

# Supporting Information

## Computational and Photoelectrochemical Study of Hydrogenated Bismuth Vanadate

*Gongming Wang,<sup>a</sup> Yichuan Ling,<sup>a</sup> Xihong Lu,<sup>a,b</sup> Fang Qian,<sup>c</sup> Yexiang Tong,<sup>b</sup> Jin Z. Zhang,<sup>a</sup>*

*Vincenzo Lordi,<sup>c</sup> Cedric Rocha Leao,<sup>\*d</sup> and Yat Li<sup>\*a</sup>*

*<sup>a</sup> Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064, USA*

*<sup>b</sup> KLGHEI of Environment and Energy Chemistry, MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China*

*<sup>c</sup> Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, CA 94551, USA*

*<sup>d</sup> Centro de Engenharia, Modelagem e Ciencias Sociais Aplicadas (CECS), Universidade Federal do ABC, Santo André, São Paulo, Brazil*

*\*Corresponding Authors. E-mails: [cedric.rocha@ufabc.edu.br](mailto:cedric.rocha@ufabc.edu.br) and [yli@chemistry.ucsc.edu](mailto:yli@chemistry.ucsc.edu)*

## Experimental Section

### Simulation method

We used the generalized gradient approximation in the PBE<sup>1</sup> version to approximate the exchange-correlation term. Core electrons were modeled with pseudo-potentials constructed with the projector augmented-wave method<sup>2</sup> and we used plane wave basis set with a cutoff of 500 eV to expand the charge density, as implemented in the VASP code.<sup>3</sup> For integrals over the Brillouin zone, we used the tetrahedron method including Bloëchl corrections<sup>4</sup> with the Monkhorst-Pack sampling scheme.<sup>5</sup> For the primitive cell, we used a mesh of 10×10×10 k-points to converge the charge density, but found no appreciable difference from results obtained with a 4×4×4 mesh in terms of the resulting band structure and projected density of states. Accordingly, for the supercells used for defect calculations, we used a 2×2×2 k-point mesh. For all systems, the atomic configurations were optimized using the conjugate gradient algorithm until all Hellmann-Feynman forces were below 0.01 eV/Å.

### Synthesis of BiVO<sub>4</sub> films

1 mmol NH<sub>4</sub>VO<sub>4</sub>, 1 mmol BiVO<sub>4</sub> and 2.5 mL concentrated HNO<sub>3</sub> were mixed together with 50 ml deionized water. NH<sub>4</sub>OH was used to neutralize the mixed solution, until no precipitate was further produced. Then, the precipitates were centrifuged out. The as-prepared bright yellow BiVO<sub>4</sub> precipitates were dispersed in 30 ml ethanol solution (precursor solution) 0.2 g polyvinylpyrrolidone was added to increase the precursor solution viscosity for spin coating. A piece of FTO glass substrate was cleaned with ethanol, acetone and then water. The precursor solution was spin coated on the FTO substrate at a rate of 2500 rpm. The BiVO<sub>4</sub>

coated FTO glass was annealed in air at 500 °C for 1h to remove organic binder. Repeat the spin coating and annealing processes for 2 times. The prepared BiVO<sub>4</sub> on FTO glass works as seeded substrate for further hydrothermal growth. The seeded-substrate was put into a 30 ml Teflon lined autoclave, filled with precursor solution containing 1 ml HNO<sub>3</sub>, 25 ml water, 0.5 mmol Bi(NO<sub>3</sub>)<sub>3</sub> and 0.5 mmol NH<sub>4</sub>VO<sub>4</sub>. The autoclave was heated in electric oven at 150 °C for 12h. The as-prepared bright yellow BiVO<sub>4</sub> film was washed with ethanol, deionized water and then annealed in air at 550 °C for 2h.

### **Hydrogen treatment**

Hydrogen treatment was carried out in a home-built tube furnace. The calcined BiVO<sub>4</sub> films were further annealed in hydrogen (1 bar, 50 sccm H<sub>2</sub> flow) for 10 minutes in a range of temperatures between 200 and 400°C.

### **Photoelectrochemical measurement**

BiVO<sub>4</sub> and hydrogen-treated BiVO<sub>4</sub> (denoted as H-BiVO<sub>4</sub>) samples were fabricated as photoanodes by soldering a copper wire onto a bare part of FTO substrate. The substrate edges and the metal contact region were sealed with insulating epoxy resin. The area of the working electrode is in a range of 0.2-0.25 cm<sup>2</sup>. Linear sweep voltammograms were collected by a CHI 660D electrochemical station, using Ag/AgCl (1M KCl) as reference, Pt wire as counter electrode, and 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH = 6.8) as an electrolyte, under a simulated sunlight (100 mW/cm<sup>2</sup>) generated with a 150 W xenon lamp (Newport 6255) coupled with an AM 1.5 global filter (Newport 81094). All linear sweep voltammograms

were collected at a scan rate of 20 mV/s. Incident-photon-to-current conversion efficiency (IPCE) were collected by the same electrochemical workstation with a solar simulator (Newport 69920, 1000W xenon lamp), coupled with an infrared water filter (Oriel 6127) and aligned monochromator (Oriel Cornerstone 130 1/8m). Electrochemical impedance spectroscopy (EIS) was collected with 5 mV perturbation and a frequency range from 100000 to 1Hz at different potentials. Mott-Schottky plots were generated from capacitance obtained from the EIS spectra at each potential with a frequency of 10k Hz. Carrier densities were calculated from the slopes of Mott-Schottky plots using the equation:

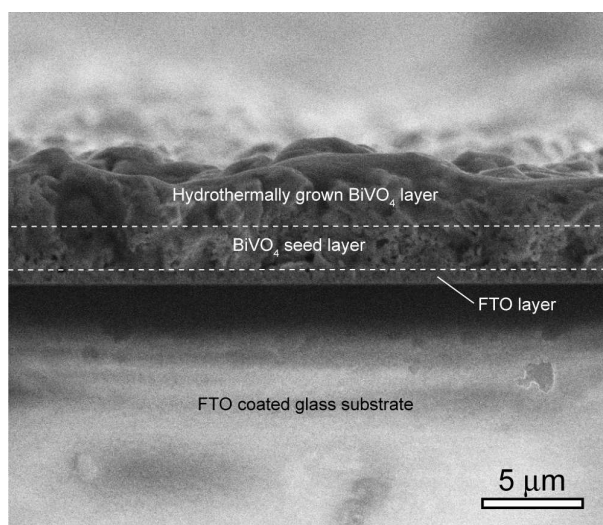
$$N_d = (2/e_0\epsilon\epsilon_0)[d(1/C^2)/dV]^{-1},$$

where  $e_0$  is the electron charge,  $\epsilon$  the dielectric constant of  $\text{BiOV}_4$ ,  $\epsilon_0$  the permittivity of vacuum,  $N_d$  the donor density, and  $V$  the applied bias at the electrode.

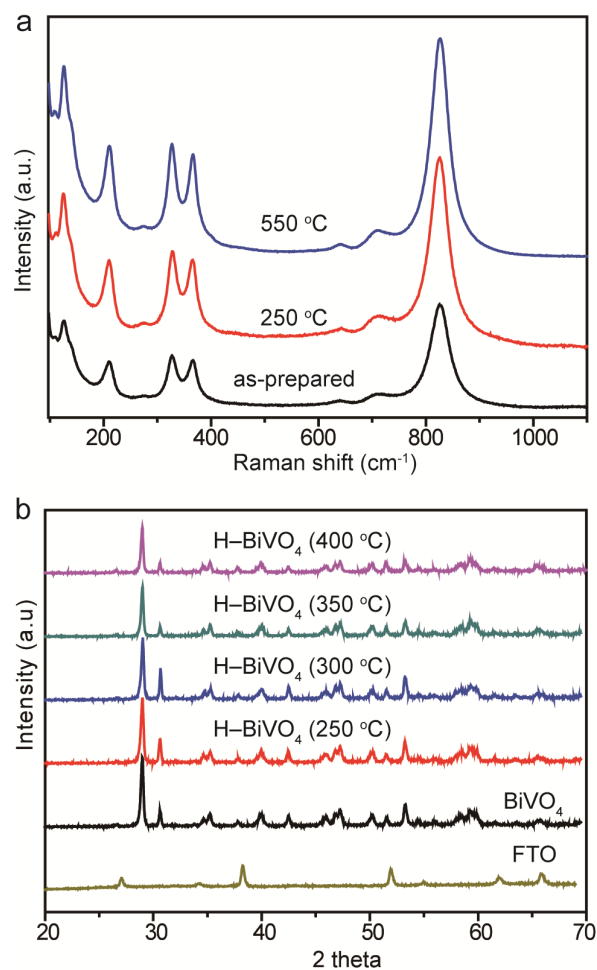
### **Material characterization**

Scanning electron microscopy (SEM) images were collected with a field-emission SEM (Hitachi S-4800II). X-ray diffraction (XRD) spectra were collected with a Rigaku Americas Miniflex Plus powder diffractometer. Diffraction spectra were recorded from a two-theta angle of 20 to 70 degree with a step size of 0.04 degree at a rate of 1 degree/min. Raman spectroscopy measurements were carried out on a Nicolet Almega XR Dispersive Raman spectrometer (laser wavelength 780 nm). X-ray Photoelectron Spectroscopy (XPS, ESCALab250, Thermo VG) with 200 W Al  $K\alpha$  radiations in twin anodes. The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as reference.

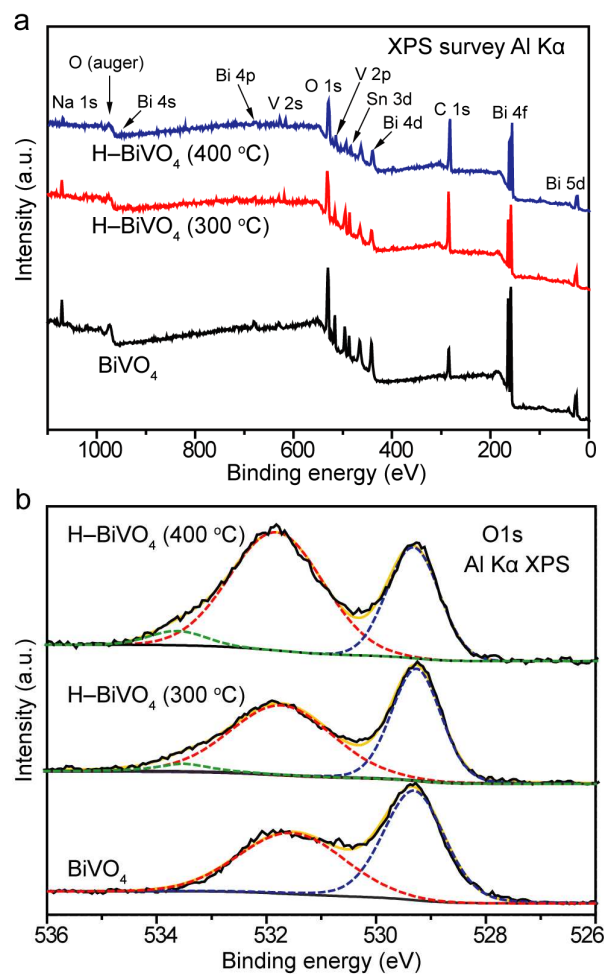
## Supplementary Figures



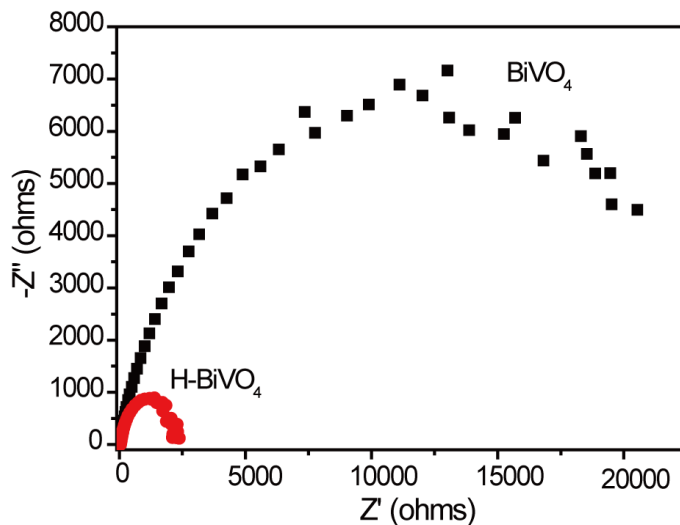
**Figure S1.** Cross-sectional SEM image of BiVO<sub>4</sub> film grown on FTO glass.



**Figure S2.** (a) Raman spectra of as-prepared BiVO<sub>4</sub> film and BiVO<sub>4</sub> films annealed in air at temperatures of 250 and 550 °C for 2h. (b) XRD patterns of bared FTO glass, air-annealed BiVO<sub>4</sub> and H-BiVO<sub>4</sub> in a range of temperatures between 250 and 400 °C.



**Figure S3.** (a) XPS survey of air-annealed  $\text{BiVO}_4$  and  $\text{H-BiVO}_4$  at 300 and 400 °C. (b) High resolution XPS O1s fitting curves of air-annealed  $\text{BiVO}_4$ ,  $\text{H-BiVO}_4$  (300 °C) and  $\text{H-BiVO}_4$ . The black curves are experimental results that were deconvoluted into two or three synthetic peaks in red, blue and purple. The green curves are the summation of the fitting curves.



**Figure S4.** Electrochemical impedance spectra collected for  $\text{BiVO}_4$  and  $\text{H-BiVO}_4$  electrode, at 0.4 V vs. Ag/AgCl under light illumination of  $100 \text{ mW/cm}^2$  in 0.5 M  $\text{Na}_2\text{SO}_4$  solution.

## References

1. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, 77, (18), 3865-3868.
2. Blochl, P. E., Projector augmented-wave method. *Physical Review B* **1994**, 50, 17953-17979.
3. Kresse, G.; Furthmüller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, 54, 11169-11186.
4. Blochl, P. E.; Jepsen, O.; Andersen, O. K., Improved tetrahedron method for brillouin-zone integrations. *Phys. Rev. B* **1994**, 49, 16223-16233.
5. Monkhorst, H. J.; Pack, J. D., Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, 13, 5188-5192.