

**Supporting Information:**

**Surface Charge Transition Levels and Hole  
Localization of Dopants in  $\text{BiVO}_4(010)$   
Photoanodes**

Changkyu Cho,<sup>†</sup> Kyunhun Lee,<sup>†</sup> Yonghyuk Lee,<sup>\*,‡</sup> and Taehun Lee<sup>\*,†,¶</sup>

<sup>†</sup>*Division of Advanced Materials Engineering, Jeonbuk National University, Jeonju 54896,  
Republic of Korea*

<sup>‡</sup>*Department of Chemical and Biochemical Engineering, Dongguk University, Seoul 04620,  
Republic of Korea*

<sup>¶</sup>*Hydrogen and Fuel Cell Research Center, Jeonbuk National University, Jeonbuk, 54896,  
Republic of Korea*

E-mail: yhyuk@dgu.ac.kr; taehun.lee@jbnu.ac.kr

## Computational Details

Table S1: Competing phases used to bound the chemical potentials. Lattice parameters are experimental and were held fixed, and only the internal coordinates were relaxed.

| Phase                                                 | Space group        | Lattice parameters (Å, deg)                          | Supercell             | Atoms |
|-------------------------------------------------------|--------------------|------------------------------------------------------|-----------------------|-------|
| CaO <sup>1</sup>                                      | $Fm\bar{3}m$ (225) | $a = 4.8105$                                         | $3 \times 3 \times 3$ | 216   |
| SrO <sup>1</sup>                                      | $Fm\bar{3}m$ (225) | $a = 5.1602$                                         | $3 \times 3 \times 3$ | 216   |
| V <sub>2</sub> O <sub>5</sub> <sup>2</sup>            | $Pmmn$ (59)        | $a = 11.512, b = 3.564, c = 4.368$                   | $1 \times 3 \times 3$ | 126   |
| $\alpha$ -Bi <sub>2</sub> O <sub>3</sub> <sup>3</sup> | $P2_1/c$ (14)      | $a = 5.844, b = 8.157, c = 7.503, \beta = 112.97$    | $2 \times 2 \times 2$ | 160   |
| $\alpha$ -MoO <sub>3</sub> <sup>4,5</sup>             | $Pnma$ (62)        | $a = 13.855, b = 3.6964, c = 3.9628$                 | $1 \times 3 \times 3$ | 144   |
| $\gamma$ -WO <sub>3</sub> <sup>6</sup>                | $P2_1/n$ (14)      | $a = 7.3271, b = 7.5644, c = 7.7274, \beta = 90.488$ | $2 \times 2 \times 2$ | 256   |

## Chemical potentials

In Equation (1) of the main text,  $\Delta N_i$  is the number of atoms of species  $i$  removed from the pristine slab to form the defect, negative for atoms added, so that the reservoir term of a substitution  $M_X$  is  $\mu_X - \mu_M$ . Bulk energies  $E_A$  are expressed per formula unit and chemical potentials per atom, both in eV. Oxygen is referenced to the O<sub>2</sub> molecule through  $\mu_O = \mu_O^0 + \Delta\mu_O$ , where  $\mu_O^0$  is the O reference of the surface-defect analysis. The host chemical potentials keep BiVO<sub>4</sub> in equilibrium with the reservoirs and lie within its stability region against the competing phases V<sub>2</sub>O<sub>5</sub>,  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> (Table S1) and O<sub>2</sub>. Each dopant chemical potential is fixed at its solubility limit, set by the formation of  $\alpha$ -MoO<sub>3</sub>,  $\gamma$ -WO<sub>3</sub>, CaO or SrO. The binary-oxide limits are upper bounds on the dopant chemical potentials. A more stable ternary phase, not considered here, would lower  $\mu_M$  and raise all formation energies of that dopant by the same amount, without changing its charge transition levels or site preference.

Anodic operation holds the surface at a high oxygen chemical potential, so the O-rich limit,  $\Delta\mu_O = 0$ , was taken as the primary condition. At  $\Delta\mu_O = 0$  the stability region of BiVO<sub>4</sub> reduces to a line segment in  $(\mu_{\text{Bi}}, \mu_{\text{V}})$ . It is bounded by the V-rich limit, where BiVO<sub>4</sub> coexists with V<sub>2</sub>O<sub>5</sub>, and by the Bi-rich limit, where it coexists with  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>. Its length is

set by

$$\Delta E_r = E_{\text{BiVO}_4} - \frac{1}{2} (E_{\text{Bi}_2\text{O}_3} + E_{\text{V}_2\text{O}_5}) = -0.834 \text{ eV}, \quad (\text{S1})$$

the energy per formula unit of forming  $\text{BiVO}_4$  from the two binary oxides. The chemical potentials are reported relative to the O-rich limits of the competing phases,  $\Delta\tilde{\mu}_i = \mu_i - \mu_i^{\text{lim}}$ , where  $2\mu_{\text{V}}^{\text{lim}} + 5\mu_{\text{O}}^0 = E_{\text{V}_2\text{O}_5}$ ,  $2\mu_{\text{Bi}}^{\text{lim}} + 3\mu_{\text{O}}^0 = E_{\text{Bi}_2\text{O}_3}$  and  $\mu_M^{\text{lim}} + 3\mu_{\text{O}}^0 = E_{\text{MO}_3}$  for  $M = \text{Mo}$  and  $\text{W}$ , and  $\mu_M^{\text{lim}} + \mu_{\text{O}}^0 = E_{\text{MO}}$  for  $M = \text{Ca}$  and  $\text{Sr}$ . The V-rich limit then lies at  $(\Delta\tilde{\mu}_{\text{Bi}}, \Delta\tilde{\mu}_{\text{V}}) = (\Delta E_r, 0)$  and the Bi-rich limit at  $(0, \Delta E_r)$ . The O-rich midpoint used in the main text is the average of the two limits and lies  $|\Delta E_r|/2 = 0.417 \text{ eV}$  from either one. It is used as the representative O-rich condition, since moving to either limit shifts each formation energy by at most 0.42 eV. The formation energies at the three conditions are shown in Figure S1 for Mo and W and in Figure S2 for Ca and Sr.

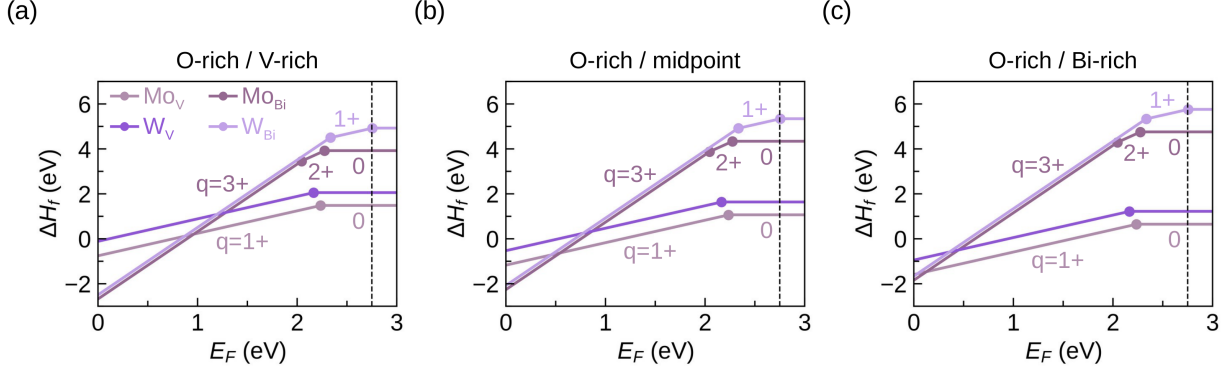


Figure S1: Formation energies of Mo and W substitutions at the (a) V-rich limit, (b) midpoint and (c) Bi-rich limit under O-rich conditions ( $\Delta\mu_O = 0$ ). The Fermi level is referenced to the VBM. Filled circles mark charge transition levels, the stable charge states are labeled, and the vertical dashed line indicates the CBM. The dopant chemical potentials are identical in all three panels, so the panels differ only through  $\mu_{Bi}$  and  $\mu_V$ .

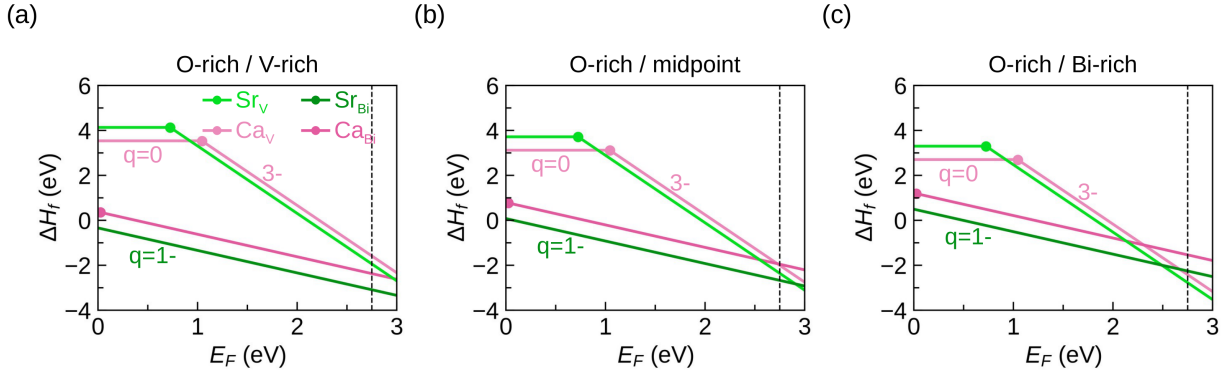


Figure S2: Formation energies of Ca and Sr substitutions at the (a) V-rich limit, (b) midpoint and (c) Bi-rich limit under O-rich conditions ( $\Delta\mu_O = 0$ ). The Fermi level is referenced to the VBM. Filled circles mark charge transition levels, the stable charge states are labeled, and the vertical dashed line indicates the CBM. The dopant chemical potentials are identical in all three panels, so the panels differ only through  $\mu_{Bi}$  and  $\mu_V$ .

## Charge transition levels

Table S2: Thermodynamic charge transition levels of the surface defects, referenced to the corrected VBM (eV).

| Defect    | Transition | $\varepsilon$ (eV) |
|-----------|------------|--------------------|
| $V_O$     | 2+/0       | 2.59               |
| $Mo_V$    | 1+/0       | 2.24               |
| $Mo_{Bi}$ | 3+/2+      | 2.05               |
|           | 2+/0       | 2.28               |
| $W_V$     | 1+/0       | 2.17               |
| $W_{Bi}$  | 3+/1+      | 2.33               |
|           | 1+/0       | 2.76               |
| $Ca_V$    | 0/3-       | 1.04               |
| $Ca_{Bi}$ | 0/1-       | 0.02               |
| $Sr_V$    | 0/3-       | 0.73               |
| $Sr_{Bi}$ | 0/1-       | —                  |

## References

- (1) Wyckoff, R. W. G. *Crystal Structures*, 2nd ed.; Interscience: New York, 1963; Vol. 1.
- (2) Enjalbert, R.; Galy, J. A Refinement of the Structure of  $V_2O_5$ . *Acta Crystallogr. Sect. C* **1986**, *42*, 1467–1469.
- (3) Ivanov, S. A.; Tellgren, R.; Rundlöf, H.; Orlov, V. G. Structural Studies of  $\alpha$ - $Bi_2O_3$  by Neutron Powder Diffraction. *Powder Diffr.* **2001**, *16*, 227–230.
- (4) Kihlborg, L. Least Squares Refinement of the Crystal Structure of Molybdenum Trioxide. *Ark. Kemi* **1963**, *21*, 357–364.
- (5) Sitepu, H.; O'Connor, B. H.; Li, D. Comparative Evaluation of the March and Generalized Spherical Harmonic Preferred Orientation Models Using X-ray Diffraction Data for Molybdate and Calcite Powders. *J. Appl. Crystallogr.* **2005**, *38*, 158–167.
- (6) Vogt, T.; Woodward, P. M.; Hunter, B. A. The High-Temperature Phases of  $WO_3$ . *J. Solid State Chem.* **1999**, *144*, 209–215.