Supporting Information

The effect of Fe (III) ions on oxygen-vacancy-rich $BiVO_4$ in photocatalytic oxygen evolution reaction

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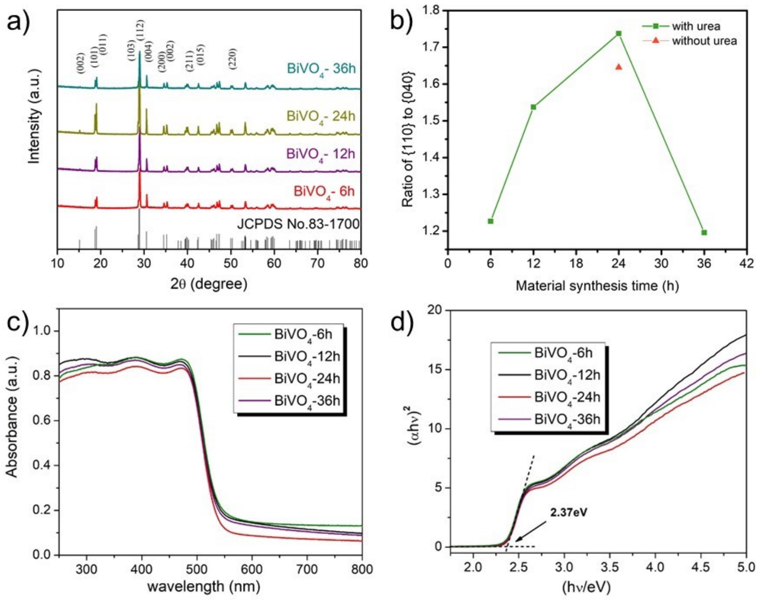

Figure S1. a) XRD patterns, b) the ratio of crystal plane {110} to {040}, c) UV-vis spectra and d) the corresponding Tauc plot of the $BiVO_4$ particles by different reaction times with the assistance of the urea.

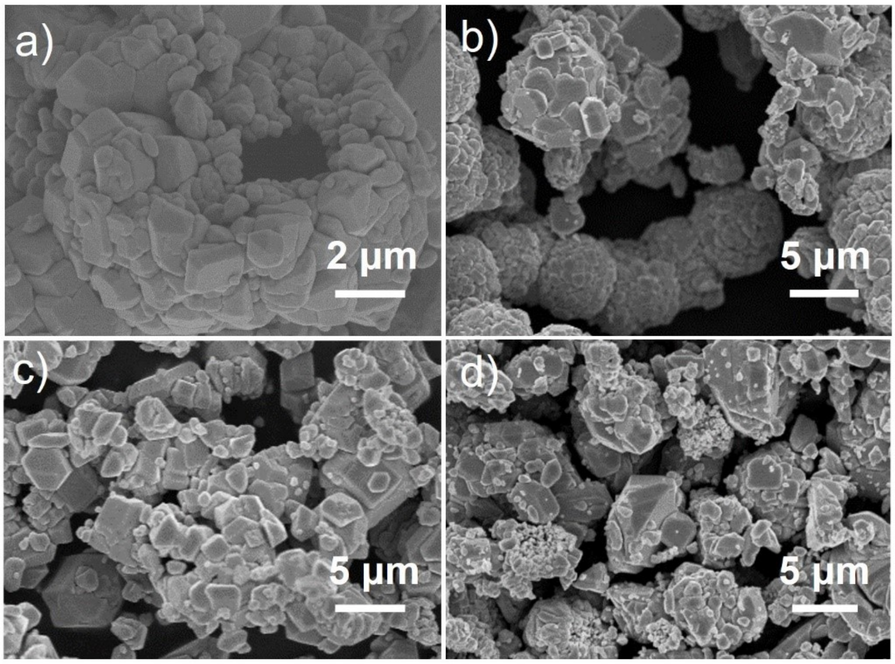

Figure S2. SEM images of the refined $BiVO_4$ particles synthesized within a) 6 h, b) 12 h, c) 24 h and d) 36 h.

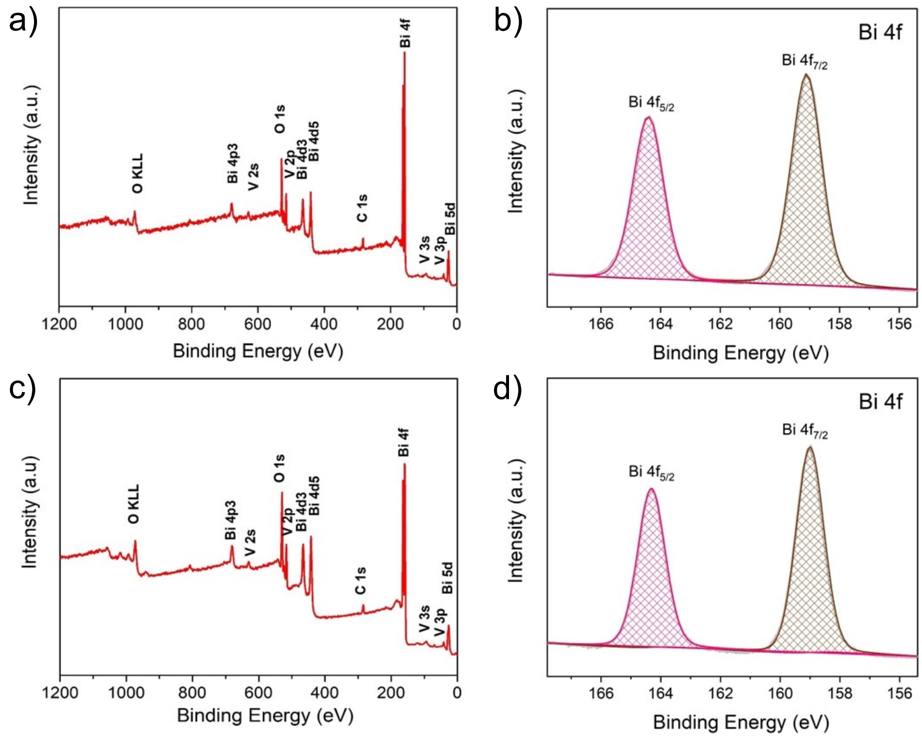

Figure S3. High-resolution XPS spectra of the refined $BiVO_4$ particles of a) sum, b) Bi 4f, of the large $BiVO_4$ particles of c) sum, d) Bi 4f.

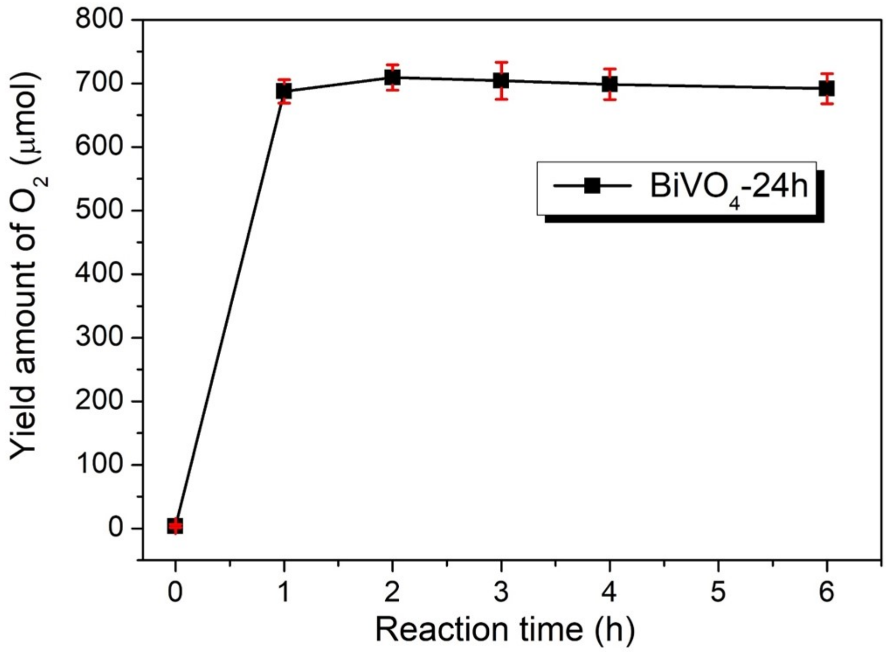

Figure S4. Photocatalytic O_2 evolution of the refined $BiVO_4$ that were prepared within 24h in $AgNO_3$ sacrificial agents.

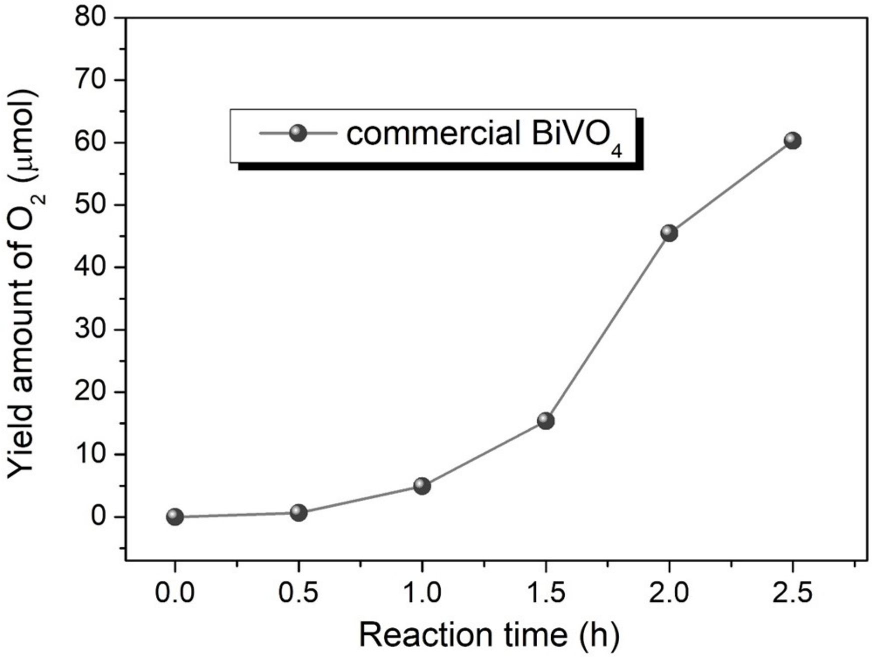

Figure S5**.** Photocatalytic O_2 evolution of commercial $BiVO_4$ in $AgNO_3$ sacrificial agents.

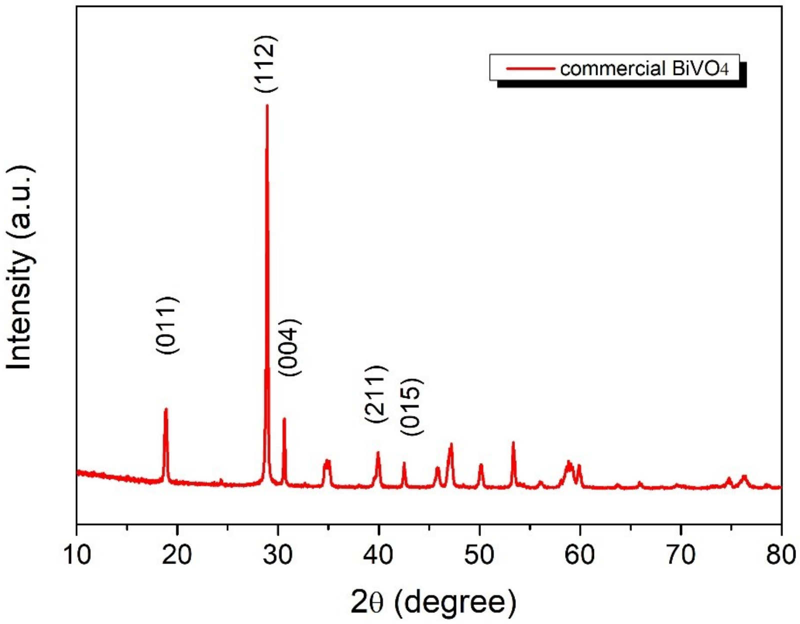

Figure S6. XRD patterns of commercial $BiVO_4$.

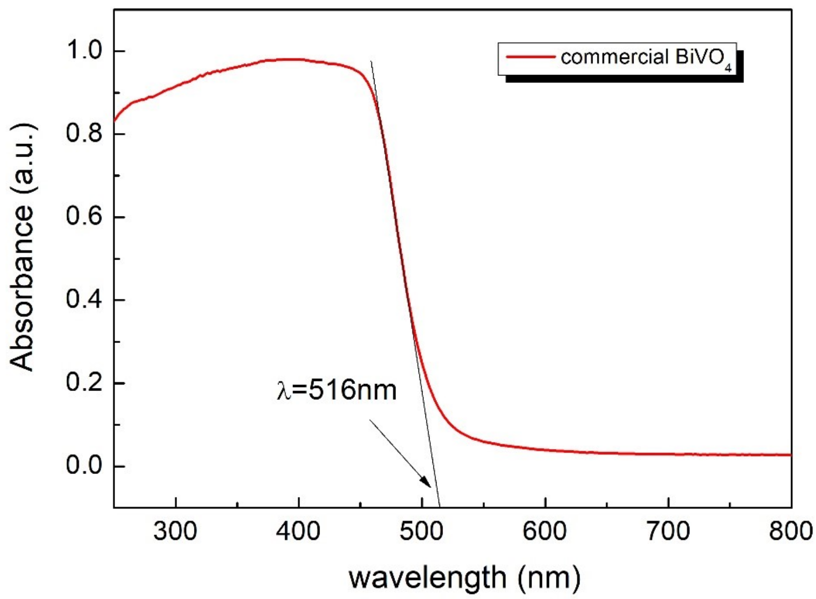

Figure S7**.** UV-vis spectra of commercial $BiVO_4$.

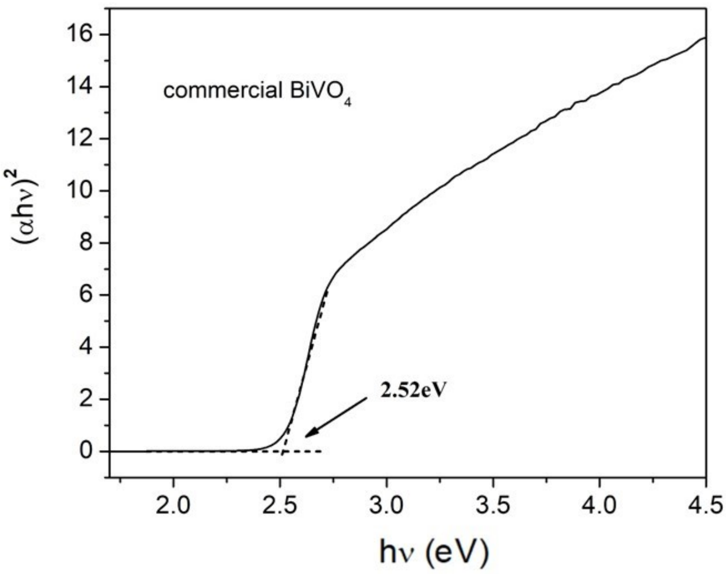

Figure S8. Tauc plot for the corresponding UV-vis spectra of commercial $BiVO_4$.

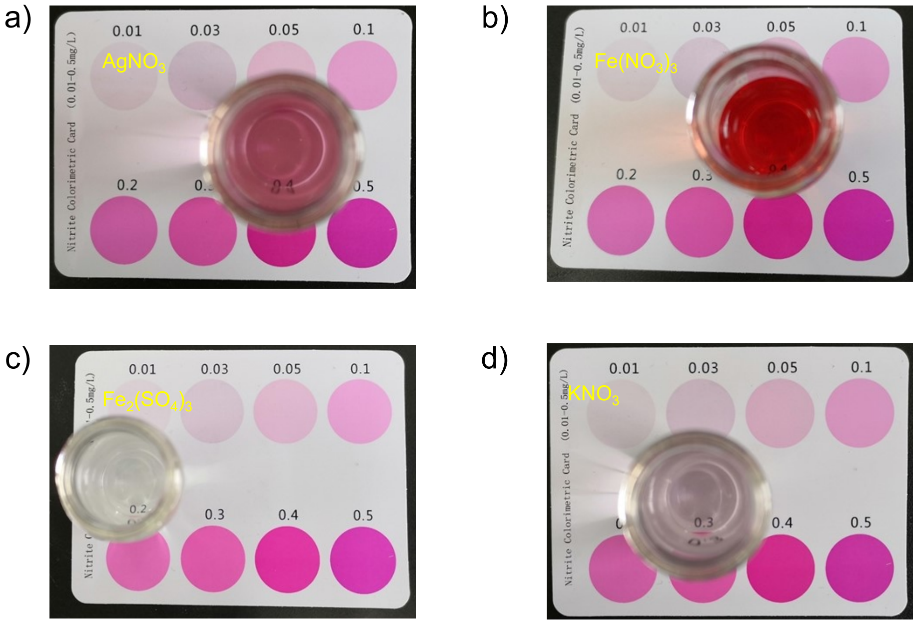

Figure S9**.** Images of the colorimetric test for the NO_2^- ion that was generated in the photocatalytic process for the refined $BiVO_4$ under a) $AgNO_3$, b) $Fe(NO_3)_3$, c) $Fe_2(SO_4)_3$ and d) KNO_3 sacrificial agents.

Figure S10. As mentioned in main text, The $BiVO_4$ film photoanode was prepared via the electrodeposition method. 0.04 M $Bi(NO_3)_3$ was dissolved in 50 ml 0.4 M KI solution which pH was adjusted to 1.7 by HNO_3. At the same time, 0.23 M p-benzoquinone was added to 20 ml ethyl alcohol. Then, these two kinds of solution were poured together and mixed under rapid stirring until the solution became clear. The Bi species layer was deposited in the above solution by applying a repetitive sequence of passing 0.1 C/cm^2 at a potential of -0.1 V versus Ag/AgCl. Then, 200 μl 0.2M $VO(acac)_2$ in DMSO was placed on BiOI and calcination at 450°C for 2 h.

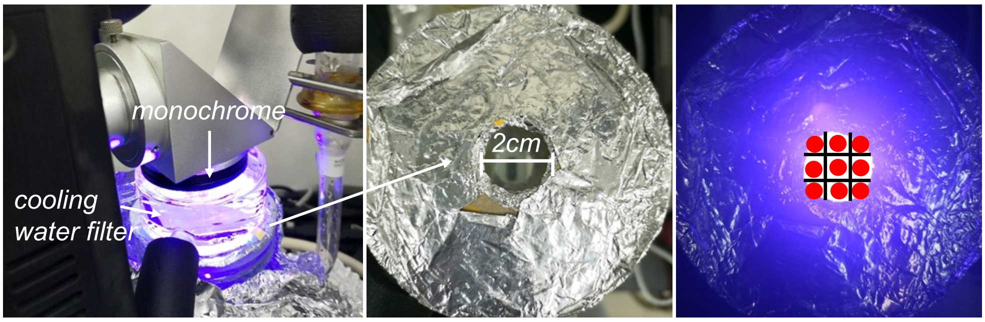

Figure S11. Light intensity test of monochromatic filter for AQE. The monochromatic light value was taken an average for 9 points. It is noticeable that when testing the monochrome filter, the cooling water filter is needed and the current density of light source must to be adjusted to minimum, to avoid the monochrome filter broken.

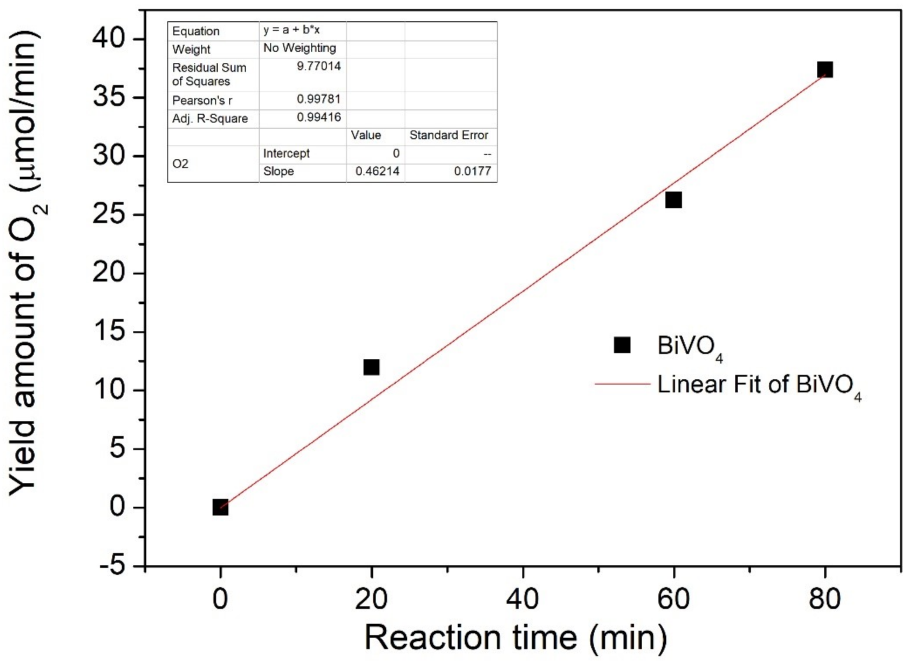

Figure S12. The apparent quantum efficiency (AQE) measurement of $BiVO_4$ at 420 nm in $AgNO_3$ solution.

According to the following equations:

$$AQE\ (\%) = \frac{Number\ of\ reacted\ electrons}{Number\ of\ incident\ photons} \times 100\%$$

$$= \frac{Number\ of\ evolved\ O_2\ molecules \times 4}{Number\ of\ incident\ photons} \times 100\%$$

$$= \frac{\mu mol \times N_A \times 10^{-6} \times 4}{\frac{I \times A \times t}{E_g \times J}} \times 100\%$$

In which $N_A = 6.02*10^{23}$, I (light intensity) = 3.589 mW/cm^2, $E_g = 1240/\lambda$, (λ=420nm), A (area) = 3.14 cm^2, t (time) = 60 s, J = $1.6*10^{-19}\, j$. It could be calculated that the AQE of $BiVO_4$ at 420 nm in $AgNO_3$ aqueous solution is 77.8%.

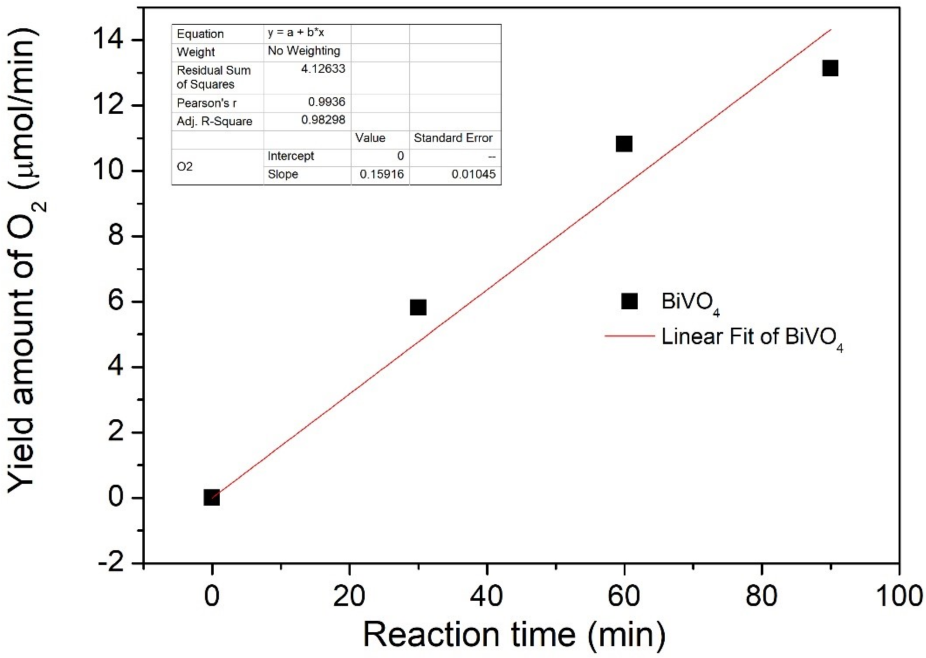

Figure S13. The apparent quantum efficiency (AQE) measurement of $BiVO_4$ at 420 nm in $Fe(NO_3)_3$ solution.

According to the above equation, in which N_A = 6.02*10^{23}, I (light intensity) = 4.91111 mW/cm^2, E_g = 1240/λ, (λ=420nm), A (area) = 3.14 cm^2, t (time) = 60 s, J = 1.6*10^{-19} *j*. it could be calculated that the AQE of $BiVO_4$ at 420 nm in $Fe(NO_3)_3$ aqueous solution is 19.6%.

Table S1. RSF of oxygen and vanadium element.

Atomic number	Element	RSF
8	O	0.780
23	V	2.116

Table S2. Comparison of oxygen evolution performance and AQE of the $BiVO_4$ samples reported in the recent literatures.

Photocatalyst	Weight of photocatalyst(g)	Sacrificial agent	Amount of Sacrificial agent(mM)	Light source	Incident light(nm)	Oxygen production rate(μmol/h)	AQE	Refs.
$BiVO_4$	0.2g	$AgNO_3$	12.5	300W Xe lamp	400 nm cutoff	680	77.8%(420nm)	This work
30-faceted $BiVO_4$	0.1g	$NaIO_3$	20	300W Xe lamp	420 nm cutoff	57.0	18.3%(430nm)	[1]
$BiVO_4$-Cl	0.1g	$AgNO_3$	5	300W Xe lamp	400 nm cutoff	230.52	34.6%(420nm)	[2]
Co_2O_3-$BiVO_4$	0.05g	$NaIO_3$	20	300W Xe lamp	400nm cutoff	31	10%(435nm)	[3]
$BiVO_4$	0.003	$Fe(NO_3)_3$	8	300W Xe lamp	400nm cutoff	-	62%(420nm)	[4]

References:

1. P. Li, X. Chen, H. He, X. Zhou, Y. Zhou and Z. Zou, *Adv. Mater.*, 2018, **30**, 1703119.
2. Q. Zhang, M. Liu, W. Zhou, Y. Zhang, W. Hao, Y. Kuang, H. Liu, D. Wang, L. Liu and J. Ye, *Nano Energy*, 2021, **81**, 105651.
3. J. Wang and F. E. Osterloh, *J. Mater. Chem. A*, 2014, **2**, 9405-9411.
4. Y. Zhao, C. Ding, J. Zhu, W. Qin, X. Tao, F. Fan, R. Li and C. Li, *Angew. Chem., Int. Ed.*, 2020, **59**, 9653-9658.