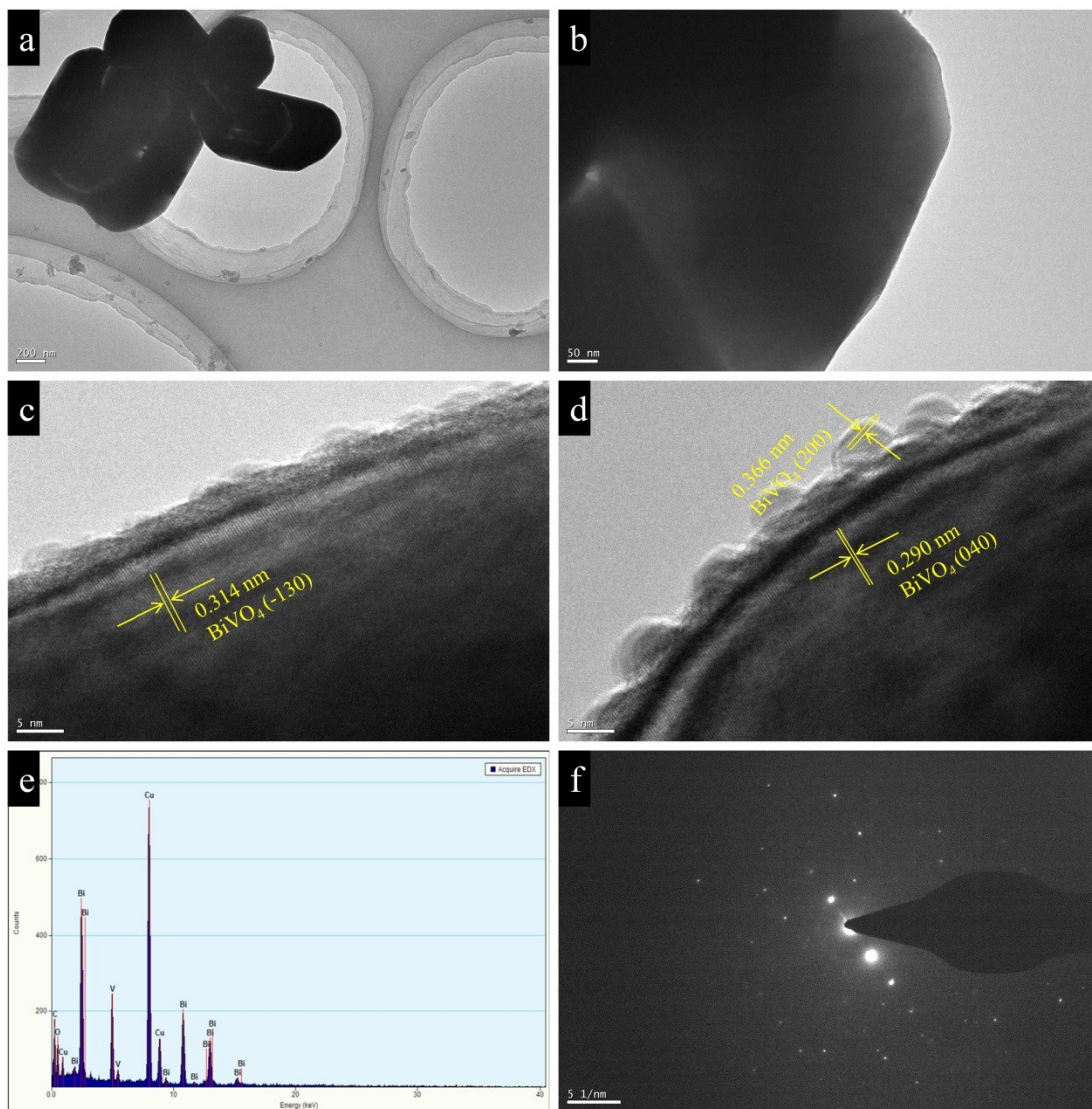


Figure S7. The TEM (a, b), HRTEM (c, d), EDX (e) images and SEAD (f) patterns of recovered bare BiVO₄.

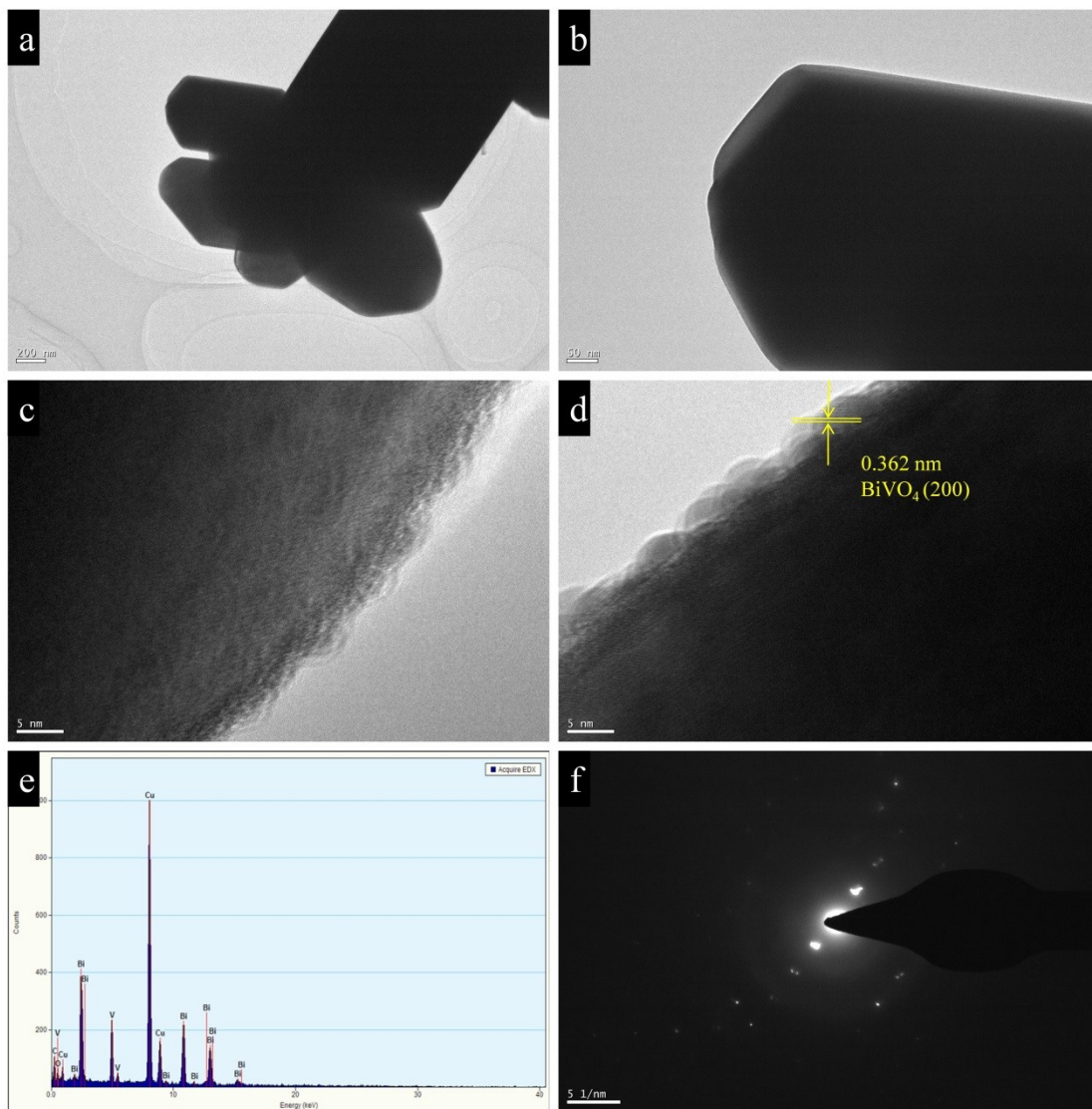


Figure S8. The TEM (a, b), HRTEM (c, d) EDX (e) images and SEAD (f) patterns of recovered BiVO_4 .

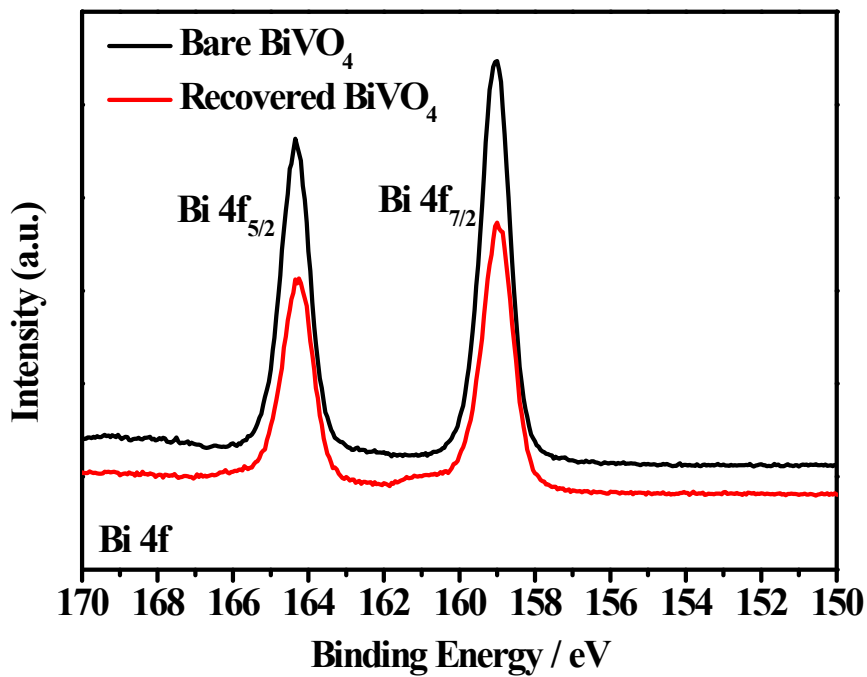


Figure S9. X-Ray photoelectron spectroscopy (XPS) spectra of Bi 4f.

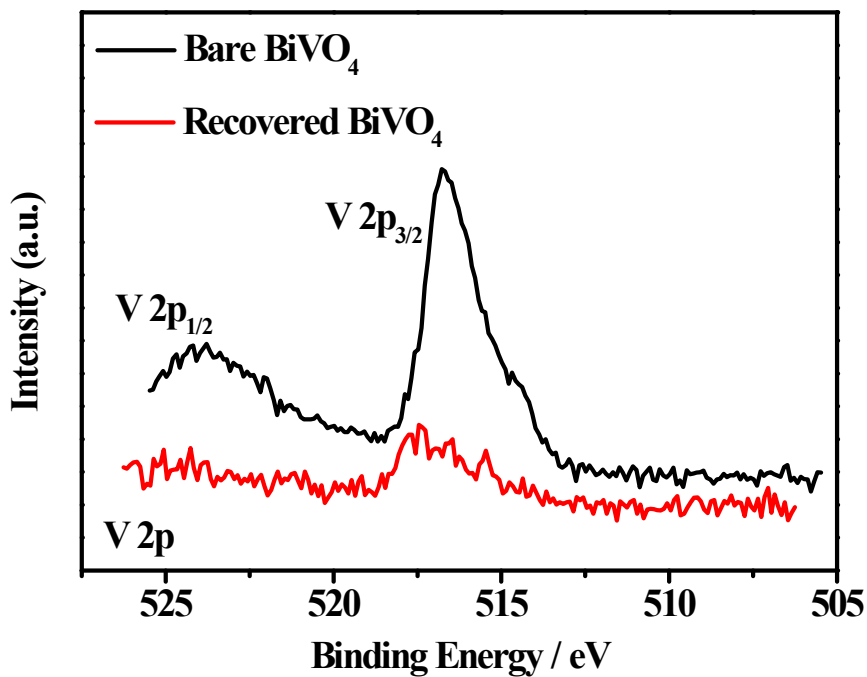


Figure S10. X-Ray photoelectron spectroscopy (XPS) spectra of V 2p.

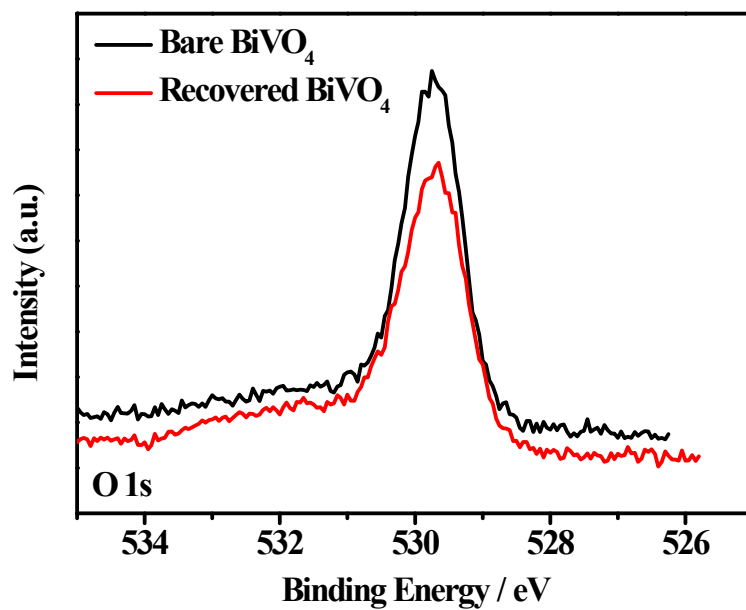


Figure S11. X-Ray photoelectron spectroscopy (XPS) spectra of O 1s.

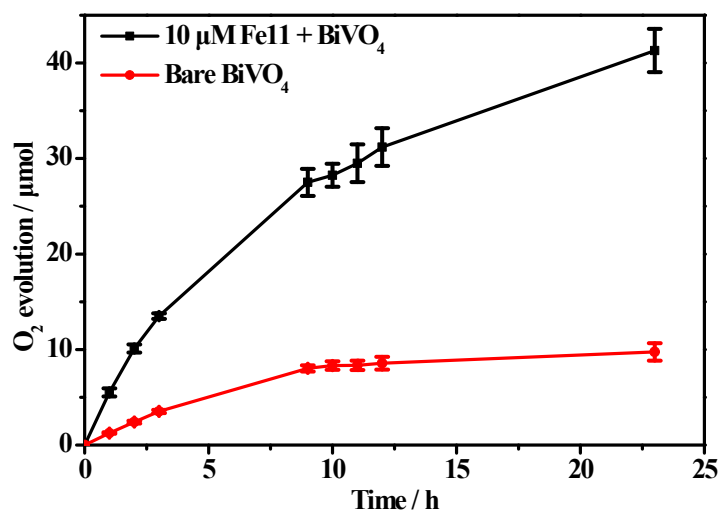


Figure S12. Long time photocatalytic water oxidation performance of BiVO₄ combined Fe11.

Table S1. The ICP-AES result of synthesized **Fe11** solution.

	Fe	Sb	W
Theoretical content (mg/L)	6.143	7.306	110.304
Measured content (mg/L)	7.637	9.273	115.5

Conditions: 500 mM sodium acetate buffer solution (pH 3) contains 10 μ M **Fe11**.

Table S2. Photocatalytic water oxidation result of BiVO₄ combined **Fe11** under pH 3, 4, 5 and 6.

Entry	Fe₁₁ POM Concentration (μ M)	pH	Amount of O ₂ (μ mol)	TOF _{initial} (h ⁻¹)	O ₂ yield (%)
1	10	3	13.6	36	6.0
2	10	4	17.4	43	7.7
3	10	5	18.7	49	8.3
4	10	6	18.8	54	8.4
5 ^a	0	3	2.3	-	1.0
6 ^b	0	3	1.7	-	0.8
7 ^c	0	4	7.3	-	3.2
8 ^d	0	4	14.1	-	6.3
9 ^e	0	5	8.8	-	3.9
10 ^f	0	5	16.4	-	7.3
11 ^g	0	6	8.9	-	4.0
12 ^h	0	6	15.8	-	7.0

Conditions: LED lamp ($\lambda = 420$ nm, 100mW/cm²); 10.0 mg BiVO₄, 10.0 mM NaIO₃, 500 mM sodium acetate buffer; total reaction volume is 15 mL and overall volume is ~32.5 mL; vigorous agitation using a magnetic stirrer; reaction time is 3h; room temperature.

^{a,c,e,g} Bare BiVO₄

^{b,d,f,h} Recovered BiVO₄

$$TOF = \frac{\text{mole of } O_2 \text{ evolution (1h's reaction)}}{\text{mole of Fe11} \times 1 \text{ h}}, \quad O_2 \text{ yield} = \frac{4 \times \text{mole of } O_2 \text{ evolution}}{6 \times \text{mole of NaIO}_3}$$

Table S3. The ICP-AES result of the filtrate after bare BiVO₄ reaction.

	Bi	V
First test content (mg/L)	0.63	0.14
Second test content (mg/L)	0.62	0.13

Conditions: 500 mM sodium acetate buffer solution (pH 3) filtrated after bare BiVO₄ reaction.

Dissolved BiVO₄ ratio calculation:

$$\begin{aligned} \text{Ratio (Bi)} &= \frac{0.625 \text{ mg} \cdot \text{L}^{-1} \times 0.015 \text{ L} \div 208.98 \times 323.92}{10 \text{ mg}} \times 100 \% \\ &= 0.14 \% \end{aligned}$$

$$\begin{aligned} \text{Ratio (V)} &= \frac{0.135 \text{ mg} \cdot \text{L}^{-1} \times 0.015 \text{ L} \div 50.94 \times 323.92}{10 \text{ mg}} \times 100 \% \\ &= 0.13 \% \end{aligned}$$

References

- 1 M. Bosing, I. Loose, H. Pohlmann and B. Krebs, *Chem. – Eur. J.*, 1997, **3**, 1232.
- 2 X. Du, J. Zhao, J. Mi, Y. Ding, P. Zhou, B. Ma, J. Zhao and J. Song, *Nano Energy*, 2015, **16**, 247.
- 3 Y. Zhao, R. Li, L. Mu and C. Li, *Cryst. Growth Des.*, 2017, **17**, 2923.