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Research Article

Keywords:

Posted Date: October 23rd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11239054/v1>

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

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Abstract

Bismuth vanadate (BiVO_4) is a benchmark oxide photoanode whose performance is governed by surface states, yet the thermodynamics and charge transition levels (CTLs) of its surface defects remain far less characterized than its bulk defect physics. Here we use dielectric-dependent hybrid density functional theory to compute formation energies and CTLs for oxygen vacancies and for substitutional n -type (Mo, W) and p -type (Ca, Sr) dopants on $\text{BiVO}_4(010)$. Under the O-rich conditions of anodic operation, Mo and W substitute on the V sublattice, which they prefer over the Bi site by 3.3 and 3.7 eV for a Fermi level at the conduction band edge. Surface oxygen vacancies are shallow donors whose $\varepsilon(2+/0)$ level lies 0.16 eV below the conduction band and are ionized over almost the whole gap. Mo_V and W_V are deeper donors at 0.51 and

0.58 eV below the conduction band. Ca_{Bi} is a shallow acceptor 0.02 eV above the valence band, whereas Sr_{Bi} has no transition within the gap and is ionized at every Fermi level. The two acceptors also place the hole differently, Ca_{Bi} on the outermost oxygen layer and Sr_{Bi} in the interior. Because photoanode operation is limited by holes reaching the surface, an acceptor that captures photogenerated holes on the outermost oxygen layer should be more useful for water oxidation than one that leaves them in the interior, which makes Ca_{Bi} the more promising *p*-type dopant of the two.

Keywords

Bismuth vanadate; Photoanode; Surface defects; Charge transition levels; Hybrid density functional theory; Hole localization

Introduction

Solar-driven photoelectrochemical (PEC) water splitting offers a direct route to store renewable energy in chemical bonds, but practical implementation requires photoelectrodes that combine strong visible-light absorption, efficient charge transport/separation, and robust interfacial catalysis.¹ Among metal oxide photoanodes, monoclinic BiVO_4 has emerged as a benchmark material because it absorbs visible light (band gap ~ 2.4 eV) and provides a valence band position sufficiently positive for oxygen evolution under PEC operational conditions.^{1,2}

Despite extensive progress, BiVO_4 photoanodes remain limited by intrinsically poor carrier transport associated with small-polaron formation, as well as surface recombination and catalytic overpotentials at the semiconductor/electrolyte interface.¹ Consequently, performance improvements have largely relied on bulk and surface defect-engineering strategies such as donor doping (e.g., Mo or W) and oxygen vacancy (V_{O}) formation to enhance electron conductivity and improve charge collection.^{3,4} Theoretically and experimentally, Mo/W

doping is also known to modify the near-surface electronic structure and can induce polaronic charge localization in the subsurface region, influencing both transport and surface chemistry.^{5,6}

Because the PEC interface is controlled by surface band bending and surface-state energetics, surface defects play a disproportionate role in determining recombination losses and interfacial charge transfer. Among plausible surface defects, oxygen vacancies have attracted particular attention, and both experiment and theory suggest that their charge state (i.e., V_O and ionized forms such as V_O^+ and V_O^{2+}) can strongly influence charge-carrier trapping and dynamics.^{7–9}

Their role under operating conditions, however, remains unsettled. Recent first-principles work indicates that surface V_O on BiVO_4 can spontaneously ionize and that ionized vacancies may enhance water oxidation by avoiding hole trapping and by modifying reaction energetics.¹⁰ At the same time, other studies have argued that oxygen vacancies can behave as deep donor-like centers at BiVO_4 surfaces and may act as recombination sites, highlighting an ongoing debate.^{11,12}

From a defect-physics perspective, the key descriptors connecting point defects to electronic functionality are the defect formation energies and charge transition levels (CTLs). While bulk defect energetics and doping trends in BiVO_4 have been systematically investigated (e.g., shallow donor behavior of oxygen vacancies and Mo/W_V , and shallow acceptor behavior of $\text{Ca}/\text{Sr}_{\text{Bi}}$),¹³ a comprehensive, comparative understanding of CTLs for surface defects remains limited. This gap is critical because surfaces differ from the bulk in coordination environment and electrostatic alignment, both of which can shift defect thermodynamics and CTLs. In contrast to the extensive literature on donor (n -type) dopant strategies, acceptor-doped or p -type BiVO_4 has been much less explored. Only very recent work has demonstrated p -type BiVO_4 enabling photocathodic O_2 reduction to H_2O_2 , and the corresponding acceptor-induced hole localization remains poorly understood, particularly at surfaces.^{13,14}

Here we address this gap by performing a systematic dielectric-dependent hybrid functional study of surface defects on $\text{BiVO}_4(010)$, focusing on oxygen vacancies and representative n -type (Mo, W) and p -type (Ca, Sr) substitutional dopants. Motivated by the established importance of n -type defects for BiVO_4 photoanodes and the comparatively limited understanding of p -type defect physics,^{13,14} we include Ca and Sr as representative acceptor dopants to assess whether their acceptor character remains shallow at the surface, in comparison with their behavior in the bulk.¹³

Using dielectric-dependent hybrid functional calculations combined with surface charged-defect corrections, we compute defect formation energies and CTLs, and we analyze the associated charge localization in the surface lattice. Our results show that i) the surface V_O is a shallow donor within 0.16 eV of the conduction band minimum (CBM), whereas the substitutional donors Mo_V and W_V lie considerably deeper, 0.51 and 0.58 eV below it, ii) Ca_{Bi} is an acceptor 0.02 eV above the valence band maximum (VBM), whereas Sr_{Bi} has no transition within the gap, and iii) the two Bi-site acceptors place the hole in different locations, Sr_{Bi} in the interior and Ca_{Bi} on the outermost oxygen layer.

This distinction is what connects the defect levels to photoelectrochemistry, since interfacial hole transfer on BiVO_4 proceeds through surface Bi–O states,¹⁵ and an acceptor that places the hole in the interior therefore leaves the reactive site unpopulated. On this criterion Ca_{Bi} emerges as a feasible p -type dopant for photoelectrochemical application, since it is preferred on the Bi sublattice over most of the gap and, although ionized under photoanode operation, captures a photogenerated hole on the outermost oxygen layer at a level shallow enough to release it again thermally.

Computational Methods

We employed the dielectric-dependent PBE0 hybrid functional,^{16,17} setting the fraction of exact exchange to $\alpha = 1/\epsilon_\infty = 0.22$ (ϵ_∞ is the high-frequency dielectric constant),^{18,19} a value

established for BiVO_4 by matching the quasiparticle self-consistent GW band gap and independently verified through the generalized Koopmans condition. Calculations were carried out using PBE0 with Truncated Coulomb and Long-Range Correction (PBE0-TC-LRC)²⁰ combined with the auxiliary density matrix method (ADMM)²¹ as implemented in CP2K.²² Core–valence interactions were treated with Goedecker–Teter–Hutter (GTH) pseudopotentials,²³ and valence wave functions were expanded in MOLOPT double- ζ polarized (DZVP) basis sets.²⁴ The electron density was represented in an auxiliary plane-wave basis with a cutoff of 600 Ry. The computed gap was corrected for spin–orbit coupling and excitonic effects by shifting the valence and conduction band edges by +0.61 and -0.54 eV, respectively.^{19,25} We modeled the $\text{BiVO}_4(010)$ surface using a periodic slab with a vacuum spacing of 30 Å to avoid spurious slab–slab interactions. The slab was built from the tetragonal phase (space group $I4_1/a$), whose (001) termination is structurally equivalent to the monoclinic (010) termination for the purposes of defect thermodynamics and polaron formation and is used here as a proxy for it.^{10,26} For brevity we refer to this surface as $\text{BiVO}_4(010)$ throughout. The lattice parameters were set to $a = b = 5.15$ Å and $c = 16.33$ Å for bulk BiVO_4 , consistent with experimental crystallographic data.²⁷

We considered surface V_{O} following the geometries and polaronic configurations established in a prior hybrid-functional study.¹⁰ Surface dopants (Mo, W, Ca, and Sr) were introduced substitutionally at the topmost-layer V or Bi sites in a $p(2 \times 2)$ $\text{BiVO}_4(010)$ slab supercell.

The formation energy of a surface defect in charge state q was defined as

$$\Delta H_{\text{f}}(q) = E^{\text{defect}} - E^{\text{pristine}} + \sum_i \Delta N_i \mu_i + q(E_{\text{VBM}} + E_{\text{F}}) + E_{\text{corr}}, \quad (1)$$

where E^{defect} and E^{pristine} are the total energies of the defect-containing and pristine slabs, respectively, and E_{corr} is the charged-slab electrostatic correction. ΔN_i is the number of atoms of species i (Bi, V, O, or dopants) removed from the pristine slab, negative for atoms

added, and μ_i is its chemical potential, defined in the Supporting Information (Table S1). The Fermi level E_F is referenced to the VBM, E_{VBM} , and is varied across the band gap. Charged-slab calculations suffer from spurious electrostatic interactions between periodic images. We corrected these effects using the Freysoldt–Neugebauer–Van de Walle (FNV) approach²⁸ and its extension to surfaces and two-dimensional systems,²⁹ with a dielectric screening parameter consistent with reported permittivity values for BiVO_4 ($\epsilon \sim 68$).³⁰

Results and Discussion

Pristine $\text{BiVO}_4(010)$ surface and its polaronic charge localization. Before discussing surface defects, we first characterize the pristine $\text{BiVO}_4(010)$ slab. The pristine slab exhibits a corrected band gap of 2.75 eV within the dielectric-dependent PBE0 approach ($\alpha = 0.22$). Bulk BiVO_4 can be understood as a framework of isolated VO_4 tetrahedra (fourfold-coordinated V) and Bi-centered oxygen polyhedra (eightfold coordination in the bulk, Figure 1a). Cleaving along the (010) plane preserves the VO_4 tetrahedral motif in the near-surface region, while the Bi coordination becomes reduced at the outermost layer.

For the stoichiometric $\text{BiVO}_4(010)$ termination, the topmost layer is composed of distorted Bi–O polyhedra together with surface-exposed VO_4 units. Within a Bi–O cutoff of 2.55 Å, the outermost Bi is best described as a BiO_5 unit, with five short bonds averaging 2.35 Å and one elongated contact of 2.57 Å that falls outside the cutoff, so that the bulk BiO_8 dodecahedron is reduced to a five-coordinate surface polyhedron.

To probe polaronic self-trapping at the surface, we introduced one excess electron (e^-) or one excess hole (h^+) into the slab and relaxed the atomic positions. In both cases (e^- or h^+), the excess charge localizes with a local lattice distortion, consistent with prior reports that charge carriers in BiVO_4 exhibit polaronic character.^{6,31–33} As shown in Figure 1b, an excess e^- localizes on a single subsurface V site, carrying an integrated spin moment of 1.0 μ_B , and expands the surrounding VO_4 unit from a mean V–O bond length of 1.72 Å to 1.80 Å.

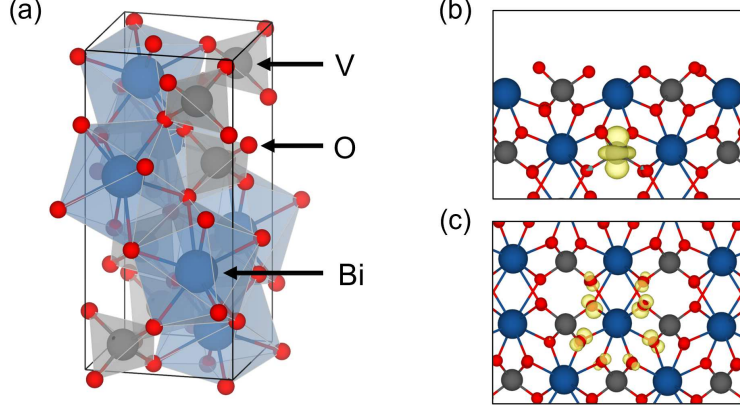


Figure 1: (a) Crystal structure of bulk BiVO₄. V is tetrahedrally coordinated to four O atoms, forming a VO₄ unit, while Bi adopts eightfold coordination with oxygen in a dodecahedral BiO₈ geometry. (b) Excess electron polaron and (c) localized excess hole at the BiVO₄(010) surface. Blue, gray, and red spheres denote Bi, V, and O atoms, respectively.

The hole behaves differently (Figure 1c), and rather than trapping on one site, it is distributed over the O 2*p* ligands of a single eightfold-coordinated Bi polyhedron in the slab interior, with no individual O carrying more than 0.15 μ_B , and contracts the mean Bi–O bond length of that polyhedron from 2.47 Å to 2.41 Å. The contrast is central to what follows, in that electrons at this surface form well-localized small polarons, whereas holes remain comparatively delocalized over a Bi–O cage unless a defect provides an undercoordinated O to trap them.

Surface oxygen vacancy. As a benchmark intrinsic donor-type surface defect, we first examine the surface oxygen vacancy on BiVO₄(010). A recent hybrid-functional study reported that the neutral V_O is thermodynamically disfavored at the BiVO₄(010) surface and that V_O spontaneously ionizes, with the released electrons preferentially stabilizing as small electron polarons in subsurface regions of the slab.¹⁰ Using a similar computational setup (asymmetric slab) and charged-defect formalism, we reproduce the same qualitative behavior for surface V_O .

Figure 2a displays the computed formation energies ΔH_f of V_O^q as a function of the Fermi level, E_F , using Equation (1). Up to the $\varepsilon(2+/0)$ transition, which lies 0.16 eV below the CBM, V_O^{2+} is the lowest-energy charge state, and only in that narrow window below the

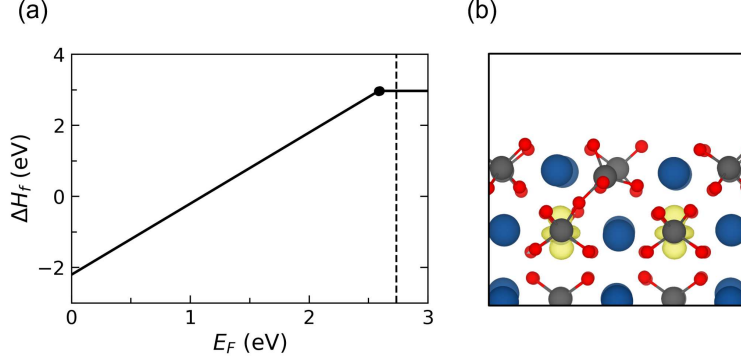


Figure 2: Surface oxygen vacancy (V_O) on $\text{BiVO}_4(010)$. (a) Formation energy of V_O in its lowest-energy charge state as a function of the Fermi level E_F , referenced to the valence band maximum (VBM). The filled circle marks $\varepsilon(2+/0)$, and the vertical dashed line indicates the CBM. (b) Polaronic charge localization associated with the neutral vacancy V_O (triplet state). Bi, V, and O atoms are shown in blue, gray, and red, respectively.

CBM does the neutral vacancy become lowest. The +1 state is never lowest at any E_F , consistent with Ref. 10. Near the CBM, where the neutral V_O is lowest, its formation is thermodynamically unfavorable, with $\Delta H_f(V_O^0) = 2.97$ eV. With $\varepsilon(2+/0)$ at 0.16 eV below the CBM in our corrected surface band gap of 2.75 eV, the vacancy is a shallow donor at the surface. Our dielectric-dependent hybrid results side with the shallow-donor picture, since V_O^{2+} remains the lowest-energy charge state across almost the whole gap and the released electrons are stabilized as polarons in stoichiometric regions rather than in vacancy-centered in-gap states.¹⁰

As shown in Figure 2b, when V_O is introduced at a topmost surface oxygen site of the (010) termination, the neutral V_O (triplet state) does not retain the two excess electrons at the vacant site. Instead, the electrons self-trap as small electron polarons on two nearby (typically subsurface) V cations, forming V^{4+} -like centers and inducing local lattice relaxations around the polaronic V sites. This localization pattern and the relaxed defect geometry are in excellent agreement with previously reported hybrid-functional results.¹⁰ Both trapped electrons carry a spin moment of $1.0 \mu_B$, and each elongates its host tetrahedron from a mean V–O bond length of $1.72 \text{ \AA}$ to $1.80 \text{ \AA}$, reproducing the intrinsic electron polaron of Figure 1b at two adjacent V sites. This behavior is consistent with facile vacancy ionization and a

donor-like character at the surface, aligning with the picture that surface oxygen vacancies on BiVO_4 tend to ionize and that ionized vacancies avoid acting as strong hole-trapping centers.^{7,8,10}

Substitutional Mo and W at the surface. We next examine *n*-type substitutional Mo and W dopants at the $\text{BiVO}_4(010)$ surface, considering both V-site substitutions (Mo_V , W_V) and Bi-site substitutions (Mo_Bi , W_Bi). Figure 3a shows $\Delta H_\text{f}(q)$ as a function of E_F , referenced to the VBM, evaluated at the O-rich midpoint of the BiVO_4 stability region, the condition midway between coexistence of BiVO_4 with V_2O_5 and with $\alpha\text{-Bi}_2\text{O}_3$. This O-rich condition reflects the oxidizing environment of anodic operation. V-site substitution is strongly preferred for both dopants, and at the CBM we obtain 1.07 eV (Mo_V) and 1.64 eV (W_V), against 4.34 eV (Mo_Bi) and 5.33 eV (W_Bi), i.e., site preferences of 3.27 and 3.69 eV in favor of the V site. At the CBM the V site remains preferred at the V-rich and Bi-rich limits, by 2.44 and 4.11 eV for Mo and by 2.86 and 4.53 eV for W (Figure S1). The preference reverses only below $E_\text{F} = 0.54$ eV for Mo and 0.77 eV for W, where the Bi-site states become lower in energy (Figure 3a).

For V-site substitution, both Mo_V and W_V behave as single donors, whose donor ionization energies lie 0.51 eV (Mo_V) and 0.58 eV (W_V) below the CBM (Table S2), substantially deeper than the surface V_O donor transition, which lies within 0.16 eV of the CBM.¹⁰ These depths differ sharply from the bulk. Both levels are far deeper than their bulk counterparts, which have been placed within a few tens of meV of the CBM (0.04 and 0.01 eV).¹³ Bulk defects were not recomputed here, and the reference values come from generalized gradient approximation (GGA) and GGA+*U* calculations in a 2.06 eV gap.¹³ Compared on the basis of each level’s distance from its own band edge, the calculated surface levels of the substitutional donors lie farther from the respective CBM than those bulk values, whereas the vacancy level stays close to the CBM in both.

To characterize the donated electron, we analyzed the spin density of the neutral V-site dopants (Figure 3b). In both Mo_V and W_V the excess electron leaves the dopant center

entirely and self-traps on a host V site with an integrated spin moment of $1.0 \mu_B$, consistent with the electron polarons reported for Mo/W-doped BiVO_4 surfaces.^{6,31–33} The two dopants differ in how deep the electron sits. At W_V it sits in the second V layer, $2.7 \text{ \AA}$ below the outermost one, whereas at Mo_V it reaches the third, $5.8 \text{ \AA}$ down and at the midplane of the slab. Both sites lie more than $6 \text{ \AA}$ from the dopant, and the range they span, from subsurface to bulk-like, matches the spread reported for polarons at BiVO_4 terminations.^{6,34} The accompanying distortion differs in character between the two dopants, and it is useful to recall that the host VO_4 tetrahedron is not regular. In the pristine slab each V carries two short bonds of $1.64 \text{ \AA}$ and two long ones of $1.81 \text{ \AA}$, a mean of $1.72 \text{ \AA}$, so the four bonds fall into two inequivalent pairs rather than being all alike. For Mo_V the polaronic unit expands while preserving that division, to 1.75 and $1.78 \text{ \AA}$ against 1.83 and $1.84 \text{ \AA}$, a mean of $1.80 \text{ \AA}$, and it remains four-coordinated.

At W_V the pairing itself does not survive the expansion, and the two pairs are replaced by one short bond and three long ones. One bond stays at the pristine short value of $1.64 \text{ \AA}$ while the other three lengthen to 1.86 , 1.93 and $1.97 \text{ \AA}$, and a fifth O lies at $2.08 \text{ \AA}$, giving a mean of $1.90 \text{ \AA}$ over five contacts within the $2.65 \text{ \AA}$ cutoff. We describe this as a distorted VO_4 unit with one additional long V–O contact rather than a converted VO_5 polyhedron. The larger and less symmetric distortion at W_V is consistent with a more strongly bound polaron than at Mo_V .

Substitutional Ca and Sr at the surface. We next examine acceptor-type substitutional Ca and Sr at the $\text{BiVO}_4(010)$ surface, on both the Bi sublattice (Ca_{Bi} , Sr_{Bi}) and the V sublattice (Ca_V , Sr_V). Figure 3a summarizes the corresponding formation energies $\Delta H_f(q)$ as a function of E_F (referenced to the VBM). At the same O-rich midpoint, with μ_{Ca} and μ_{Sr} fixed by CaO and SrO, Bi-site substitution is preferred over V-site substitution for both alkaline-earth dopants over most of the gap. At the VBM the Bi-site acceptors form with $\Delta H_f = 0.77 \text{ eV}$ (Ca_{Bi}) and 0.08 eV (Sr_{Bi}), against 3.12 and 3.72 eV on the V site, a Bi-site preference of 2.35 and 3.64 eV . The Bi-site preference is consistent with the large size of

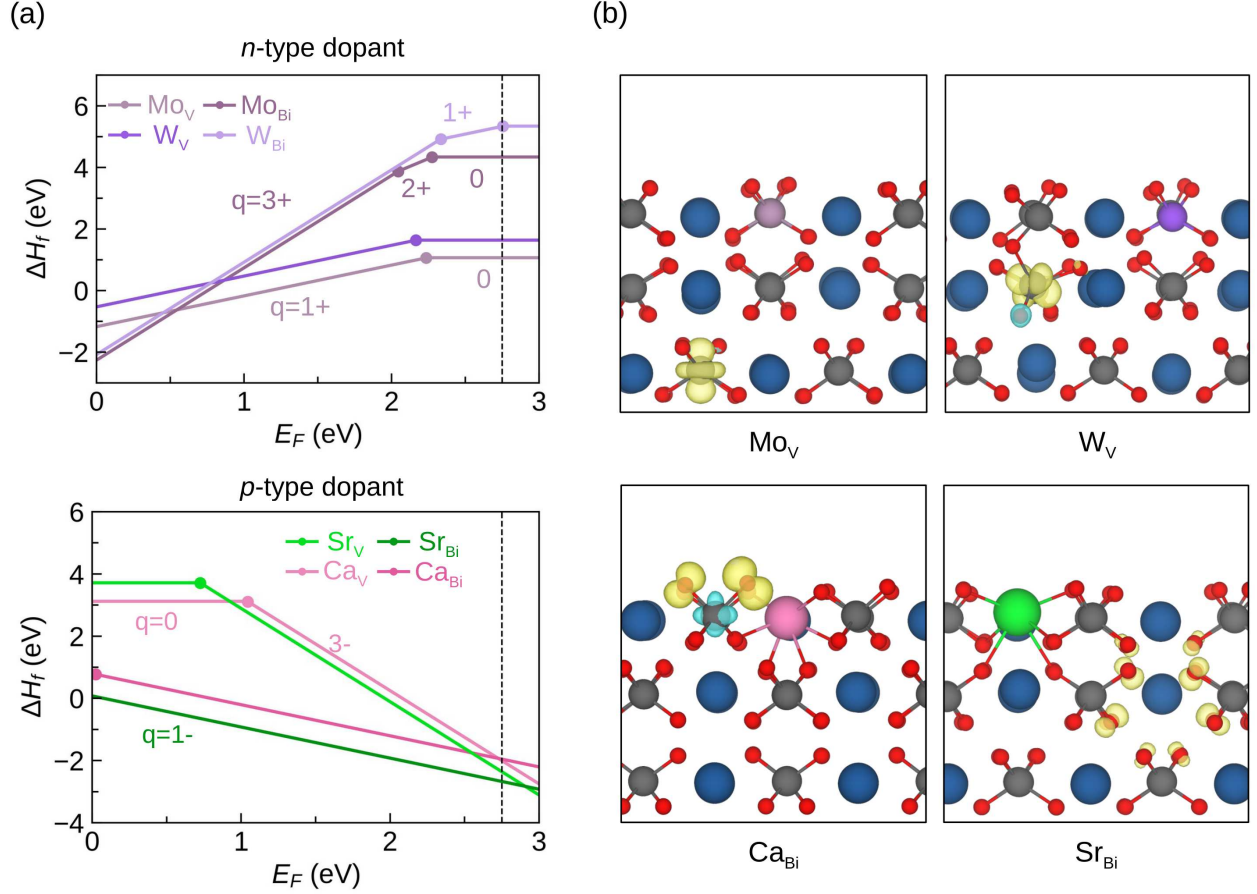


Figure 3: (a) Formation energies of *n*- and *p*-type substitutional dopants on the BiVO₄(010) surface as a function of the Fermi level. All curves are evaluated at the O-rich midpoint. The Fermi level is referenced to the VBM. The different charge states are marked, and the vertical dashed line indicates the CBM at 2.75 eV. (b) Spin densities of neutral dopant states. Mo, W, Ca and Sr atoms are indicated in mauve, purple, pink and green, respectively. The isosurface value of spin densities is set to 0.01 e/Bohr^3 .

both alkaline-earth cations relative to tetrahedral V⁵⁺, with the close match in ionic radius and coordination preference between Ca²⁺ and Bi³⁺, and with the lower Bi-site formation energies reported for Ca-doped BiVO₄.^{13,14}

Ca_{Bi} is a shallow acceptor, with $\varepsilon(0/1-)$ only 0.02 eV above the VBM (Table S2). Sr_{Bi} has no transition within the gap. Its -1 state is the lowest in energy at every E_F , and $\varepsilon(0/1-)$ falls 0.39 eV below the VBM, so the dopant is ionized under any accessible condition (Table S2). By contrast, Ca_V and Sr_V act as deep acceptors with a single $\varepsilon(0/3-)$ transition at 1.04 and 0.73 eV above the VBM, since their -1 and -2 states are never lowest in energy

(Table S2). Unlike the donors, the Bi-site acceptors are not deeper at the surface than in the bulk. The Bi-site acceptor levels reported for the bulk lie 0.08 and 0.09 eV above the VBM,¹³ and bulk Ca_{Bi} has been placed at 0.13 eV with the same class of dielectric-dependent hybrid functional.¹⁴ Our surface level for Ca_{Bi} is shallower than either bulk estimate, and Sr_{Bi} has no level in the gap.

Polaronic hole localization for the neutral acceptors is shown in Figure 3b, and the two dopants behave differently, in line with their different levels. In Sr_{Bi}^0 the hole is distributed over the O 2*p* ligands of a single eightfold-coordinated Bi polyhedron below the surface, with no individual O carrying more than 0.15 μ_{B} , and the mean Bi–O bond length of that polyhedron contracts from 2.47 Å to 2.42 Å. This is the localized excess hole of Figure 1c, and it is not associated with the dopant, the Bi that hosts it lying 6.4 Å from the Sr. This agrees with the absence of a Sr_{Bi} level in the gap, since the dopant does not bind the hole.

In Ca_{Bi}^0 , by contrast, the hole is displaced to the outermost layer and shared by two neighboring oxygens, which carry 0.84 and 0.43 μ_{B} . Both sit above the topmost Bi plane and each retains only one long Bi–O contact, of 2.93 and 2.95 Å. Their host surface Bi polyhedra therefore lose one of the six oxygens they hold within 2.9 Å on the pristine surface, and the five that remain shorten from 2.35 Å to 2.29 and 2.30 Å. A nearby V carries 0.35 μ_{B} of antiparallel spin. The two spin-bearing oxygens also approach each other, from 2.71 Å on the pristine surface to 2.49 Å, which makes them the closest O–O pair in the slab. In both cases the spin density avoids the alkaline-earth dopant itself and the surrounding VO_4 units are barely perturbed (for Ca_{Bi}^0 , the mean V–O bond length stays within 0.02 Å of the pristine value), consistent with O 2*p* hole character rather than dopant-centered states.

This contrast bears on where holes are available at the surface. On the dry stoichiometric slab our excess hole stays in the interior, whereas at the hydrated BiVO_4 –water interface the hole polaron gains about 0.2 eV of binding energy on localizing in the surface layer, so that hydration itself favors surface holes.³⁵

Holes at BiVO_4 surfaces have a further, distinctly surface channel available to them. Two

adjacent lattice oxygens can pair into an O–O dimer that traps a hole pair strongly, with a computed binding energy of -1.32 eV and a CTL 0.66 eV above the VBM at the surface, deepening to -2.42 eV and 1.21 eV at the aqueous interface.¹⁸ Peroxide-derived states of this kind appear near the VBM on O-rich $\text{BiVO}_4(010)$ terminations and act as hole traps, and they have been proposed as precursors of the oxygen-evolution step.³⁴ Our Ca_{Bi} result sits directly on this axis, though short of the dimer itself. The dopant places hole density on two adjacent undercoordinated oxygens of the outermost layer without invoking the solvent, and draws the two together by 0.22 Å relative to the pristine surface. At the resulting separation of 2.49 Å they are the closest O–O pair in the slab but still 1.04 Å longer than the peroxide bond of the dimer (1.45 Å), so no dimer is formed. Sr_{Bi} , by contrast, leaves the hole where it sits on the undoped surface.

Implications of p -type dopants for PEC performance. For the acceptors, the relevant comparison is with the reactive species identified for water oxidation. In an n -type photoanode E_{F} lies near the CBM, so both Bi-site acceptors are ionized and carry no hole of their own. Their role is then to capture photogenerated holes, and the neutral states of Figure 3b describe the configuration after capture. Mechanistic simulations of the first proton-coupled electron-transfer (PCET) step at the BiVO_4 –water interface place the reactive hole at the surface with pronounced Bi–O character, with transfer to the adsorbate mediated by the Bi–O bond.¹⁵ Ca_{Bi} places 0.84 and 0.43 μ_{B} of hole density on two undercoordinated O of the outermost layer, whereas Sr_{Bi} leaves the hole in the interior. Since the Ca_{Bi} level lies within about $k_{\text{B}}T$ of the VBM at room temperature, a captured hole can also be released thermally, so the site acts as a shallow and reversible hole reservoir next to the reactive surface. Sr_{Bi}^- does not bind the hole, which in Sr_{Bi}^0 sits in the interior as in the undoped slab. Once a photogenerated hole is captured, Ca_{Bi} holds it on outer-layer oxygens at a level only 0.02 eV above the VBM, which keeps it both surface-localized and shallow. The oxygens involved would be hydroxylation sites under operating conditions.^{15,32}

The same acceptors compensate the n -type carriers of the photoanode, so their use

presupposes doping confined to the surface at low concentration, or co-doping with Mo or W that sustains the bulk conductivity. In *p*-type BiVO₄ photocathodes for O₂ reduction,¹⁴ by contrast, the ionized V_O²⁺ donors would have to be suppressed, since they compensate the acceptors.¹⁰

Conclusions

Using dielectric-dependent hybrid density functional theory with charged-defect corrections for slab geometries, we determined formation energies and charge transition levels for representative surface defects on BiVO₄(010). The pristine surface traps an excess electron as a small polaron on a subsurface V, whereas an excess hole stays distributed over the O 2*p* ligands of an interior Bi–O polyhedron. Surface oxygen vacancies are ionized over almost the whole gap and release their electrons into the same polaronic states.

Among the substitutional dopants the preferred sublattice is set by the dopant rather than by the surface, so the site assignments established for the bulk carry over to the surface. Mo and W favor V sites, by 3.3 and 3.7 eV at the O-rich midpoint with E_F at the CBM, and Ca and Sr favor Bi sites over most of the gap. What the surface appears to change is depth, since the substitutional donors sit an order of magnitude deeper than the bulk levels reported at the GGA level, while Ca_{Bi} stays within 0.02 eV of the VBM and Sr_{Bi} has no level in the gap. The two Bi-site acceptors differ in whether they bind a photogenerated hole and where. Sr_{Bi} leaves it in the interior, as in the undoped slab, while Ca_{Bi} holds it on the outermost oxygen layer. Since photoanode operation is limited by holes reaching the surface, this suggests Ca_{Bi} as the more promising *p*-type dopant of the two and identifies whether and where a dopant binds the hole as a design variable.

Acknowledgement

This research was supported by National University Development Project at Jeonbuk Na-

tional University in 2023.

Supporting Information Available

Competing phases used to bound the chemical potentials (Table S1), the chemical-potential definitions under O-rich conditions, formation energies of Mo and W (Figure S1) and of Ca and Sr (Figure S2) at the V-rich limit, midpoint and Bi-rich limit, and thermodynamic charge transition levels (Table S2).

References

- (1) Park, Y.; McDonald, K. J.; Choi, K.-S. Progress in Bismuth Vanadate Photoanodes for Use in Solar Water Oxidation. *Chem. Soc. Rev.* **2013**, *42*, 2321–2337.
- (2) Lee, D.; Wang, W.; Zhou, C.; Tong, X.; Liu, M.; Galli, G.; Choi, K.-S. The Impact of Surface Composition on the Interfacial Energetics and Photoelectrochemical Properties of BiVO₄. *Nat. Energy* **2021**, *6*, 287–294.
- (3) Pilli, S. K.; Furtak, T. E.; Brown, L. D.; Deutsch, T. G.; Turner, J. A.; Herring, A. M. Cobalt-Phosphate (Co-Pi) Catalyst Modified Mo-Doped BiVO₄ Photoelectrodes for Solar Water Oxidation. *Energy Environ. Sci.* **2011**, *4*, 5028–5034.
- (4) Abdi, F. F.; Firet, N.; van de Krol, R. Efficient BiVO₄ Thin Film Photoanodes Modified with Cobalt Phosphate Catalyst and W-Doping. *ChemCatChem* **2013**, *5*, 490–496.
- (5) Ding, K.; Chen, B.; Fang, Z.; Zhang, Y.; Chen, Z. Why the Photocatalytic Activity of Mo-Doped BiVO₄ Is Enhanced: A Comprehensive Density Functional Study. *Phys. Chem. Chem. Phys.* **2014**, *16*, 13465–13476.
- (6) Cen, J.; Li, S.; Zheng, J.; Pan, F. Electron Polarons in the Subsurface Layer of Mo/W-Doped BiVO₄ Surfaces. *RSC Adv.* **2019**, *9*, 819–823.
- (7) Selim, S.; Pastor, E.; García-Tecedor, M.; Morris, M. R.; Francàs, L.; Sachs, M.; Moss, B.; Corby, S.; Mesa, C. A.; Gimenez, S.; Kafizas, A.; Bakulin, A. A.; Durrant, J. R. Impact of Oxygen Vacancy Occupancy on Charge Carrier Dynamics in BiVO₄ Photoanodes. *J. Am. Chem. Soc.* **2019**, *141*, 18791–18798.
- (8) Cheng, C.; Fang, Q.; Fernández-Alberti, S.; Long, R. Controlling Charge Carrier Trapping and Recombination in BiVO₄ with the Oxygen Vacancy Oxidation State. *J. Phys. Chem. Lett.* **2021**, *12*, 3514–3521.

- (9) Hermans, Y.; Murcia-López, S.; Klein, A.; Jaegermann, W. BiVO₄ Surface Reduction upon Water Exposure. *ACS Energy Lett.* **2019**, *4*, 2522–2528.
- (10) Österbacka, N.; Ouhbi, H.; Ambrosio, F.; Wiktor, J. Spontaneous Oxygen Vacancy Ionization Enhances Water Oxidation on BiVO₄. *ACS Energy Lett.* **2024**, *9*, 153–158.
- (11) Wang, W.; Strohbeen, P. J.; Lee, D.; Zhou, C.; Kawasaki, J. K.; Choi, K.-S.; Liu, M.; Galli, G. The Role of Surface Oxygen Vacancies in BiVO₄. *Chem. Mater.* **2020**, *32*, 2899–2909.
- (12) Nikačević, P.; Hegner, F. S.; Galán-Mascarós, J. R.; López, N. Influence of Oxygen Vacancies and Surface Facets on Water Oxidation Selectivity toward Oxygen or Hydrogen Peroxide with BiVO₄. *ACS Catal.* **2021**, *11*, 13416–13422.
- (13) Yin, W.-J.; Wei, S.-H.; Al-Jassim, M. M.; Turner, J.; Yan, Y. Doping Properties of Monoclinic BiVO₄ Studied by First-Principles Density-Functional Theory. *Phys. Rev. B* **2011**, *83*, 155102.
- (14) Seo, D.; Somjit, V.; Wi, D. H.; Galli, G.; Choi, K.-S. p-Type BiVO₄ for Solar O₂ Reduction to H₂O₂. *J. Am. Chem. Soc.* **2025**, *147*, 3261–3273.
- (15) Zhuang, Y.-B.; Pasquarello, A. Mechanism of First Proton-Coupled Electron Transfer of Water Oxidation at the BiVO₄–Water Interface. *Angew. Chem. Int. Ed.* **2025**, *64*, e202507071.
- (16) Alkauskas, A.; Broqvist, P.; Pasquarello, A. Defect Levels through Hybrid Density Functionals: Insights and Applications. *Phys. Status Solidi B* **2011**, *248*, 775–789.
- (17) Skone, J. H.; Govoni, M.; Galli, G. Self-Consistent Hybrid Functional for Condensed Systems. *Phys. Rev. B* **2014**, *89*, 195112.
- (18) Ambrosio, F.; Wiktor, J. Strong Hole Trapping Due to Oxygen Dimers in BiVO₄: Effect on the Water Oxidation Reaction. *J. Phys. Chem. Lett.* **2019**, *10*, 7113–7118.

- (19) Wiktor, J.; Reshetnyak, I.; Ambrosio, F.; Pasquarello, A. Comprehensive Modeling of the Band Gap and Absorption Spectrum of BiVO_4 . *Phys. Rev. Mater.* **2017**, *1*, 022401.
- (20) Guidon, M.; Hutter, J.; VandeVondele, J. Robust Periodic Hartree–Fock Exchange for Large-Scale Simulations Using Gaussian Basis Sets. *J. Chem. Theory Comput.* **2009**, *5*, 3010–3021.
- (21) Guidon, M.; Hutter, J.; VandeVondele, J. Auxiliary Density Matrix Methods for Hartree–Fock Exchange Calculations. *J. Chem. Theory Comput.* **2010**, *6*, 2348–2364.
- (22) Kühne, T. D. et al. CP2K: An Electronic Structure and Molecular Dynamics Software Package—Quickstep: Efficient and Accurate Electronic Structure Calculations. *J. Chem. Phys.* **2020**, *152*, 194103.
- (23) Goedecker, S.; Teter, M.; Hutter, J. Separable Dual-Space Gaussian Pseudopotentials. *Phys. Rev. B* **1996**, *54*, 1703–1710.
- (24) VandeVondele, J.; Hutter, J. Gaussian Basis Sets for Accurate Calculations on Molecular Systems in Gas and Condensed Phases. *J. Chem. Phys.* **2007**, *127*, 114105.
- (25) Ambrosio, F.; Wiktor, J.; Pasquarello, A. pH-Dependent Catalytic Reaction Pathway for Water Splitting at the BiVO_4 –Water Interface from the Band Alignment. *ACS Energy Lett.* **2018**, *3*, 829–834.
- (26) Hu, J.; Chen, W.; Zhao, X.; Su, H.; Chen, Z. Anisotropic Electronic Characteristics, Adsorption, and Stability of Low-Index BiVO_4 Surfaces for Photoelectrochemical Applications. *ACS Appl. Mater. Interfaces* **2018**, *10*, 5475–5484.
- (27) Sleight, A. W.; Chen, H.-Y.; Ferretti, A.; Cox, D. E. Crystal Growth and Structure of BiVO_4 . *Mater. Res. Bull.* **1979**, *14*, 1571–1581.
- (28) Freysoldt, C.; Neugebauer, J.; Van de Walle, C. G. Fully Ab Initio Finite-Size Corrections for Charged-Defect Supercell Calculations. *Phys. Rev. Lett.* **2009**, *102*, 016402.

- (29) Freysoldt, C.; Neugebauer, J. First-Principles Calculations for Charged Defects at Surfaces, Interfaces, and Two-Dimensional Materials in the Presence of Electric Fields. *Phys. Rev. B* **2018**, *97*, 205425.
- (30) Zhou, D.; Pang, L.-X.; Wang, D.-W.; Reaney, I. M. BiVO₄ Based High-*k* Microwave Dielectric Materials: A Review. *J. Mater. Chem. C* **2018**, *6*, 9290–9313.
- (31) Wang, W.; Favaro, M.; Chen, E.; Trotochaud, L.; Bluhm, H.; Choi, K.-S.; van de Krol, R.; Starr, D. E.; Galli, G. Influence of Excess Charge on Water Adsorption on the BiVO₄(010) Surface. *J. Am. Chem. Soc.* **2022**, *144*, 17173–17185.
- (32) Wiktor, J.; Ambrosio, F.; Pasquarello, A. Role of Polarons in Water Splitting: The Case of BiVO₄. *ACS Energy Lett.* **2018**, *3*, 1693–1697.
- (33) Österbacka, N.; Ambrosio, F.; Wiktor, J. Charge Localization in Defective BiVO₄. *J. Phys. Chem. C* **2022**, *126*, 2960–2970.
- (34) Lee, Y.; Cho, C.; Lee, K.-T.; Lee, T. Surface Reconstruction Tunes Band Edges and Lattice-Oxygen Reactivity on BiVO₄(010) Photoanodes. *J. Mater. Chem. A* **2026**, *14*, 27568–27576.
- (35) Wiktor, J.; Pasquarello, A. Electron and Hole Polarons at the BiVO₄–Water Interface. *ACS Appl. Mater. Interfaces* **2019**, *11*, 18423–18426.

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