Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Boost quantum efficiency of $BiVO_4$ photoanode by increasing oxygen vacancies for highly-efficient solar water oxidation

Bin Li, [a, b] Qi Qin, [a] Chuanyong Jian, [a, b] Qian Cai, [a] and Wei Liu [a] *

[a] CAS Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China

[b] University of Chinese Academy of Sciences, Beijing, 100049, China

*Corresponding authors: E-mail: liuw@fjirsm.ac.cn

Experimental section

Photoelectrochemical measurements:

Photocurrent-potential curves were monitored using linear sweep voltammogram in a voltage window of 0.2~1.3 V vs. RHE with a scan rate of 10 mV/s. The conversion between potentials vs. Ag/AgCl and RHE is performed according to the Nernst equation below: [1]

$$E_{RHE} = E_{Ag/AgCl} + 0.059 * \text{pH} + E^{0}_{Ag/AgCl}$$

Where E_{RHE} is the potential referred to a reversible hydrogen electrode (RHE), and $E_{Ag/AgCl}$ is the measured potential against Ag/AgCl reference electrode. The incident-photon-to-current-efficiency (IPCE) as a function of wavelength for the prepared photoanodes was measured at a bias of 1.23 V vs. RHE by a CHI660e electrochemical workstation, and the monochromator was incremented in the spectral range (300-600 nm) with a sampling interval of 20 nm and a current sampling time of 10s. The IPCE was calculated by equation: [2]

$$\mathrm{IPCE}\ (\%) = \frac{1240 \times J_{ph}}{P_{mono} \times \lambda} \times 100\%$$

Where J_{ph} presents the photocurrent density ($\mathrm{mW \cdot cm^{-2}}$) obtained from the electrochemical workstation. P_{mono} is the intensity of the incident monochromatic light ($\mathrm{mW \cdot cm^{-2}}$), and λ is the wavelength (nm) of the monochromatic light.

Applied bias photon-to-current efficiency (ABPE) can be calculated using the following equation: [2]

$$\mathrm{ABPE}\ (\%) = \frac{(1.23 - V_b) \times J_{ph}}{P_{light}} \times 100\%$$

Where J_{ph} presents the photocurrent density ($\mathrm{mW \cdot cm^{-2}}$) obtained from the electrochemical workstation. V_b refers to the applied bias vs. RHE (V), and P_{total} is the total light intensity of AM 1.5 G (100 $\mathrm{mV \cdot cm^{-2}}$).

To confirm the inference, we calculated the transient decay time using the following equation: [3]

$$D = \frac{I_t - I_s}{I_m - I_s}$$

Where I_t represents current at time t, I_s represents the stabilized current, and I_m represents the current spike. The transient decay time can be defined as the time at which Ln $D = -1$.

Chopped-light amperometric J-t measurements were performed at an applied potential of 1.23 V under chopped light irradiation (light on or off cycles: 10 s). Mott-Schottky (MS) spectra were measured in the dark (increment: 10 mV, open circles:

1000 Hz, filled circles: 500 Hz). Electrochemical impedance spectroscopy (EIS) measurements for all the photoanodes were conducted by applying AC voltage amplitude of 10 mV within the frequency range from 10^5 to 10^{-2} Hz.

Solid current-voltage (I-V) measurements: Solid-state conductivity measurements were carried out by a 2-point measurement setup which consisted of a USMCO micromanipulator and precision semiconductor parameter analyzer (4156C, Agilent technologies, Japan). All I-V curves were measured with 20 mV/s sweep rate in the voltage window from -300 mV to 300 mV.

The charge carrier density (N_d) can be calculated using the following equation: [4]

$$N_d = \frac{2}{e\varepsilon\varepsilon_o} \times \left[\frac{d\left[\frac{1}{C^2}\right]}{dV_s} \right]^{-1}$$

The electronic charge is 1.6×10^{-19} C, vacuum permittivity (ε_0) is 8.86×10^{-12} F • m^{-1}, and relative permittivity (ε) is 68 for $BiVO_4$ photoanode. V_s (V) is the applied potential for MS curves. C (F • cm^{-2}) is the space charge capacitance in the semiconductor obtained from MS curves.

Figures

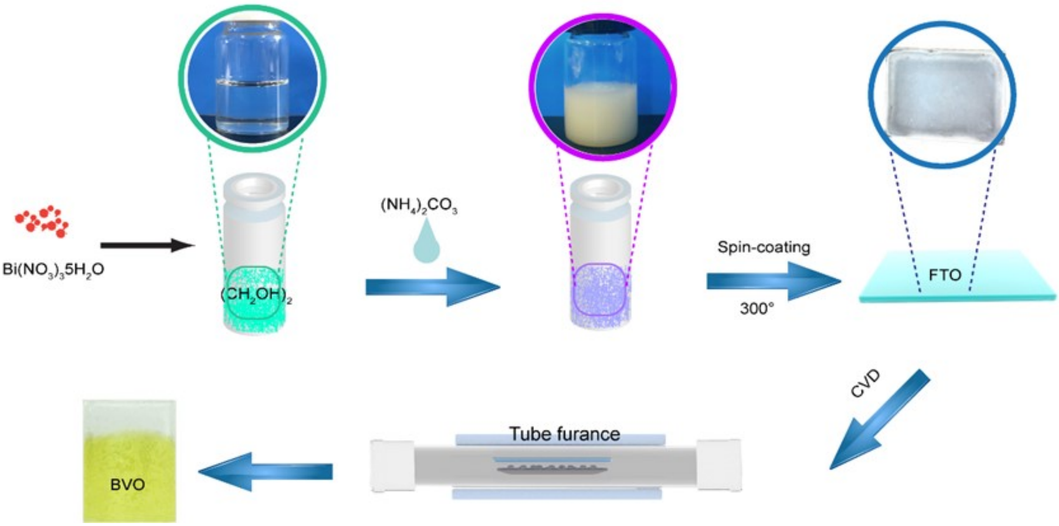

Fig. S1 Schematic of the fabrication process flow of $BiVO_4$ films.

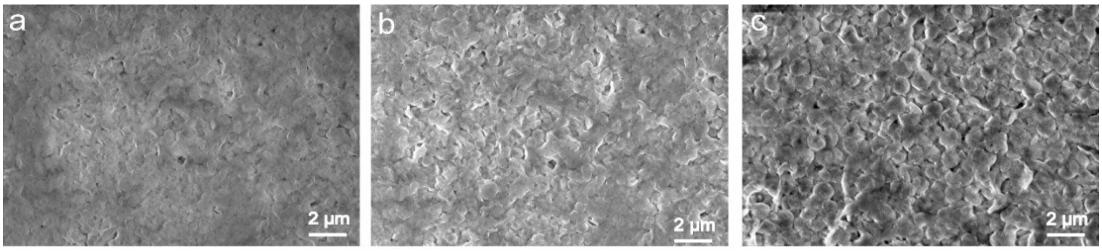

Fig. S2 Top view SEM images of three different $(BiO)_2CO_3$ films. It can be clearly seen that the $(BiO)_2CO_3$ particle size is around 1 μm.

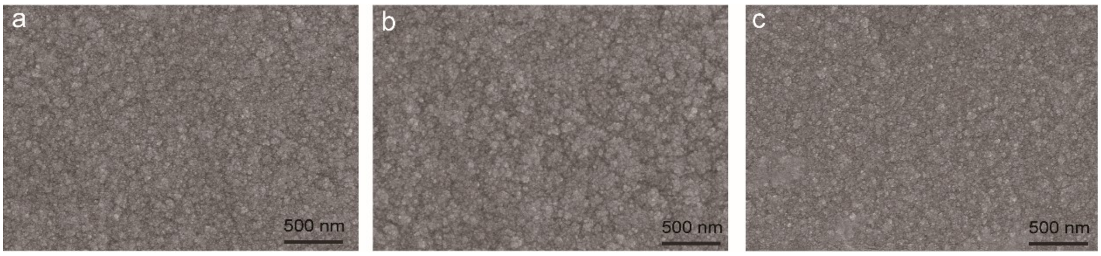

Fig. S3 Top view SEM images of Bi_2O_3 films after annealing the $(BiO)_2CO_3$ films in air at different temperature in the range from 250 °C to 350 °C.

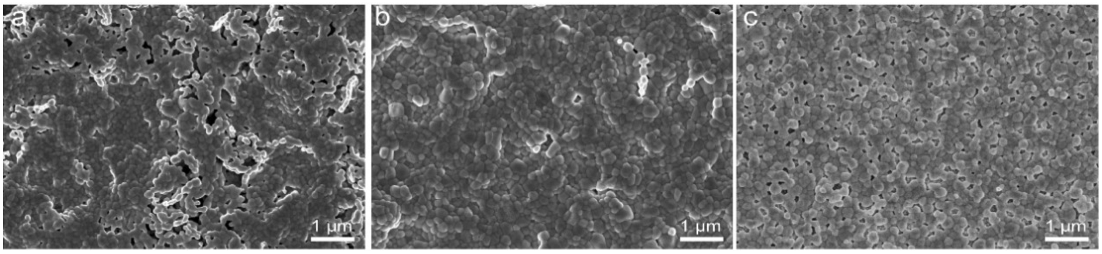

Fig. S4 Top view SEM images of $BiVO_4$ films.

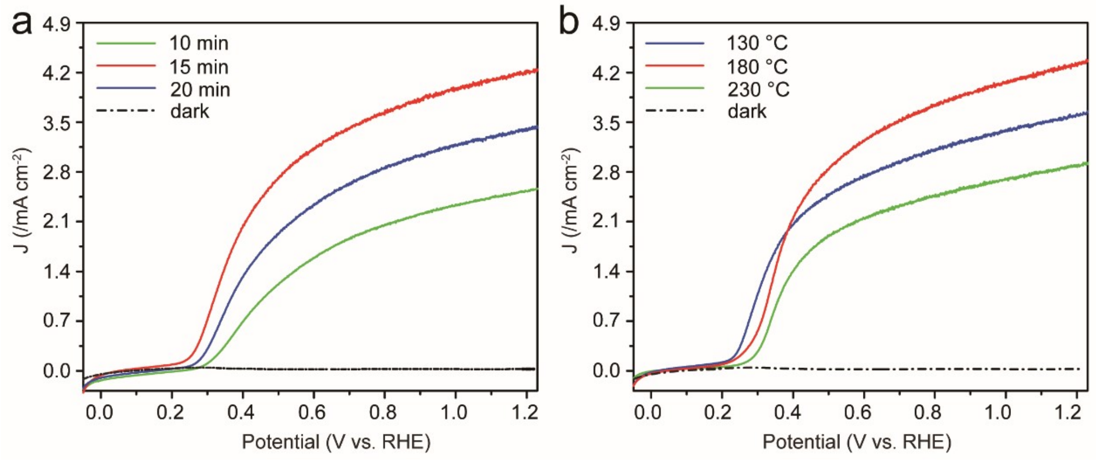

Fig. S5 Photocurrent density vs. applied potential curves of the BVO-2 films of (a) different annealing times, (b) calcination temperature in air under back illumination through an AM 1.5 G filter with the intensity of 100 mW • cm^{-2} in 1 M potassium electrolyte with 0.2 M Na_2SO_3.

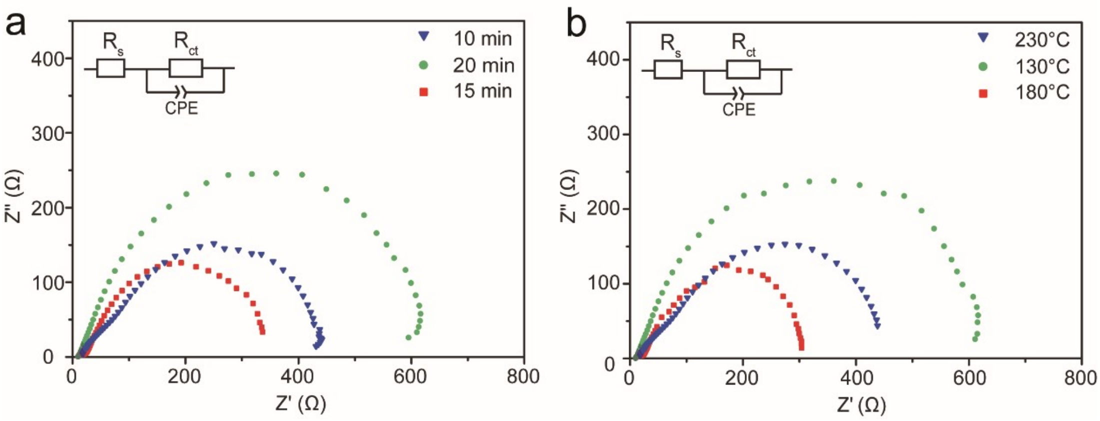

Fig. S6 I_s plots under AM 1.5 G illumination of the BVO-2 films annealed by different time and temperature. All measurements were taken in 1 M potassium borate electrolyte with 0.2 M Na_2SO_3.

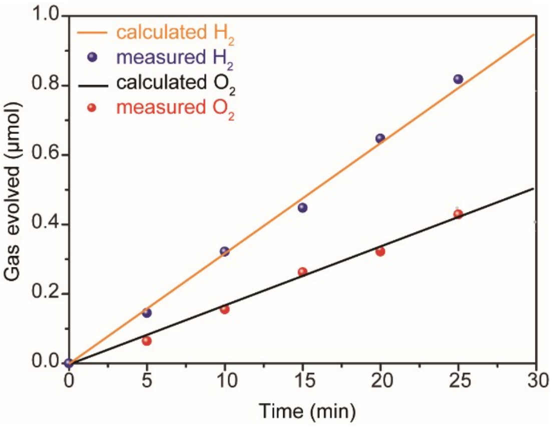

Fig. S7 Fluorescence probe measurement of O_2 and H_2 generation from a BVO-2 electrode at 1.23 V vs RHE under AM 1.5G, 100 mW/cm^2 illumination

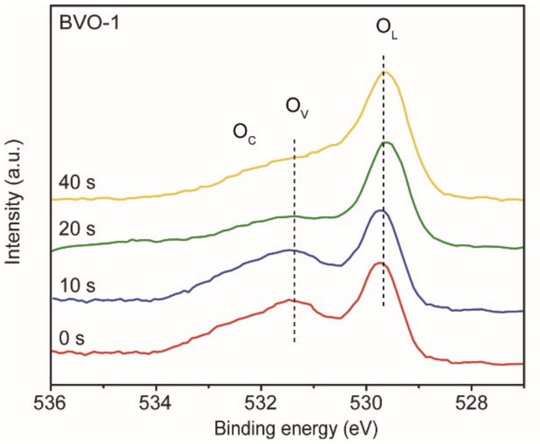

Fig. S8 Depth-profile XPS of different BVO-1.

Table

Table S1. PEC performance comparison of $BiVO_4$ anodes reported in literature.

Catalyst	Electrolyte	pH	$J^{[a]}$ ($mA \cdot cm^{-2}$)	Reference
$BiVO_4$	1 M KB	2.44	4.36	This work
$BiVO_4$	1 M KB	2.38	5.5	Adv. Mater. 2018,1800486
$BiVO_4$	0.5 M KPi	1.5	4.8	Science. 2014,343,990.
$BiVO_4$	0.1 M $K_2B_4O_7 \cdot 4H_2O$	/	2.75	Adv. Energy Mater. 201802198.
Mo: $BiVO_4$	0.5 M KB	~1.2	~2.7	Energy Lett. 2018, 3, 1648.
$BiVO_4$	1 M KB	0.75	2	Energy Lett. 2017, 2, 1062.
$BiVO_4$	1 M KB	2.5	3.4	Angew. 201703491.
$BiVO_4$	0.4 M KPi	~1.5	/	ACS Catal.2017, 7, 1868.
$BiVO_4$	0.1 M KPi	~1	~2	Angew. 2016, 55, 1769.
Sb-Doped $SnO_2/BiVO_4$ Core/Shell	1 M KB	/	1.6	Nano lett. 2016, 16, 3463.
Co_3O_4/ $BiVO_4$	0.5 M KPi	~0.6	~3.4	J. Am. Chem. Soc. 2015, 137, 8356.
$BiVO_4$	0.5 M Na_2SO_4	1.5	/	Nano. 2014, *8*, 7088.
$BiVO_4$	0.1 M KH_2PO_4	~0.2	~2	J. Am. Chem. Soc. 2012, 134, 2186.
$BiVO_4$	natural seawater	0.5	/	Energ.Environ.Sci. 2011, 4, 4046
Mo: $BiVO_4$	0.5 M Na_2SO_4	1	/	Energ.Environ.Sci. 2011, 4, 5028
$WO_3/BiVO_4$	0.5 M Na_2SO_4	~1.6	/	Nano lett. 2011, 11, 1928
W: $BiVO_4$	0.1 M KPi	1	~1.6	J. Am. Chem. Soc. 2011, 133, 18370.
$BiVO_4$	natural seawater	0.5	/	Energ.Environ.Sci. 2011, 4, 4046.

[a] refers the current density produced at 1.23 V vs RHE with sacrificial reagent

Reference

[1] L. Zhang, E. Reisner, J. Baumberg, *Energy Environ. Sci.*, 2014, **7**, 1402-1408.

[2] Z. Chen, T. F. Jaramillo, T. G. Deutsch, A. Kleiman-Shwarsctein, A. J. Forman, N. Gaillard, R. Garland, K. Takanabe, C. Heske, M. Sunkara, E. W. McFarland, K. Domen, E. L. Miller, J. A. Turner, H. N. Dinh, *J. Mater. Res.*, 2010, **25**, 3-16.

[3] J. M. Wu, Y. Chen, L. Pan, P. Wang, Y. Cui, D. Kong, L. Wang, X. Zhang, J. Zou, *Appl. Catal. B Environ.*, 2018, **221**, 187-195.

[4] M. Ye, J. Gong, Y. Lai, C. Lin, Z. Lin, *J. Am. Chem. Soc.*, 2012, **134**, 15720-15723.