Electronic Supplementary Information (ESI)

Highly Symmetrical, 24-Faceted, Concave $BiVO_4$ Polyhedron Bounded by Multiple High-Index Facets for Prominent Photocatalytic O_2 Evolution under Visible Light

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Experimental Section

Reagents: Bismuth nitrate pentahydrate (AR 99%), Ammonium metavanadate (AR), sodium hydroxide (AR) and ethanol absolute (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Analytical grade sodium dodecylbenzensulfonate(SDBS) and nitric acid were purchased from Chengdu Kolong Chemical Reagent Co., Ltd and Nanjing Chemical Reagent Co., Ltd, respectively. All chemicals were used as received, unless otherwise stated. Deionized water was prepared with a Milli-Q puritysystem (18.2 MΩ).

Synthesis of S_{24} : 2 mmol $Bi(NO_3)_3 \cdot 5H_2O$ and 0.5 g SDBS were dissolved in a nitric acid solution (noted as A solution). 2 mmol NH_4VO_3 were dissolved in a sodium hydroxide solution (noted as B solution). Then B solution was added into the A solution under vigorous stirring. After 30 min stirring, an appropriate amount of 2 M sodium hydroxide solution was also added into the prepared solution to adjust the acid concentration to 0.1M. The final 40 mL solution was transferred into a 100 ml Teflon-lined autoclave and maintained at 180 ℃ for 2 h, followed by naturally cooling to room temperature. The resulting solid products were collected through centrifugation at 12000 rpm for 5 min and were washed with deionized water and ethanol for several times, and finally dried in vacuum at 60°C for 12h.

Prepare of S_b: the reference sample S_b was obtained by the solid-state reaction (SSR) of raw materials of Bi_2O_3 and V_2O_5 at 900 ^{0}C for 12 hours.

Characterizations: X-ray diffraction (XRD) was conducted on a Bruker D8 Advance diffractometer using Cu Kα radiation (λ = 0.15406 nm), where the data was collected in the 2θ range of 20–80° at a step size of 0.02°. FE- SEM images of solid products were measured on a Nova Nanosem 200 system operated at an acceleration voltage of 15 kV. Both transmission electron microscopy (TEM) and high-resolution

transmission electron microscopy (HRTEM) were performed on JEOL-3010 instrument. XPS was performed on a spectrometer from Kratos Axis Ultradld, using Mono Al Kα (1486.71eV) radiation at a power of 120 W (8 mA, 15 kV). All binding energies were referenced to the C 1s peak (284.6 eV) arising from adventitious carbon.

Photocatalytic H_2O splitting test : Photocatalytic activity in O_2 production was evaluated using a 400 mL Pyrex flask with a closed gas circulation and evacuation system. A 300 W Xe lamp with a UV-cut off filter ($\lambda \geqslant 420$ nm) was employed as the light source. In a typical experiment, 100.0 mg as-prepared photocatalyst powders was dispersed by using Magnetic stirring in the 270 mL aqueous solution using 0.05 M $AgNO_3$ as the sacrificial reagent. Before irradiation, the suspension was pumped to remove any dissolved oxygen in order to guarantee that the reaction system was under anaerobic condition. Typically, amount of evolved gas was determined using a gas chromatograph (Shimadzu GC-2014C, argon carrier) equipped with a thermal conductivity detector (TCD). The apparent quantum efficiency (AQY) was also measured under the same reaction conditions except using LED as the light source (5 W, 420 nm, Beijing Perfectlight Technology). The AQY was calculated according to equation (1)

$$\mathrm{AQY}(\%) = \frac{\text{number of } O_2 \text{ molecules evolved} \times 4}{\text{number of incident photons}} \times 100 \quad \text{..... (1)}$$

$$= \frac{4nN_A hc}{PS\lambda t} \times 100$$

Computational Details: VASP code[1,2] with the projector augmented wave (PAW) pseudopotentials[3] is employed to carry out the optimization of monoclinic scheelite

$BiVO_4$ unit cell and surfaces. The Perdew-Burke-Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA) is used for the exchange correlation.[4] The bulk lattice parameters of $BiVO_4$ are relaxed using 400 eV as the cutoff energy and 6×6×3 Monkhorst-Pack type of k-points sampling. According to the experiment parameters of monoclinic scheelite $BiVO_4$,[5] β angle, which should be 90.383º, was set as 90º for simplification. Fig. S10a show the optimized bulk structure. The calculated lattice parameters are a=5.1773Å, b= 11.7609Å, c= 5.1450Å, β=90º, which keep in good conformity with the experiment data.[5]

GGA-PBE is used to relax the six exposed surfaces of $BiVO_4$ single crystal synthesized experimentally, which are depicted in Fig. S10. The surfaces were represented by slab models repeated periodically with a vacuum region of 15 Å. There are 144 atoms in (010) and (110) surface, and 192 atoms in (012), (210), (115) and (511) surfaces. We used 3×3×1 Monkhorst-Pack type k-points sampling for (010) and (110) cells, 2×1×1 k-points sampling for (012) cell, and 1×2×1 k-points sampling for (210), (115) and (511) cells. The top half of slab and adsorbants are relaxed and the bottom half of slab is fixed as the positions in bulk.

References

1 G. Kresse, J. Furthmuller, *Computational Materials Science* 1996, **6**, 15.

2 G. Kresse, J. Furthmüller, *Physical Review B*, 1996, **54**, 11169.

3 P. E. Blöchl, *Physical Review B*, 1994, **50**, 17953.

4 J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

5 A. W. Sleight, H. Y. Chen, F A. erretti, D. E. Cox, *Mater. Res. Bull.*, 1979, **14**, 1571.

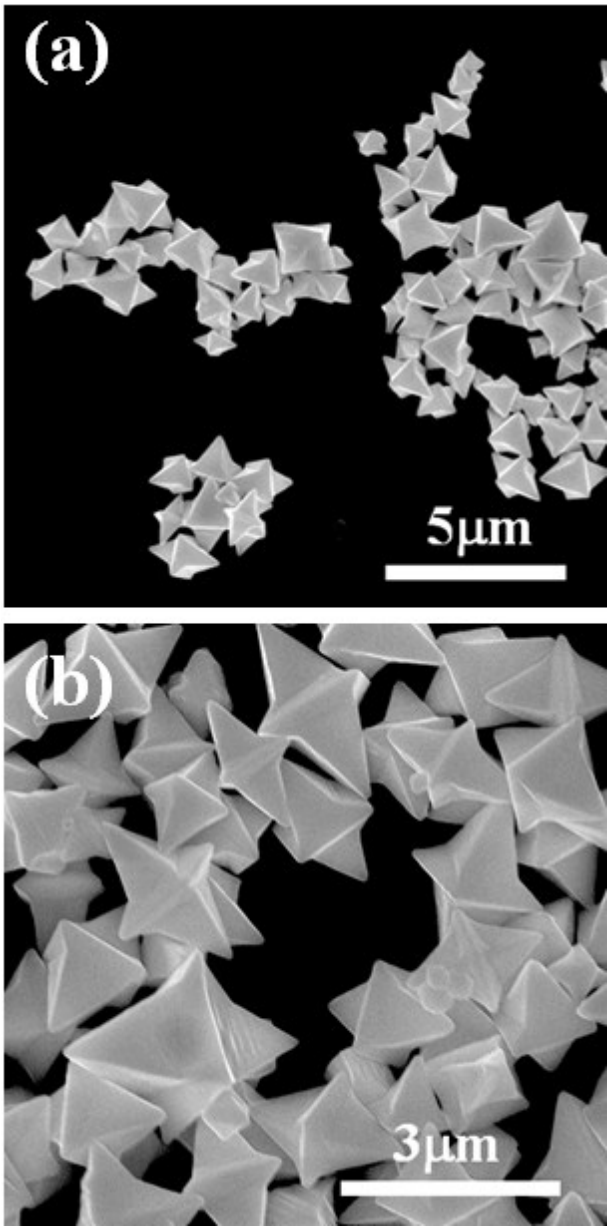


Fig. S1 (a and b) FE-SEM images of S_{24} at different magnification.

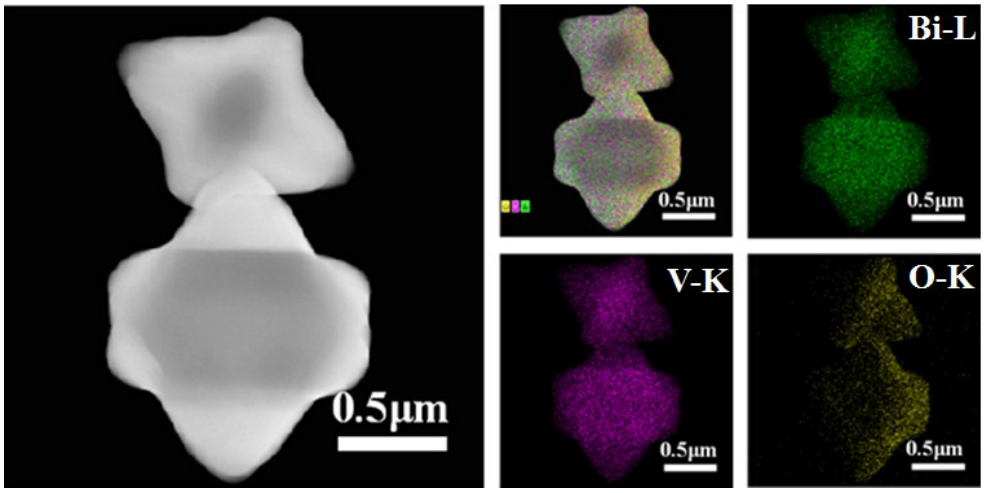


Fig. S2 EDX elemental mapping of S_{24} sample, clearly showing Bi (green), V (purple), and O (yellow) evenly distributed in the sample.

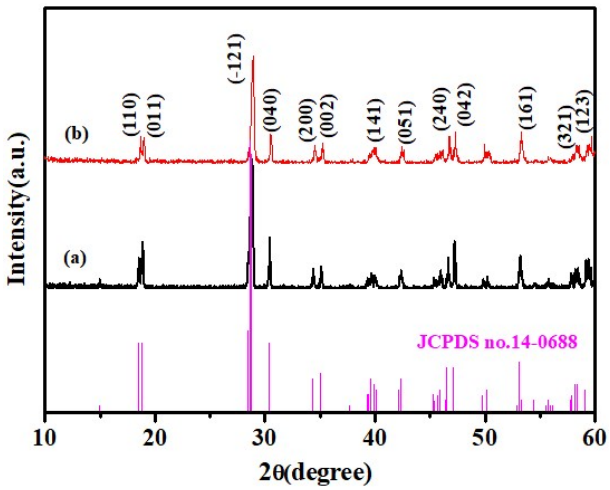


Fig. S3 XRD patterns of various $BiVO_4$ materials: (a) S_b and (b) S_{24}.

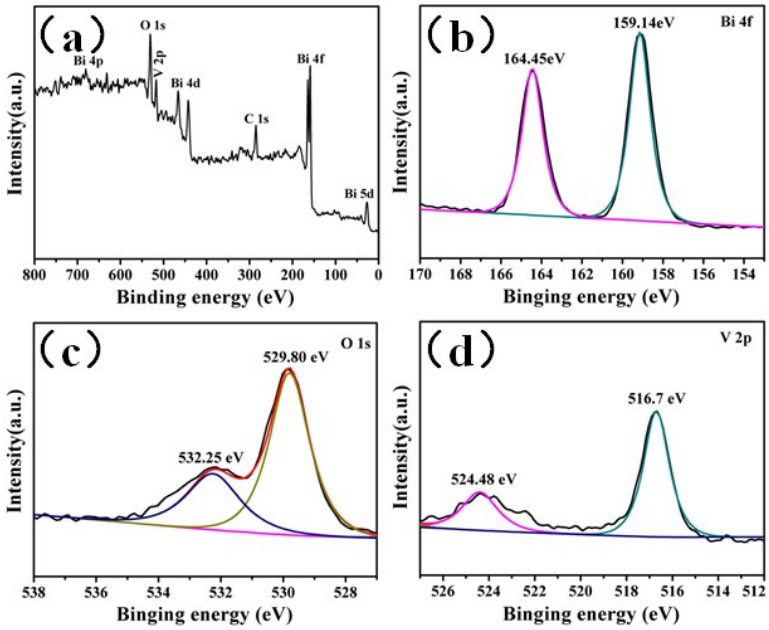


Fig. S4 (a) XPS fully scanned spectra of S_{24} sample; High resolution XPS spectra for (b) Bi 3d for Bi^{3+}, (c)V 2p for V^{5+}, (d) O 1s for O^{2-}.

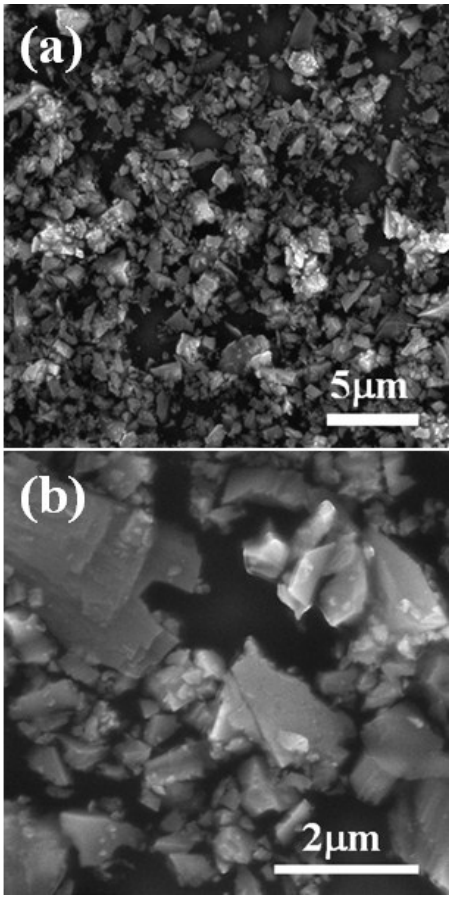


Fig. S5 (a and b) FE-SEM images of S_b at different magnification.

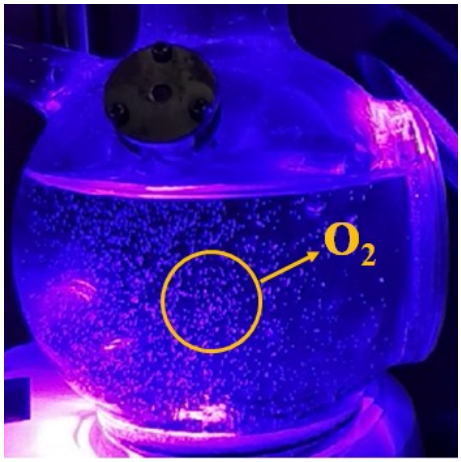


Fig. S6 photograph of photocatalytic O_2 evolution over the S_{24} obtained by Supplementary Moive1 under LED irradiation with 420 nm.

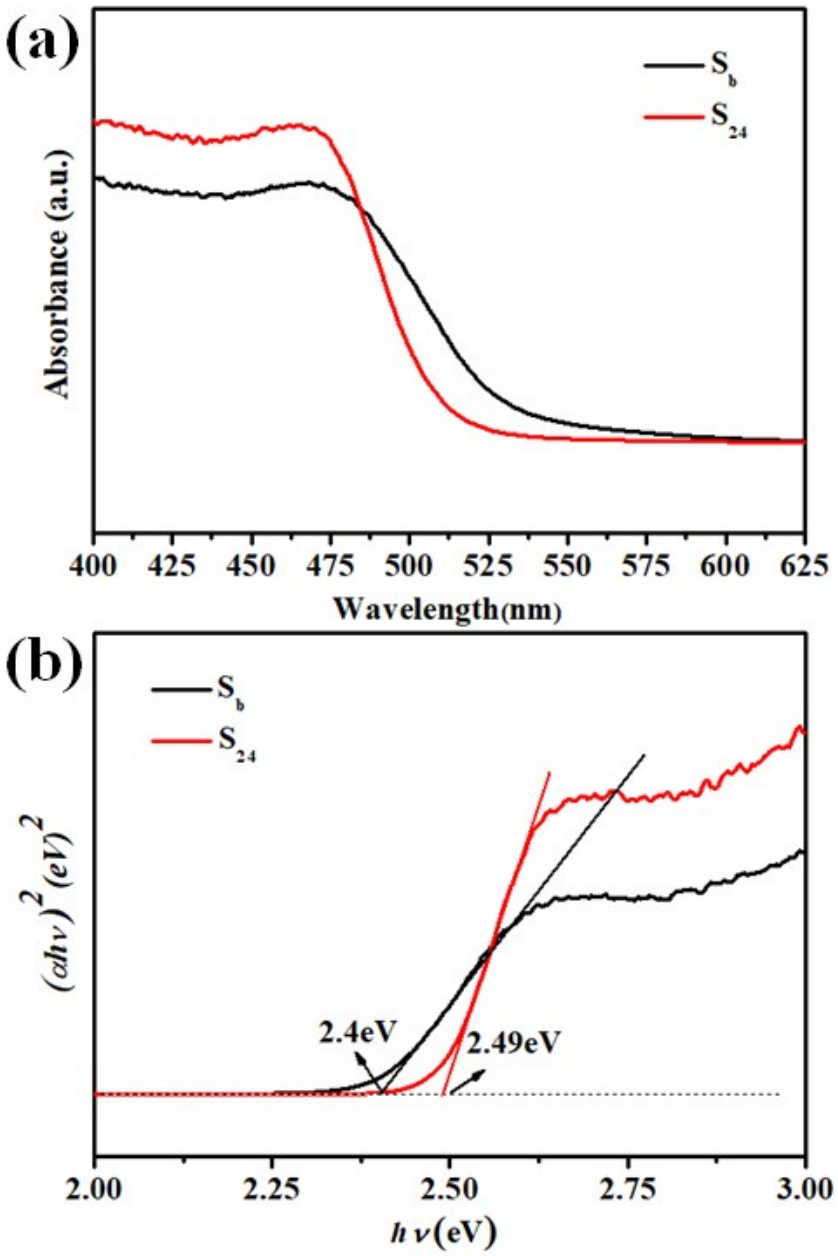


Fig. S7 (a) UV/Vis absorption spectra of S_b and S_{24}. (b) plots of $(\alpha h\nu)^2$ versus $h\nu$ for S_B and S_{24} sample, by which the values of the energy band gaps of the products could be estimated, corresponding to those in (a).

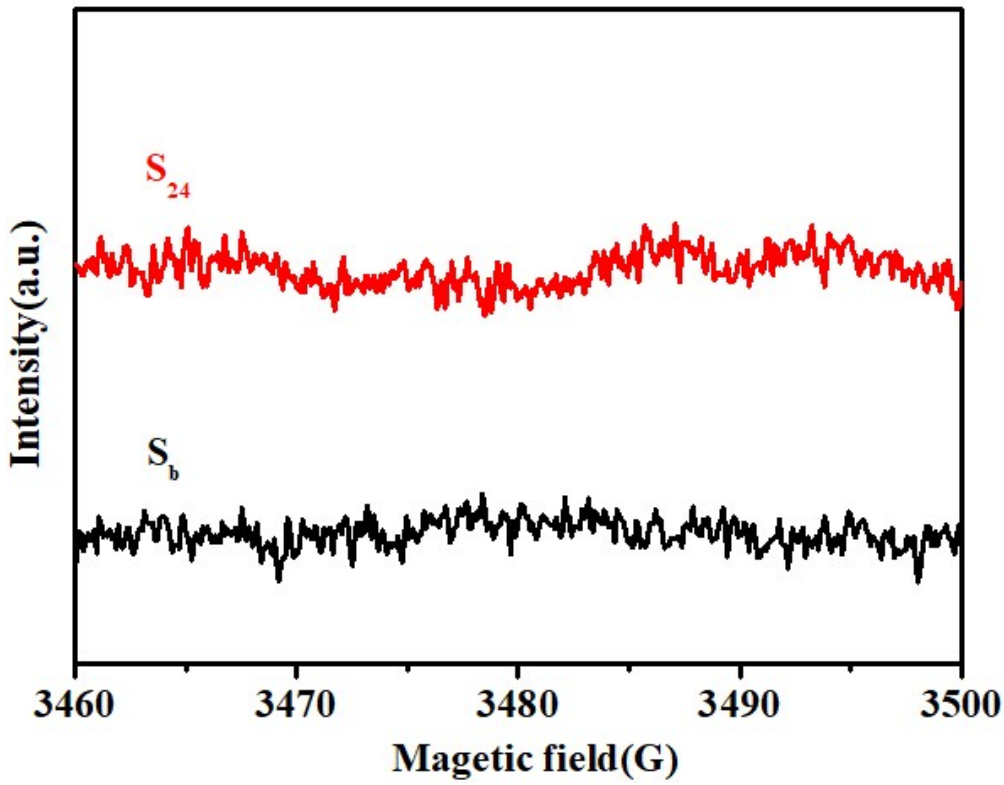


Fig. S8 EPR spectra of S_b and S_{24}.

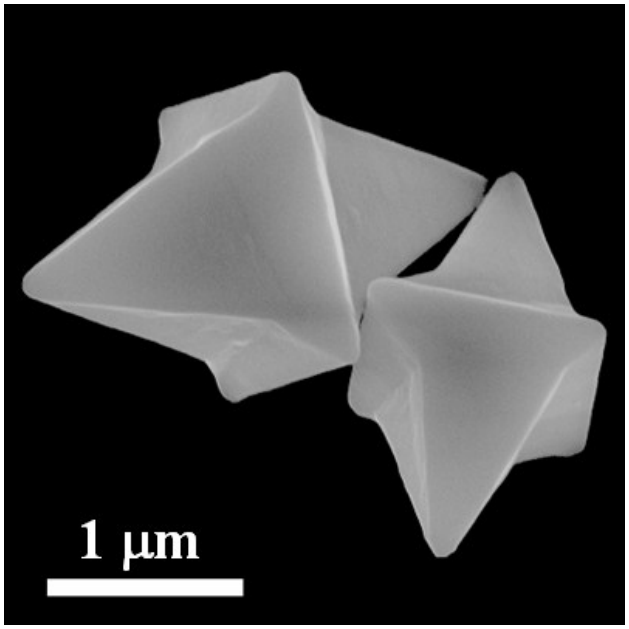


Fig. S9 The SEM images of the S_{24} after O_2 evolution reactions.

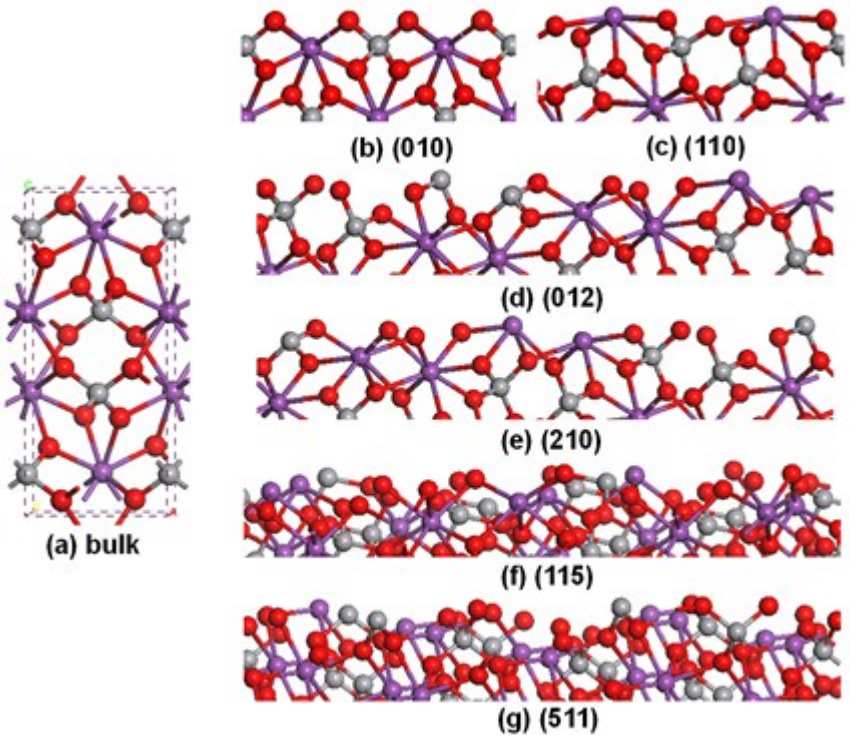


Fig. S10 Illustration of monoclinic bulk $BiVO_4$ (a) and stoichiometric surface (010) (b), (110) (c), (012) (d), (210) (e), (115) (f) and (511) (g). The red, purple and gray spheres represent O atoms, Bi atoms and V atoms, respectively.

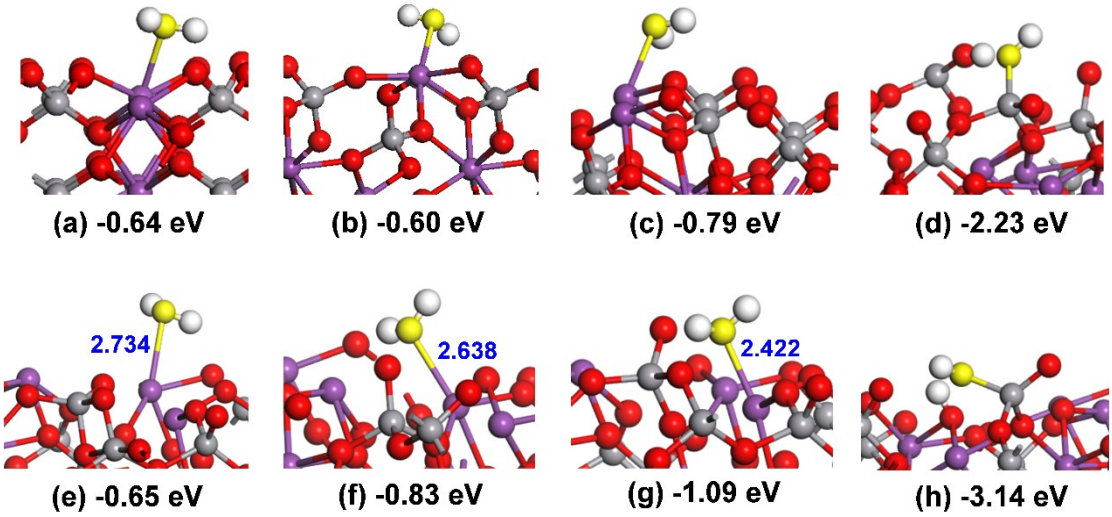
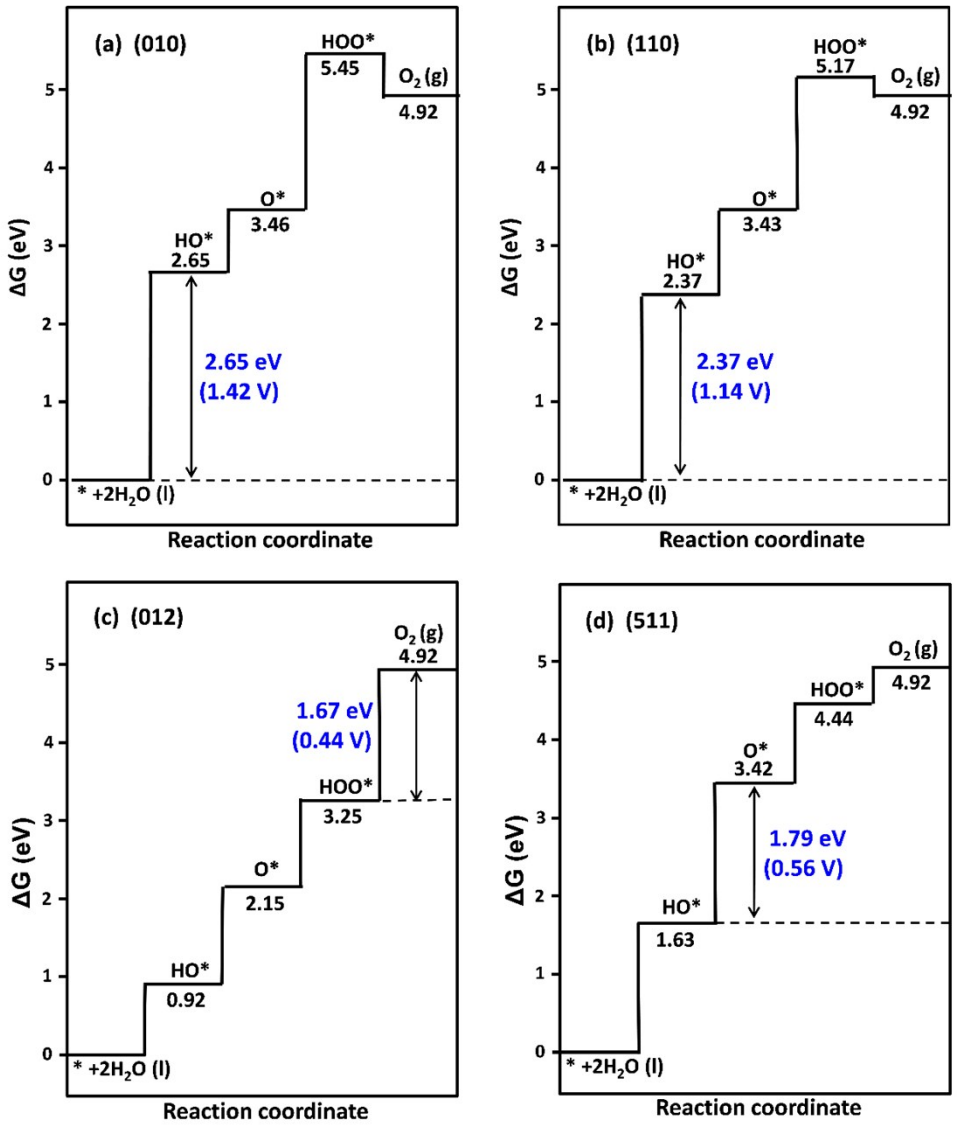


Fig. S11 Relaxed adsorption configurations for H_2O adsorbed on the (a) (010), (b) (110), (c) and (d) (012), and (e), (f), (g), and (h) (511) surfaces, and the corresponding adsorption energies. The red, purple, gray, yellow and white balls stand for oxygen from $BiVO_4$, bismuth, vanadium, oxygen from water and hydrogen atoms, respectively. The Bi-O bond lengths described in blue as shown in (e), (f), and (g).



~~**Fig. S12** Free energy diagrams for four steps of OER on (a) (010), (b) (110), (c) (012), and (d) (511) surface of $BiVO_4$ at U = 0, pH = 0 and T = 298 K. The ΔG (vertical sold line with arrows) value of the rate-determining step for every surface is shown.~~

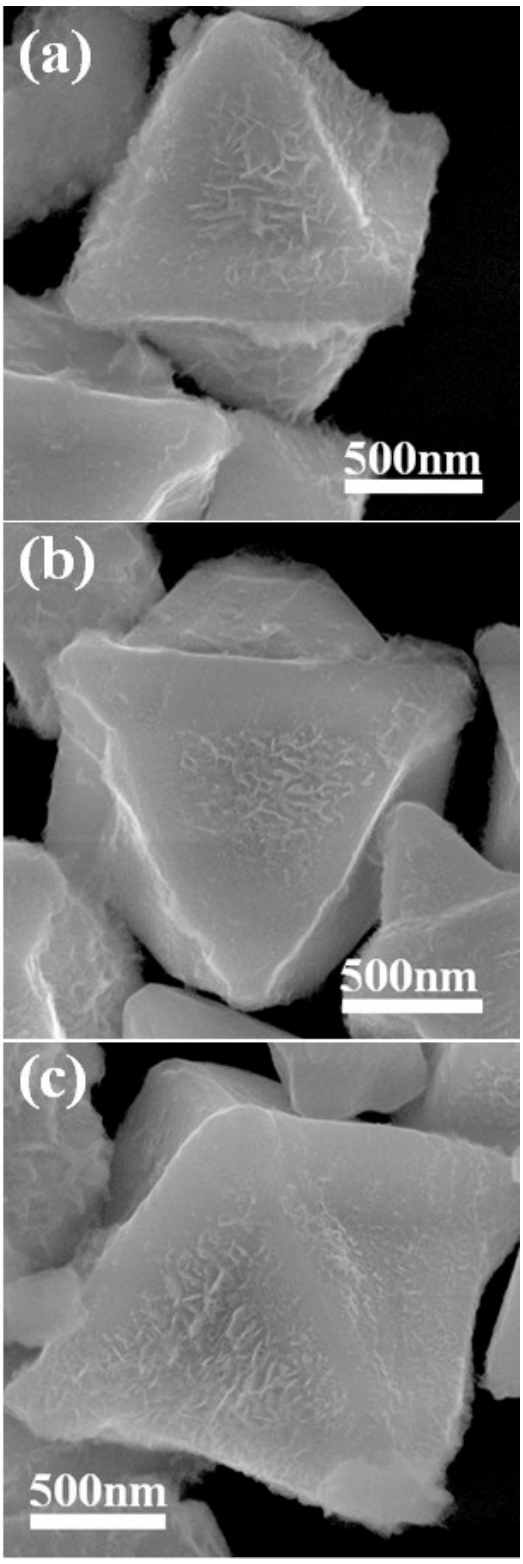


Fig. S13 SEM images of S_{24} with MnO_X.

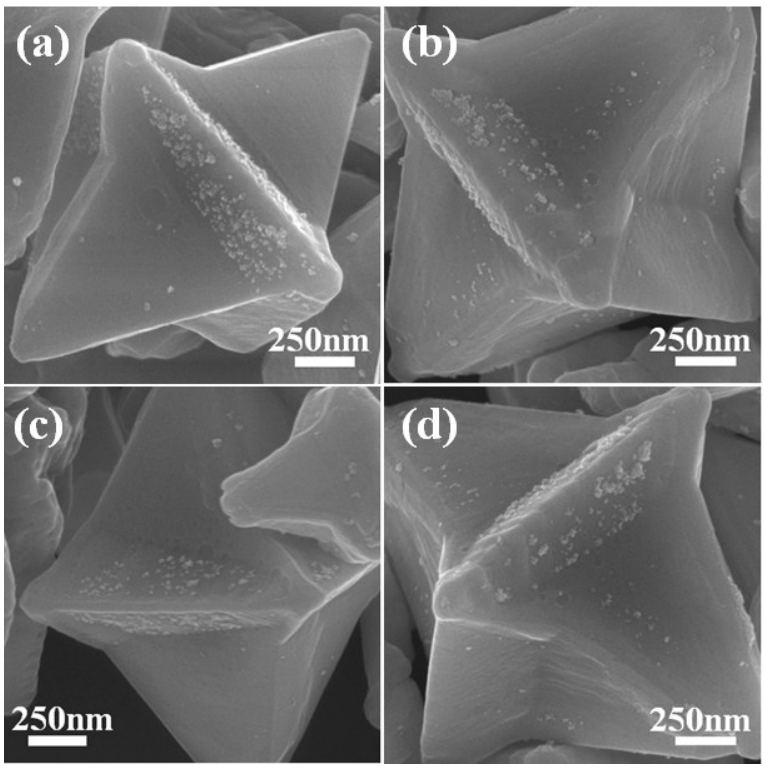


Fig. S14 SEM images of S_{24} with Pt.

Table S1 Comparison of quantum efficiency of the 24-faceted, concave $BiVO_4$ polyhedron with the well-known catalysts reported in the recent literatures.

Photocatalytic	AQY (%)	Reference
24-facets $BiVO_4$ Polyhedron	30.7 (420 nm)	This work
Ultrathin monoclinic $BiVO_4$ nanosheets	26.1 (420 nm)	*ACS Catal.* **2018,** 8, 8649−8658
30-facets $BiVO_4$ Polyhedron	18.3 (430 nm)	*Adv.Mater.***2018**, *30*, 1703119
$BiVO_4$ Powder	9.0 (450 nm)	*J. Am. Chem. Soc.* **1999,** 121, 11459−11467.
Pristine $BiVO_4$	8.3 (420 nm)	*Chem. Mater.* **2016,** 28, 1318−1324
Facted $BiVO_4$	0.50 (450 nm)	*Nano Energy, 2018,51, 764-773*
Pristine BVO_4 nanotubes	0.55(420 nm)	*ACS Appl. Nano Mater. 2018, 1, 2589*
Bare $BiVO_4$	0.5 (420 nm)	*J. Catal.* **2016**, *338*, 168–173
Bare $BiVO_4$	0.52 (420 nm)	*Chem. Engineer J.* **2015**, *281*,102–108