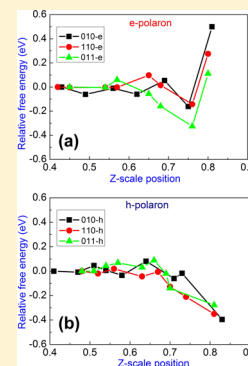


Photocatalytic Facet Selectivity in BiVO_4 Nanoparticles: Polaron Electronic Structure and Thermodynamic Stability Considerations for Photocatalysis

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Supporting Information

ABSTRACT: Selective charge separation among different crystal facets of a semiconductor is an intriguing phenomenon for which there is no firm and full theoretical foundation currently. In this work, we report on a density functional theory + *U* characterization of band alignment and electron and hole polaron stabilities among the (010), (110), and (011) facets of bismuth vanadate BiVO_4 (BVO). Computation-derived band alignment indicates that the conduction band minima are at nearly the same level among the three facets but that the valence band maxima exhibit a shift. We also modeled electron and hole polarons as localized electrons and holes on vanadium and oxygen, respectively, and determined their relative stabilities from a “bulk” region to a surface region. Calculated stabilities reveal similar stability profiles across the various facets, with electron polarons most stable when localized on subsurface V atoms and hole polarons most stable on surface O atoms. Calculations indicate a small stability preference for electron polarons toward the (011) facet and for hole polarons toward the (110) facet, whereas, experimentally, interfacial reduction is observed to take place selectively on the (010) facet and oxidation on the (110) and (011) facets. Facet selectivity could be occurring on the basis of thermodynamics (electron or holes showing a stronger affinity for some facets over others) or kinetics (electron or hole transport and/or redox processes being more efficient toward/on some facets over others) or a combination of both. This work establishes that thermodynamic stability alone is not responsible for the observed facet selectivity in BVO. Therefore, we surmise that polaron transport kinetics and interfacial redox kinetics are likely to have a role in facet selectivity in BVO. These issues will be the subject of future publications.



1. INTRODUCTION

Separation of photogenerated electrons and holes^{1–3} toward different facets of a semiconductor is a key approach to enhancing photocatalytic efficiency. One strategy toward this end, for example, is to deposit suitable reduction and oxidation co-catalysts on different facets of a light-absorbing semiconductor crystal. The co-catalysts draw electrons or holes, a process that leads to improved photocatalytic activity.⁴ A number of semiconductor photocatalysts, for example, TiO_2 ,⁵ Cu_2O ,³ SrTiO_3 ,² WO_3 ,⁶ BiOCl ,⁷ and BiVO_4 (BVO),¹ exhibit inherent charge separation across different facets, a characteristic that results in enhanced photocatalytic conversion. Among these facet-selective semiconductors, bismuth vanadate BiVO_4 (BVO) is the most notable photocatalytic semiconductor, with reduction and oxidation reactions taking place separately on the (010) and (110) facets under photoirradiation.

In traditional catalysis,⁸ catalyst particles can be controllably synthesized with different sizes and shapes. In these situations, several distinct surfaces are exposed and catalytic reactions can

take place on particular surfaces due to their different surface structures. These are in fact facet effects. In their photocatalytic experiment, Li et al.¹ demonstrated that, without illumination, there is no electron/hole separation and no redox reactivity among the (010) and (110) facets of BVO, even though the surface structures of the (010) and (110) facets are indeed different (as discussed below). Thus, facet effects in traditional catalysis are quite different from facet effects in photocatalysis, whereby separation of photogenerated charges across different facets of a semiconductor may take place. The fundamental reasons for this intrinsic property in selected photocatalytic materials remain unclear. In an earlier study of BVO, we attempted to rationalize the observed facet selectivity by characterizing the intrinsic mobility of electrons and holes along different crystal directions, independently from consid-

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ering the thermodynamic surface or interfacial stability and redox kinetics factors.⁹ Here, we deal with the thermodynamics aspects. Our hypothesis is that differences in electrostatics due to the broken symmetry of solid/vacuum or solid/electrolyte interfaces may play a role in the charge separation among different facets.

Recent discussions of facet selectivity in the literature have been in the context of the band structure. Bai et al.¹⁰ determined that in BiOCl, for example, the valence band (VB) edge of the (110) facet is ~ 0.36 eV higher than that of the (001) facet (an extremely large energy difference in comparison to $k_B T \sim 26$ meV at 300 K), suggesting that holes may migrate from the (001) facet to the (110) facet with a high probability. Wang et al.⁷ supported this proposition. Yates et al.¹¹ advocated the idea that surface band bending is an important factor in the charge separation among different facets of a semiconductor. Beyond band alignment and band bending, a different but complementary approach to the facet selectivity discussion involves small polarons¹² (both electron and hole polarons) with their localized electronic structures and their stability at or near surfaces. For example, Deskins et al. investigated the stability of electron polarons on a (110) surface of TiO₂ rutile¹³ and found that electron polarons are most stable in the first subsurface layer. Carey and McKenna investigated the stability of electron and holes polarons in TiO₂ anatase.¹⁴

Here, we apply the same methodology,¹³ also applied by other groups,^{15–18} to investigate electron and hole polaron stability from “bulk” to “surface” in BVO slabs. Experimentally, the small polaron nature of the charge carriers in BVO is well established. Rettie et al.¹⁹ measured the alternating current field and Hall effects and showed that the conductivity mechanism is one of small polaron hoppings at temperatures between 250 and 400 K with an electron polaron activation energy of $\Delta G^* \sim 0.30$ eV. Abdi et al.²⁰ and Ziwrtsch et al.²¹ provided time-resolved evidence of small hole polaron formation by time-resolved terahertz spectroscopy characterization. These authors stated that the analysis of their data was consistent with the description of hole polarons as O (2p) holes with a hole polaron activation energy of $\Delta G^* \sim 0.09$ eV. Note that our previously calculated and reported electron and hole polaron activation energies are ~ 0.37 and ~ 0.16 eV, respectively,²² in satisfactory agreement with the experiment. For holes, we uncovered the bimodal nature of hole transport.²²

We note a prior report by Chen et al.²³ of hole polaron stability data, bulk versus surface, in the quest for characterizing experimentally and computationally the electronic structure of the oxyl intermediate in the water oxidation reaction on SrTiO₃. See Table S13 in the Supporting Information (SI) of these authors' paper. Two points of interest here are as follows: (i) These authors used a density functional theory (DFT) + *U* level of theory (with $U_{\text{eff}} = 7$ eV) very comparable to what we used here and in our previous work. (ii) These authors' calculations showed that a surface hole polaron is more stable than a bulk hole polaron by ~ 0.38 eV, a value quite comparable to what we obtained here for BVO, as described below in our more extensive study.

Computationally, Kweon and Hwang²⁴ [using the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional] reported that an excess hole shows a tendency to localize at a surface rather than in the bulk. However, we note that the models of hole localization on Bi atoms as Bi holes reported by Kweon et

al.^{24,25} and more recently by Wiktor et al.²⁶ (with PBE0 hybrid functional) are not consistent with the experimental results of Abdi et al.²⁰ and Ziwrtsch et al.²¹ In the present work, hole polarons are found to be localized on O atoms as in our earlier work on BVO,^{9,22} which is in accord with the interpretation of the experimental data. We discuss briefly this point in Section 7 of the SI.

In the present work, we investigated systematically band alignment and polaron stability across the (010), (110), and (011) facets of BVO to assess whether thermodynamic factors are responsible for the observed selective charge separation among these facets of BVO. Facet selectivity could have its foundation on thermodynamics or kinetics or both. Thermodynamically, electron and holes would have to show a distinct preference for some facets over others. Kinetically, transport would have to be more facile along some directions over others; additionally, redox processes (reduction and oxidation) would have to be much more efficient on some facets over others.

This paper is concerned with the thermodynamics considerations. The overall conclusion arising from this work is that both electron and hole polarons exhibit stronger stability near or at facet surfaces than deeper in the bulk region but with little selective preference across facets. There appears to be no facet selectivity based on the thermodynamic stability of electron/holes. These findings suggest that other factors such as redox kinetics may be at play in facet selectivity. These points will be investigated in future research. The paper is organized as follows: the details of our computational approach are given in Section II, results and discussions are presented in Section III, and conclusions are given in Section IV.

II. COMPUTATIONAL DETAILS

To determine electron and hole polaron structures and stabilities, we carried out spin-polarized DFT calculations using the Vienna Ab initio Simulation Package (VASP) code^{27,28} and adopted the Perdew–Burke–Ernzerhof (PBE) parametrization²⁹ of the exchange and correlation potential in the generalized gradient approximation (GGA).³⁰ We also used the DFT + *U* approach to overcome the self-interaction error of DFT.^{31–33} We used effective Hubbard ($U_{\text{eff}} = U - J$ in Hubbard theory) values of $U_{\text{eff}}(\text{V}) = 10$ eV on vanadium atoms when calculating electron polarons and $U_{\text{eff}}(\text{O}) = 9$ eV on oxygen atoms when calculating hole polarons following our earlier work.⁹ More about our use of DFT + *U* is discussed below. The electronic wave functions were expanded in plane waves with an energy cutoff of 400 eV. Self-consistent DFT energies were converged to 10^{-4} eV, and geometry optimizations were deemed converged when the residual forces on the atoms were smaller than 0.01 eV/Å.

II.I. Structure. We used the monoclinic scheelite (ms-) phase of BVO as a stoichiometric model system since, experimentally, ms-BVO exhibits the highest photocatalytic activity under visible light irradiation. The cell parameters were taken from the experiment ($a = 5.196$ Å, $b = 11.705$ Å, $c = 5.094$ Å, $\alpha = 90^\circ$, $\beta = 90.38^\circ$, and $\gamma = 90^\circ$), and the atomic positions within the unit cell were optimized using a $5 \times 5 \times 2$ mesh of *k*-points. Optimization of the unit cell parameters at the DFT + *U* level of theory yields the higher-symmetry tetragonal scheelite structure (ts-BVO) that has experimental parameters very close to the ms-scheelite structure ($a = c = 5.147$ Å, $b = 11.722$ Å, and $\alpha = \beta = \gamma = 90^\circ$) as it is slightly more stable than the ms-scheelite structure. In previous work,

Kweon et al.^{25,34} showed that PBE is not able to yield the ms structure as the lowest-energy structure, but only the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional³⁵ does. At our DFT + U level of theory, the difference in energy between the ms and ts structures is ~ 0.1 eV. The root-mean-squared deviation (RMSD) between Bi atoms in the ms and ts experimental structures is $\text{RMSD}(\text{Bi}) \sim 0.026$ Å, for V atoms $\text{RMSD}(\text{V}) \sim 0.034$ Å, for O atoms $\text{RMSD}(\text{O}) \sim 0.084$ Å, and for all atoms $\text{RMSD}(\text{all}) \sim 0.076$ Å. Because of the closeness in parameters of the two structures, we decided to use the ms-BVO experimental cell parameters for this work to obtain polaron energy profiles, as ms-BVO is the phase used in the experiment. It cannot be excluded that this choice may lead to predictions of incorrect surface structures, although, owing to the small differences in bulk structures, one may expect the surface differences to be relatively small. We note that, with respect to the band gap E_g (experimental $E_g \sim 2.4$ eV), we obtained $E_g \sim 2.1$ eV with our DFT + U calculations. In contrast, Kweon and Hwang obtained $E_g \sim 3.41$ eV with HSE, whereas Wiktor et al.²⁶ obtained $E_g \sim 3.61$ eV with PBE0. Overall, owing to the small magnitude of the differences between the structures, we believe that our use of the monoclinic structure as in the experimental work rather than the DFT + U optimized structure is unlikely to affect our conclusions about polaron stability to any significant extent.

II.II. Polarons. Electron polarons were modeled by adding one excess electron to the system, whereas hole polarons were modeled by removing an electron from the system. To model the localized small polaron character of the charge carrier, we resorted to a number of “techniques” (sometimes a combination of them) to create an initial density whereby the excess electrons or the holes were localized predominantly on a single atom (a vanadium atom for electron polarons and an oxygen atom for hole polarons). In some instances, we lengthened the bonds around the site of localization site by ~ 0.2 Å. In other instances, we started with larger $+U_{\text{eff}}$ values and we gradually brought the $+U_{\text{eff}}$ value down. In other instances, we replaced a V atom by a Cr atom initially and used the “doped” wave function as the initial wave function for an undoped calculation.

We note that the localized character of polarons is the defining feature of small polarons.¹² Functionals of the density for DFT in the generalized gradient approximation (GGA) such as PBE do not yield localized electronic structures for electron and hole polarons in BVO and in many other inorganic semiconductors. It is well accepted that the DFT + U and hybrid DFT level of theories are two suitable approaches to modeling small polarons.^{36,37} A previous work on electron and hole polarons in BVO yielded computed data (hopping barriers) using DFT + U ^{9,22} and hybrid DFT²⁶ consistent with experimental measurements. Polaronic lattice distortions around electron and hole polaron sites involve a lengthening of the bonds that can be rationalized on the basis of electronic structure arguments.³⁸ They are highlighted in the SI material. The computed polaronic distortions have been found to be confined to the primitive cell. Nonetheless, we used supercells to reduce the periodic image interaction effects when modeling the (010), (110), and (011) slabs. We used successfully the same methodology to characterize the electron and hole polaron mobilities in bulk ms-BVO previously, obtaining good agreement with the experiment. For example, electron and hole hopping activation energies were as follows: calculated $\Delta G^* \sim 0.37$ eV for an electron polaron versus experimental $\Delta G^* \sim$

0.30 eV, and calculated $\Delta G^* \sim 0.16$ eV for a hole polaron versus experimental $\Delta G^* \sim 0.09$ eV,²² as we had for several oxides previously.

II.III. Choice of $+U_{\text{eff}}$ and Convergence with Respect to $+U_{\text{eff}}$. We chose effective Hubbard ($U_{\text{eff}} = U - J$ in Hubbard theory) values of $U_{\text{eff}}(\text{V}) = 10$ eV for electrons and $U_{\text{eff}}(\text{O}) = 9$ eV for holes following our earlier work.⁹ As mentioned above, the polaron hopping barriers were found to be in good accord with the experiment when using these $+U_{\text{eff}}$ values, as well as not very sensitive to the actual U_{eff} values.

It is of interest to know the behavior of the density of states (DOS), band edges, polaron stability energies, and work functions as a function of $+U_{\text{eff}}$. With regard to band gap and band edges and the ability to form electron and hole polarons, we refer the reader to our previous work.⁹ The calculated band gap (~ 2.1 eV) varies little (~ 0.1 eV) with changes in $+U_{\text{eff}}$. This indicates that the band edges vary at most by the same amount. Furthermore, since we cannot and do not compare directly energies of electron polarons with those of hole polarons, the absolute changes in positions of VB and conduction band (CB) band edges do not come into play. We analyze only the relative stability of electron/hole polarons from bulklike sites to near-surface sites.

The values of $+U_{\text{eff}}$ selected here are values that give rise to good degrees of localization of electron and hole polarons compared to smaller values of $+U_{\text{eff}}$ as explained in our earlier work.⁹ We note that Herlihy³⁹ et al. used a value of $+U_{\text{eff}}(\text{O}) = 7$ eV on O atoms to study the structure of an oxyl radical intermediate during water oxidation on SrTiO_3 . Additionally, Erhart et al.⁴⁰ determined that $+U_{\text{eff}}(\text{O}) = 8$ eV on O atoms mimics well data obtained from the hybrid functional HSE.³⁵ These values are a little smaller than our $+U_{\text{eff}}(\text{O}) = 9$ eV for O atoms when modeling hole polarons.

To critically assess our selection of $U_{\text{eff}}(\text{V}) = 10$ eV for electron polarons and $U_{\text{eff}}(\text{O}) = 9$ eV for hole polarons, we used the ms-BVO bulk structure to evaluate the piece-wise linearity of our DFT + U energies $E(q)$ with respect to the point defect charge q . This assessment follows closely the discussion by Lany and Zunger,³⁷ Lany,³⁶ and Erhart et al.⁴⁰ We repeated these calculations for smaller values of $U_{\text{eff}}(\text{V})$ and $U_{\text{eff}}(\text{O})$. The data is given and displayed in Section 8 of SI. The U values of $U_{\text{eff}}(\text{V}) = 10$ eV and $U_{\text{eff}}(\text{O}) = 9$ used in our prior work and here do not appear to overcorrect the self-interaction error as these levels of theory show little deviation in piece-wise linearity of the energy as a function of the charge state. One can perhaps make a case that smaller $U_{\text{eff}}(\text{O})$ values (~ 8 or 7 eV) might be a more optimal choice. We believe that such a choice would be unlikely to alter the qualitative findings from this work. Indeed, the preference “surface over subsurface” of holes reported by Chen et al.²³ with $U_{\text{eff}}(\text{O}) = 7$ eV is close to what we obtain here. Overall, we interpret the tests as suggesting that the polaron energy profiles would not change significantly upon using smaller $+U_{\text{eff}}(\text{O})$ values and our overall conclusions would stand.

II.IV. Slabs and Vacuum Lengths. When dealing with electron and hole polaron energy profiles, the (010) facet was modeled with a slab of 2×2 lateral size and 11 Bi layers. The Brillouin zone was sampled using a $2 \times 2 \times 1$ k -point mesh. The (110) and (011) facets were modeled with slabs of (1×2) and (2×1) lateral sizes, respectively, and 12 Bi layers, with the Brillouin zone sampled with $2 \times 2 \times 1$ k -point meshes. A vacuum length of 15 Å was used for all of the three surfaces. To check convergence with respect to slab thickness and

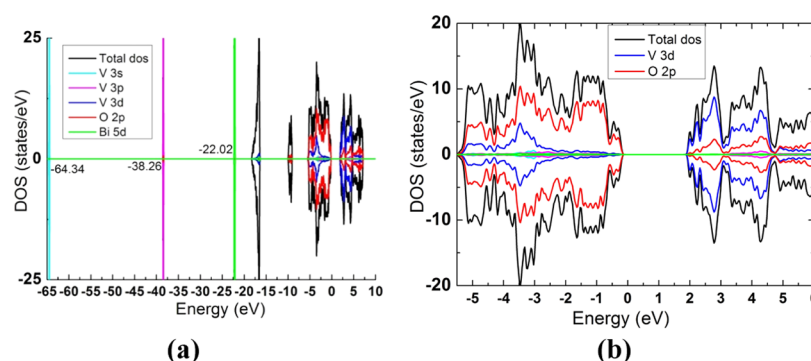


Figure 1. Total and projected density of states (PDOS) of bulk BiVO_4 using DFT + U [$U_{\text{eff}}(\text{V}) = 5 \text{ eV}$] with the small core valence configuration of V ($3s^2 3p^6 4s^2 3d^3$), the configuration of O ($2s^2 2p^4$), and the configuration of Bi ($5d^{10} 6s^2 6p^3$). (a) Energy range of -65 to $+10 \text{ eV}$ to show the position of the semicore states V ($3s$), V ($3p$), and Bi ($5d$) used in band alignment across slabs. (b) Energy range of -6 to $+6 \text{ eV}$ to emphasize the valence and conduction bands. The corresponding calculated band gap is $\sim 2.0 \text{ eV}$ compared to the experimental band gap of $\sim 2.4 \text{ eV}$.

vacuum thickness, we tested thicknesses of 14 Bi layers with 15 Å vacuum and 12 Bi layers with 20 Å vacuum for the (011) surface. The coordinates for the 15 Å vacuum systems (CIF files) are given in the [Supporting Information \(SI\)](#).

When dealing with band alignment and work function, the three surfaces were modeled with slabs of 1×1 lateral sizes. The Γ -centered k -point meshes of the Brillouin zone sampling for the (010), (110), and (011) were set at $(7 \times 7 \times 1)$, $(2 \times 5 \times 1)$, and $(5 \times 2 \times 1)$ based on the Monkhorst–Pack scheme.⁴¹ All slabs modeled in this work were stoichiometric and symmetric. Accordingly, no slab-dipole correction was necessary. The thickness of slab for the (010) facet included 11 bismuth Bi layers ($\sim 46.16 \text{ Å}$), whereas for the (110) and (011) facets, slabs comprised 12 Bi layers ($\sim 41.86 \text{ Å}$).

To check the convergence of the slab models, we tested vacuum lengths of 15, 20, 25, and 30 Å for all three surfaces. The work function was calculated from the total local potential excluding the exchange–correlation potential, in other words, the Hartree potential also referred to as the electrostatic potential. VASP creates a file labeled LOCPOT from which we extracted the work function. Far away from the surface in the vacuum, the flatness of the Hartree potential is a sign that the vacuum length is large enough. The work function was taken as the difference between the Fermi level (valence band maximum as given by VASP) and the asymptotic potential in the vacuum. Unless explicitly stated (for semicore state band alignment), we used the following electronic valence configurations: O ($2s^2 2p^4$), large core V ($3p^6 4s^1 3d^4$), and Bi ($6s^2 6p^3$). We used also the small core V ($3s^2 3p^6 4s^1 3d^4$) electronic configuration for V to determine the sensitivity of the semicore levels to the choice of the pseudopotential. The results justified using the large core pseudopotential for polaron energies and work functions.

We tested the effect of $+U_{\text{eff}}$ on the work function for the (010) slab, using the valence electronic configurations O ($2s^2 2p^4$), V ($3p^6 4s^1 3d^4$) (larger core), and Bi ($6s^2 6p^3$). Unless explicitly stated for energy alignment calculations, this set of valence configurations was used throughout. The data for work function versus $+U_{\text{eff}}$ is shown in [Figure S8](#) with the values of the vacuum level given in [Table S5](#). The data show that the work functions remained essentially unchanged upon variations in $+U_{\text{eff}}$.

Finally, we used the (011) facet to test whether the polaron energy profiles were affected by slab thickness and vacuum thickness: we used a slab thickness of 14 Bi layers ($\sim 31.53 \text{ Å}$)

with a vacuum length of 15 Å and a slab thickness of 12 Bi layers ($\sim 27.30 \text{ Å}$) with a vacuum length of 20 Å. The energy profiles of the electron and hole polarons were also essentially unchanged. Accordingly, we believe the profiles obtained in this work are qualitatively accurate to draw conclusions as it is done below.

II.V. Band Alignment. Band alignments among the three surfaces need a common reference energy level. We found that the V ($3s$), V ($3p$), and Bi ($5d$) states lie deep on the energy scale, well separated from the valence band (see results below). Thus, the bands corresponding to these states are very narrow as these states are not involved in covalent/ionic bonding. A critical point to make is that the chemical environments of V or Bi sites deep in the bulk and far from the slab surfaces are the same whether we are considering the (010), (110), or (011) slabs. The V and Bi atoms deep in the slab resemble V and Bi atoms in stoichiometric bulk, and their descriptions should converge to be identical for all three slabs as the slabs grow in thickness. We chose the V ($3s$), V ($3p$), or Bi ($5d$) states from V and Bi atoms deep in the slabs as reference energy levels and shifted the DOS for the three surfaces to align these DOS peaks.

II.VI. Polaron Energy Alignment. To investigate the stability of electron and hole polarons, we calculated their structures and energies when localized at various sites, from near surface to deep bulk. As already mentioned, to overcome the self-interaction error of standard DFT methods, we employed the DFT + U approach³⁸ to obtain localized polaron structures. We obtained the absolute DFT energies of electron polarons and hole polarons by adding an extra electron or by removing an electron from the system. We discussed extensively earlier our choices of $+U_{\text{eff}}$ on V and on O atoms. We localized electron polarons on vanadium sites in V ($3d$) orbitals and hole polarons on oxygen sites in O ($2p$) orbitals. It is important to note that the slab parameters for the (010) and (011) facets, such as thickness and size, are different. Thus, it is not possible to compare absolute DFT energies. Comparisons of relative energies from a bulklike region to a surface region within slabs are valid. We took most bulklike sites (ones that are furthest from the slab surfaces) for the zero of energy for all three slabs, and with this definition, relative energies can be compared across slabs.

II.VII. Modeling the Aqueous Phase. All calculations described up to now were based on solid/vacuum interface models. To investigate the effect of the aqueous phase that is a

part of the experiment situation, we carried out calculations that included a polarizable continuum model of the aqueous phase with a dielectric constant $\epsilon = 80$. We used the program VASPsol for these calculations.⁴² In brief, the energy profiles obtained in solid/vacuum models were not qualitatively altered when using solid/aqueous phase models.

III. RESULTS AND DISCUSSION

III.I. Electronic Structure of Bulk BiVO_4 . The density of states (DOS), including the V (3s), V (3p), and Bi (5d) states, is shown in Figure 1 based on our DFT + U [$U_{\text{eff}}(\text{V}) = 5 \text{ eV}$] calculations. The DOS figure helps select states that one might use for the alignment of the DOS across the three slabs (010), (110), and (011) with the goal of assessing their redox abilities. To align the DOS for different stoichiometric slabs, we looked for states that are narrow and deep. Being narrow is a sign that the band is atomlike with little dispersion because of a small overlap between atoms of a given type. Being deep also emphasizes the atomlike character and small overlap. It stands out in Figure 1a that the bands associated with the semicore states are deep, narrow, and far from the valence band. These states can be safely used as reference energy levels for energy alignment across the various slabs. Indeed, all atoms should have the same oxidation state in all slabs. The top of the valence band is made up of O (2p) states, and the bottom of the conduction band is made up of V (3d) states. When considering the three slabs, our contention will be that atoms deep inside the slabs will be essentially bulklike and their associated levels will be essentially identical from one slab to the other. Note that the DOS presented in Figure 1 is in essential agreement with other published DOS plots for BiVO_4 . The Bi 6s and 6p levels contribute to the VB and CB, but they appear buried.⁴³ This is because Figure 1a is meant to emphasize the core levels V (3s) and V (3p) and Bi (5d), which we want to use for band alignment below.

III.II. Surface Structures. The optimized structures of the (010), (110), and (011) surfaces are shown in Figure 2. Because we used slabs and vacuum spaces of varying thickness to test polaron stabilities within and across slabs, we found it convenient to use a fractional coordinate, referred to as z -scale varying from 0.0 to 1.0 for each slab. As seen in Figure 2, $z = 0.5$ resides at the middle of a slab and $z = 0.0$ and 1.0 at the middle of the vacuum space. The depth of an atom in a slab is related to its z -coordinate.

On the (010) surface, O's have twofold coordination, V's have fourfold coordination, and Bi's have sixfold coordination, whereas in the bulk, O's have threefold coordination, V's have fourfold coordination, and Bi's have eightfold coordination. The surface coordination environment on the (110) surface is the same as on the (011) surface. The difference in coordination between the (010) and (011) surfaces lies only in that the surface Bi atoms have only fivefold coordination on the (011) surface compared to sixfold coordination for the (010) surface. The coordination of the surface O's is the same for the (010) and (011) surfaces, but in both cases, the surface O's have lower coordination than bulk O's. The lower coordination of the O's on the surfaces (010) and (011) and the O lone pair electrons being exposed are likely the reasons that holes on surface O's are more stable than holes on bulk O's, as shown later.

The surface energies of the three slabs are almost the same, a finding that we established in our earlier work⁹ and summarized here. The slabs are all stoichiometric. The surface

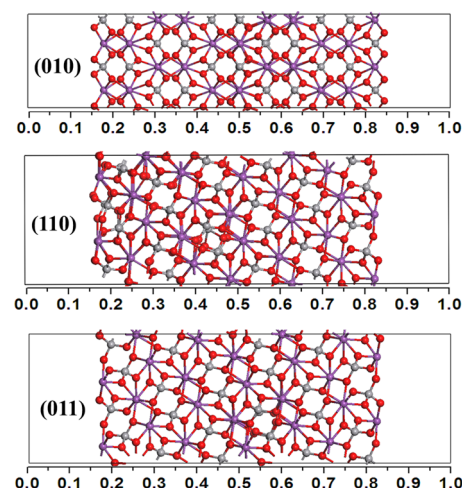


Figure 2. Surface structures of (010), (110), and (011) slabs with fractional coordinates as z -scale. $z = 0.5$ is at the middle of the slab and $z = 0.0$ and 1.0 are at the middle of the vacuum space. Bi atoms are shown as purple balls, V atoms as gray balls, and O atoms as red balls. The similarity between the pictures for (110) and (011) arises from the lattice parameters a and b being nearly identical. At the (010) surface, the V atoms are fourfold coordinated as in the bulk; the Bi atoms are sixfold coordinated in contrast to their eightfold coordination in the bulk; and the O atoms are twofold coordinated, compared to threefold coordinated in the bulk. For the (110) and (011) surfaces, essentially the same for both, the coordination of the V and O atoms is the same as on the (010) surface, but the Bi atoms are only fivefold coordinated. The CIF files of these three slabs are provided in the SI.

energies were calculated according to $\gamma = (E_{\text{slab}} - nE_{\text{BiVO}_4})/2A$, where E_{slab} and E_{BiVO_4} are the total energies of the slab and bulk, respectively; n is the number of BiVO_4 units in the slab; and $2A$ is the total exposed area of the two identical sides of the slabs. The calculated surface energies were found to be 0.20, 0.20, and 0.21 J/m² for (010), (011), and (110) slabs, respectively.

The calculated total density of states (DOS) and projected density of states (PDOS) for the three surfaces are plotted in Figure 3. The computed band gaps for the (010), (110), and (011) slabs are 1.92, 2.00, and 1.96 eV, respectively, all of them smaller than the experimental bulk value of $\sim 2.40 \text{ eV}$, as expected from DFT or DFT + U calculations. The PDOS plots show that the valence band maximum (VB-max) is mainly O (2p) in character and the conduction band minimum (CB-min) is mainly composed of V (3d). The DOSs for the (110) and (011) surfaces are similar, which is due to the a and c cell parameters being very similar and the slabs having the same surface structures.

III.III. Band Alignment. As mentioned above, we first considered the valence electronic configurations O ($2s^2 2p^4$), V ($3p^6 4s^1 3d^4$) (larger core), and Bi ($5d^{10} 6s^2 6p^3$) for O, V, and Bi, respectively. We used the 5d states of Bi atoms deep inside the slab as the reference energy level. We then used a slightly more extended valence configuration for V atoms, V ($3s^2 3p^6 4s^1 3d^4$) (smaller core), whereas the valence electronic configurations of O and Bi remained unchanged. We used the 5d states of the Bi atoms and the 3s and 3p states of the V atoms deep inside the slab as reference energy levels. We calculated the DOSs for the (010) and (011) facets with varying vacuum lengths. The DOSs for the (110) and (011)

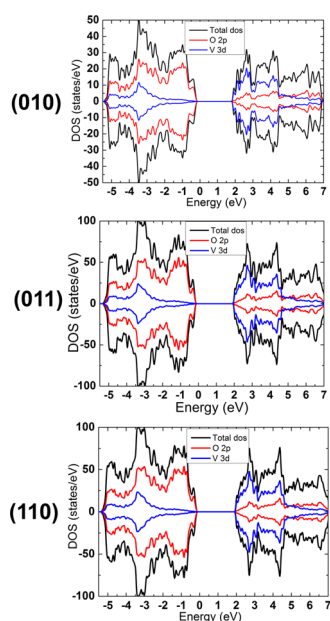


Figure 3. Total and projected density of states for the (010) slab, the (110) slab, and the (011) slab. The Fermi levels (maxima of the valence band) are set at energy = 0.0 eV. Here, the valence electronic configurations of the atoms were O ($2s^2 2p^4$), V ($3p^6 4s^1 3d^4$), and Bi ($5d^{10} 6s^2 6p^3$). The similarity between the (110) and (011) DOS plots arises from the lattice parameters a and c being nearly identical.

facets are very similar. Selected band levels for the (010), (110), and (011) slabs are given in Table 1 (the larger core of V) and Table 2 (the smaller core of V), and alignments are displayed in Figure 4. To align the bands on the basis of a given band reference [V (3s) or V (3p) or Bi (5d)], the reference band was shifted to be at the same energy for all of the slabs while maintaining the band energy differences among each slab.

It appears that the band levels are essentially converged upon increasing the vacuum length. The most significant difference between the larger-core- and smaller-core-calculations is a change in the conduction band minimum, CB-min, level, which is higher on the energy scale by ~ 0.06 eV with the smaller core. This is consistent with the fact that the smaller core affords a more flexible and more accurate description of core–valence interactions. With regard to facet selectivity, the overall conclusion is that, after performing band alignments, the band edges that are the energy levels of the photogenerated electrons and holes show no strong preference or selectivity toward either the (010) or (011) facets.

III.IV. Work Function. As a first step, we used the (010) slab to obtain the dependence of the work function with respect to the thickness of the slab at a fixed vacuum length. With a vacuum length = 15 Å, the values of the work function are ~ 7.04 , 7.00, 6.98, and 7.00 eV with the slab thickness containing 8, 9, 10, and 11 Bi layers, respectively. The work function is well converged with respect to slab thickness. We continued to use the (010) slab thickness of 11 Bi layers. For the (110) and (011) slabs, a slab thickness with 14 Bi layers (~ 31.53 Å) appears to be equivalent to a (010) slab thickness with 11 Bi layers (~ 31.16 Å). The work function curves with a vacuum length of 15 Å are shown in Figure 5. The similarity between (110) and (011) slabs was already noted earlier; therefore, we show only the (011) data along with the (010) data.

As a second step, we calculated the work functions of the (010), (110), and (011) slabs with a slab thickness of ~ 31 Å in all three cases [corresponding to 11 Bi layers for the 010 slab and 14 Bi layers for the (011) and (110) slabs as mentioned above] but with varying vacuum thickness. The results are shown in Table 3 below for vacuum lengths up to 25 Å. For the (010) slabs, the work function converges to a value of $W_{(010)} \sim 7.00$ eV, whereas for the (011) slab, it converges to $W_{(011)} \sim 6.00$ eV. The difference in work function $\Delta W = W_{(010)} - W_{(011)}$ is the key parameter that comes into the stability discussion later on. The work function for the (010) surface is ~ 1.00 eV larger than that for the (011) surface. It is easier to remove an electron into the vacuum from the (011) facet surface than from the (010) facet surface.

III.V. Electron and Hole Polaron Energy Profiles. We investigated electron and hole stabilities from the bulk region to the surface region of the slabs by means of the small polaron model. For this, we considered the energy of an excess electron and of a hole separately in each slab.

The methodology involved taking the structures of neutral slabs, creating small distortions around V or O sites to obtain localization of the excess electron or hole on specific sites, and allowing the structures to fully relax, keeping the cell parameters unchanged. For all three slabs, electron and hole polarons were localized on selected sites. Spin density contours of an excess electron and a hole for slabs (010) and (011) are shown in Figures S1 and S2 in the SI. Electron polarons are localized on the selected vanadium sites of the slabs, and a large fraction of the spin density of holes is localized on single oxygen atoms. DOSs for a typical system with an excess electron and a hole are shown in Figures S3 and S4 in the SI. Gap states appear in the band gap, indicating that electron and hole polarons are formed. Structures associated with electron polarons and hole polarons are shown in Figures S5 and S6 in

Table 1. Selected Band Levels for the (010), (110), and (011) Slabs with Different Vacuum Thicknesses Using the Valence Electronic Configurations for O, V, and Bi: O ($2s^2 2p^4$), V ($3p^6 4s^1 3d^4$) (Larger Core), and Bi ($5d^{10} 6s^2 6p^3$)^a

surface1/surface2/surface3-vacuum length (Å)	Bi-5d-max (eV)	VB-max (eV)	CB-min (eV)
(010)/(011)/(110)-15	−22.13/−22.03/−22.04	−0.14/−0.10/−0.09	1.78/1.90/1.87
(010)/(011)/(110)-20	−22.11/−22.04/−22.03	−0.12/−0.09/−0.10	1.80/1.89/1.88
(010)/(011)/(110)-25	−22.13/−22.03/−22.05	−0.14/−0.10/−0.12	1.78/1.88/1.88
(010)/(011)/(110)-30	−22.13/−22.02/−22.03	−0.14/−0.09/−0.10	1.78/1.89/1.88
bulk	−22.01	−0.13	1.88

^aBi-5d-max = top of the Bi-5d band of the four Bi atoms in the middle of the slabs as shown in Figure 2, VB-max = top of the valence band, and CB-min = bottom of the conduction band. Band-level entries include three values corresponding to “surface1”, “surface2”, and “surface3”; surface1 is (010), surface2 is (011), and surface3 is (110). The vacuum length is indicated in the left column.

Table 2. Selected Band Levels for the (010), (011), and (110) Slabs with Different Vacuum Lengths Using the Valence Electronic Configurations for O, V, and Bi: O ($2s^2 2p^4$), V ($3s^2 3p^6 4s^1 3d^4$) (Small Core), and Bi ($5d^{10} 6s^2 6p^3$)^a

surface/surface/surface-vacuum (Å)	V-3s-max (eV)	V-3p-max (eV)	Bi-5d-max (eV)	VB-max (eV)	CB-min (eV)
(010)/(011)/(110)-15	-64.42/-64.29/-64.34	-38.32/-38.21/-38.24	-22.11/-22.03/-22.05	-0.14/-0.09/-0.11	1.84/1.95/1.93
(010)/(011)/(110)-20	-64.39/-64.28/-64.31	-38.32/-38.21/-38.23	-22.08/-22.02/-22.02	-0.14/-0.09/-0.11	1.84/1.95/1.96
(010)/(011)/(110)-25	-64.42/-64.28/-64.34	-38.32/-38.21/-38.26	-22.11/-22.02/-22.02	-0.14/-0.09/-0.11	1.84/1.95/1.93
(010)/(011)/(110)-30	-64.40/-64.29/-64.31	-38.32/-38.21/-38.23	-22.11/-22.03/-22.02	-0.14/-0.09/-0.11	1.84/1.95/1.96
bulk	-64.33	-38.26	-22.02	-0.11	1.87

^aV-3s-max, V-3p-max, and Bi-5d-max = top of V (3s), V (3p), and Bi (5d) bands, respectively, of the four V and Bi atoms in the middle of slabs as shown in Figure 2; VB-max = top of the valence band; and CB-min = bottom of the conduction band.

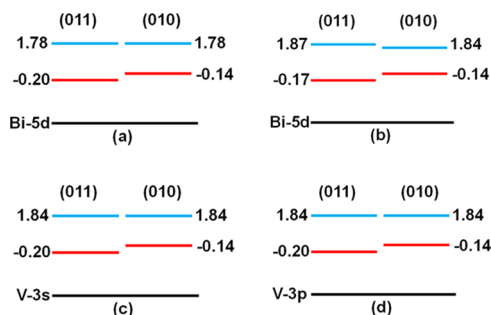


Figure 4. Alignment of bands for the (010) and (011) slabs. Blue, red, and black lines represent CB-min, VB-max, and bands (Bi 5d, or V 3s, or V 3p), respectively, used to align the bands. For (a), the valence electronic configurations for O, V, and Bi were O ($2s^2 2p^4$), V ($3s^2 3p^6 4s^1 3d^4$), and Bi ($5d^{10} 6s^2 6p^3$), respectively. For (b)–(d), the valence electronic configurations for O and Bi remained unchanged and the valence configuration of V was extended to include the 3s electrons V ($3s^2 3p^6 4s^1 3d^4$). In (a), we used the data from Table 1 (larger core for V) to align the Bi (5d) bands of the (010) and (011) slabs. In (b)–(d), we used the data from Table 2 (smaller core for V) to align the bands for the (010) and (011) slabs. In (a) and (b), we aligned the Bi (5d) levels, in (c) we aligned the V (3s) levels, and in (d) we aligned the V (3p) levels.

the SI. They exhibit lattice distortions typically associated with the formation of electron or hole polarons (lengthening of V–O bonds by ~ 0.1 Å for electron polarons, and lengthening of O–V and O–Bi bonds by ~ 0.15 Å for holes).

For generating profiles “energy vs depth” for electron and hole polarons, we used the (010), (110), and (011) slabs with 11, 12, and 12 Bi layers (31.16, 27.30, and 27.30 Å, respectively) and a vacuum length of 15 Å. Energies and relative energies for electron polarons and hole polarons are given in Tables S1 and S2 in SI, respectively. Recall that the slabs do not have the same number of constituent atoms;

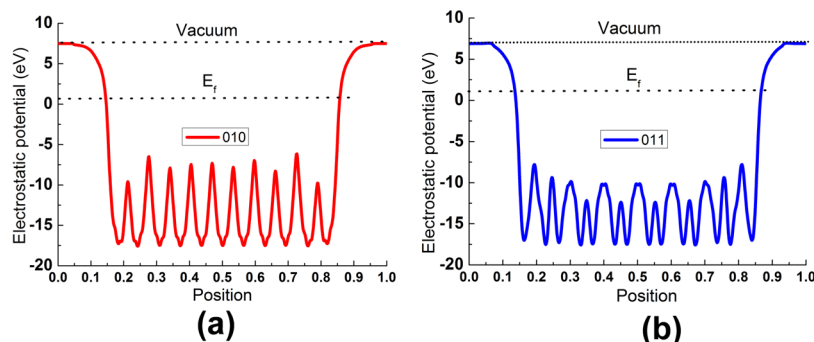
Table 3. Work Function for the (010) and (011) Facets for Varying Vacuum Thickness^a

vacuum thickness (Å)	$W_{(010)}$ (eV)	$W_{(011)}$ (eV)	ΔW (eV)
15	7.00	5.93	1.07
20	7.00	6.00	1.00
25	6.99	6.01	0.98

^aThe thickness of the slabs is ~ 31 Å in all cases [11 Bi layers for the (010) slab and 14 Bi layers for the (011) slab]. ΔW is the difference in work function $\Delta W = W_{(010)} - W_{(011)}$.

therefore, DFT energies are not directly comparable across slabs.

The relative energy profiles are shown in Figure 6a for electron polarons and in Figure 6b for hole polarons. For each curve, the profile shows that energies vary little in the bulk region (z -scale around ~ 0.5) but more significantly in the surface regions (z -scale around ~ 0.7 and up). The most stable sites for electron polarons are in the second V layer, with the least stable sites in the first V layer. The most stable sites for hole polarons are in the first O layer. It is informative to recall that at 300 K, $k_B T \sim 0.0259$ eV. Boltzmann populations for energy differences of $2 k_B T$ (~ 0.0518 eV), $3 k_B T$ (~ 0.0777 eV), $4 k_B T$ (~ 0.1036 eV), $5 k_B T$ (~ 0.1295 eV), ..., $8 k_B T$ (~ 0.2072 eV) are ~ 13.5 , ~ 5.0 , ~ 1.8 , ~ 0.6 , ..., $\sim 0.03\%$, respectively. Accordingly, the preference for a second-layer V site is very large, and the likelihood that an electron polaron might localize on a surface V atom is extremely low. Similarly, the preference for a surface site for a hole polaron is extremely high in terms of the Boltzmann population. Recall that changes due to the choice of $+U_{\text{eff}}$ were discussed earlier in Section II. The energy profiles of electron and holes polarons were found to be affected very little by the choice of $+U_{\text{eff}}$. The data are shown in Figure S7 in the SI with the values given in Tables S3 and S4.

**Figure 5.** Work functions for (a) (010) surface and (b) (011) surface for a slab thickness of ~ 31 Å and a vacuum thickness of 15 Å.

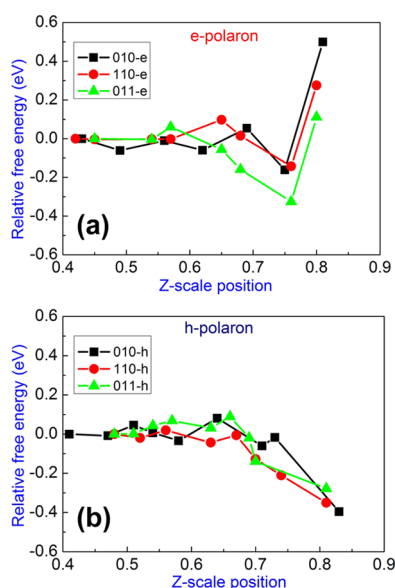


Figure 6. (a) Electron and (b) hole polaron relative energy profiles from the bulk to the surface for the (010), (110), and (011) slabs. The depth (position) of any electron/hole site is defined by its z-scale (see the text; the center of a slab is at “position = 0.5”, and the slab surface is toward “position = 1.0”).

III.VI. Alignment of Polaron Energy Profiles. So far, we obtained the energy profiles from the bulk to the surface for electron and hole polarons for all slabs and surfaces. They show the same essential features for electron as for hole polarons across the various slabs and surfaces. Our general observation is that both electrons and holes prefer surface or near-surface sites rather than bulk sites. However, we are not in a position, from a DFT + *U* energy point of view, to state whether any surface prefers electrons or holes or whether a surface prefers electrons and another surface prefers holes. This is because energies for electron polarons and hole polarons are not directly comparable from slab to slab, as the slabs have different thickness and different number of atoms.

In the limit of thick slabs, an electron polaron or a hole polaron localized at a site in the middle of the slab (z-scale ~ 0.5) should have the same stability, regardless of the indices of the slab surface. Accordingly, it is valid to show all of the electron polaron relative energy profiles on a single graph whereby all of the relative energies in the middle of the slabs are set to be equal to 0.0 eV. This is done in Figure 6 (top) for electron polarons and in Figure 6 (bottom) for hole polarons. The picture that emerges from Figure 6 is that energy profiles for electron polarons across the (010), (110), and (011) slabs have significant similarities, with electron polarons showing a great affinity for the second layer of V atoms, regardless of facet

indices. In the same vein, hole polarons show a great affinity for surface O atoms, regardless of facet indices.

It is interesting to remark the preference for electron and hole localization is in the second V atom layer and in the surface O layer, respectively. We believe the preference arises from the lattice distortion energy associated with small polarons, as surface and near-surface atoms have a reduced coordination environment so that the lattice distortions can only be absorbed by fewer coordinating atoms. This was discussed by Deskins et al.¹³ and is reminiscent of the findings of Deskins et al.⁴⁴ for titania and Ganduglia-Pirovano et al.^{45–47} for ceria. However, in the latter two cases, the electron polarons were generated by oxygen vacancies in contrast to being generated by sunlight absorption.

III.VII. Modeling the Aqueous Phase. All data so far refer to calculations without a model of the liquid phase at the facet/ aqueous phase interfaces. We note that the dielectric constant of BVO is large,⁴⁸ nearly comparable to that of liquid water. Electron and hole polarons are strongly localized charged species that show a preference for surface sites (for the holes) and subsurface sites (for electrons). The high dielectric constant of the aqueous phase suggests that the polarization of the aqueous phase will make the near-surface polarons gain stability compared to the “bulk-site” polarons. We used a polarizable dielectric continuum of the aqueous phase (dielectric constant ~ 78) embodied in the program VASPsol⁴² to calculate the “solvated” DFT energies. The actual data is given in Section 9 of the SI. The relative stability energies at polaron sites, without and with the aqueous phase model, are gathered in Tables 4a and 4b. It can be seen that the model of the aqueous phase makes the polarons a little more stable than before when they were stable and a little less unstable when they were unstable. The aqueous phase has a stabilizing effect both for electron polarons and hole polarons. In any case, the similarities in trends remain the same across the various surfaces.

IV. CONCLUSIONS

In summary, we have studied band alignment and polaron stability among (010), (011), and (110) facets of BiVO₄. For band alignment, we used the Bi (5d), V (3s), and V (3p) states as reference energy levels. The results show that the differences in CB-min and VB-max among the three surfaces are very small. We obtained the relative polaron stability from the bulk to the surface for the three facets. We found that electron polarons are most stable at subsurface V sites for any of the facets, whereas hole polarons are most stable on O surface sites. Experimentally, it is observed¹ that the photogenerated charge carriers in BVO separate between the (010) facet (electron carriers) and the (110) and (011) facets (hole carriers). This work suggests that thermodynamic stability alone is not sufficient to explain facet selectivity. Our previous

Table 4a. Relative Energies (eV) of Electron Polarons from the Bulk to the Surface for the (010), (110), and (011) Slabs^a

010-e			110-e			011-e		
-z-	ΔE	ΔE_{sol}	-z-	ΔE	ΔE_{sol}	-z-	ΔE	ΔE_{sol}
0.43	0.0000	0.0000	0.43	0.0000	0.0000	0.45	0.0000	0.0000
0.75	-0.1614	-0.1778	0.78	-0.1429	-0.1692	0.78	-0.3245	-0.3014
0.82	0.4968	0.4415	0.80	0.2756	0.2529	0.80	0.1119	0.1637

^az is the z-scale coordinate of the polaron site. ΔE 's are the relative stabilities from the bulk to the surface for slab/vacuum models, and ΔE_{sol} 's are the relative stabilities for slab/water models.

Table 4b. Relative Energies (eV) of Hole Polarons from the Bulk to the Surface for the (010), (110), and (011) Slabs^a

010-h			110-h			011-h		
-z-	ΔE	ΔE_{sol}	-z-	ΔE	ΔE_{sol}	-z-	ΔE	ΔE_{sol}
0.41	0.0000	0.000	0.48	0.0000	0.0000	0.48	0.0000	0.0000
0.73	-0.0170	-0.0204	0.74	-0.2105	-0.2023	0.70	-0.1395	-0.1444
0.83	-0.3958	-0.2905	0.81	-0.3485	-0.3172	0.81	-0.1409	-0.1456

^az is the z-scale coordinate of the polaron site. ΔE 's are the relative stabilities from the bulk to the surface for slab/vacuum models, and ΔE_{sol} 's are the relative stabilities for slab/water models.

work²² suggested that electron and hole mobilities are not direction-selective. Thus, it appears that facet selectivity may involve differences in redox reactivity between electrons and holes. We will investigate this issue in future research.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b05929.

Crystallographic data files (ZIP)

Spin density of excess electrons or holes on V or O ions on the (010) and (011) facets; total and projected density of states of one electron or hole for (010) and (011) facets; structural parameters for one excess electron or hole around the V or O ions for (010) and (011) facets; electron and hole energy profiles tested with different U_{eff} values, slab lengths, and vacuum lengths; energies and relative energies of electron and hole polarons from the bulk to the surface for (010), (110), and (011) slabs; convergence of DOSs, band edges, work functions, and polaron stability energies with different values of $+U_{\text{eff}}$; electronic structure of a hole polaron in BVO; relation of total energy $E(N)$ and the fractional electron number N ; and polaron energies and relative energies with the use of a model of solvation for describing the aqueous phase (PDF)

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T.L., C.L., and M.D. contributed equally to the design of the study. T.L. and M.D. contributed equally to the calculations and the preparation of the manuscript. Q.Z. carried out the calculations for the relation of total energy $E(N)$ and N . Y.L. carried out the VASPsol calculations.

Notes

The authors declare no competing financial interest.

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