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Bismuth Vanadate as a Platform for Accelerating Discovery and Development of Complex Transition-Metal Oxide Photoanodes

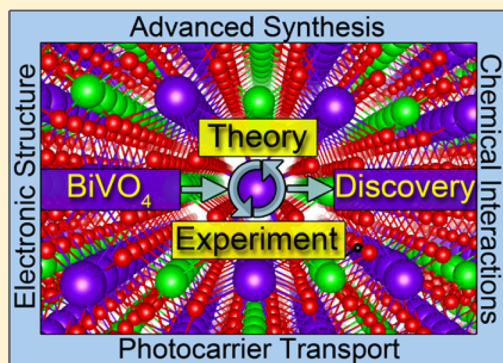
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Supporting Information

ABSTRACT: Development of practical systems for photoelectrochemical conversion of solar energy to chemical fuel requires light absorbers that are efficient, durable, and scalable. Because no material currently meets all three requirements, intensive semiconductor discovery efforts are underway, with a major focus on complex metal oxides. Discovery and development of next-generation light absorbers can be accelerated by gaining mechanistic insights into the function of existing systems. BiVO₄ embodies many key characteristics of the broader class of transition-metal oxides. Thus, it is well-suited as a platform for elucidating the critical roles of charge localization, defects, and chemical interactions on photoelectrochemical performance characteristics. In this Perspective, we discuss how comprehensive characterization of electronic structure and semiconductor properties can advance theoretical models, approaches to addressing inefficiencies and instabilities, and prediction of new materials. Studies of BiVO₄ provide a general framework for understanding mechanisms in emerging materials and a foundation for discovering new ones.



The capture of solar energy and its direct conversion to chemical fuel in artificial photosystems provides a promising route to sustainably meet global energy demands and to overcome the current reliance on fossil fuels.¹ Such a future technology would address pressing energy storage needs associated with intermittent solar power, while also providing a route to renewable and carbon-neutral transportation fuels. Among envisioned approaches, photoelectrochemical (PEC) energy conversion has attracted considerable interest for storing solar energy in chemical bonds via generation of hydrogen or carbon-based fuels.^{2–4} These systems are typically based on semiconductor light absorbers, photoanodes that drive oxidation reactions and photocathodes that drive reduction reactions, coupled to catalysts and interfaced with an aqueous electrolyte. However, a central challenge in development of viable solar fuel generators lies in the lack of semiconductors that are simultaneously efficient, stable, and scalable; no materials have yet been identified that meet all three of these basic criteria.⁵ This materials gap is particularly evident for the case of photoanodes, which must drive the oxygen evolution reaction under highly oxidative conditions in which many materials rapidly corrode.

Two parallel approaches have been pursued to address challenges associated with stability: (i) application of thin-film coatings that protect chemically sensitive, yet highly efficient,

light absorbers by physically isolating them from the reactive environment^{6,7} and (ii) discovery and development of new semiconductors that are intrinsically stable under PEC reaction conditions. The former approach has enabled the integration of materials that were previously incompatible with aqueous reaction environments into functional solar-to-fuel devices.^{8,9} While thin-film corrosion protection strategies are important for making immediate progress in the field and allow studies of functionally efficient systems, it would be premature to conclude that the nexus between efficiency, stability, and scalability has been reached. Indeed, corrosion protection strategies often rely on expensive synthesis methods applied to expensive semiconductor stacks, require pinhole-free layers over large areas, and have not been rigorously tested for long-term viability under reaction conditions that are most relevant for solar energy conversion. Therefore, the quest continues for new semiconductors that are (photo)chemically stable, possess band gaps suitable for efficiently capturing the solar spectrum, have band-edge energetic positions that maximize photovoltage

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generation, and are composed of elements that can be deposited over large area at low cost.

Discovery of materials that meet these demanding requirements could establish a path toward a viable technology with potential for real impact on the renewable energy landscape. At the same time, history shows that translation of material discoveries to functional technologies can take decades of development. For addressing pressing needs in renewable energy conversion and storage, time is of the essence.

Accelerated discovery and development of next-generation systems can be aided by targeted study of mechanisms of energy transduction, as well as strategies for controlling function, in representative materials platforms.

Accelerated discovery and development of next-generation systems can be aided by targeted study of mechanisms of energy transduction, as well as strategies for controlling function, in representative materials platforms. This Perspective describes the qualities that make BiVO_4 an appealing platform for such studies and provides an example methodology of how comprehensive study of its basic semiconductor properties, starting with electronic structure and extending to functional evaluation, can help to accelerate the understanding of efficiency loss mechanisms and can aid in the development and application of design rules for overcoming them.

The Case for BiVO_4 . Ideally, basic studies of mechanism should provide insights that can be generalized. Among currently identified semiconductor photoanodes, monoclinic scheelite BiVO_4 is a material platform that meets this requirement because it encompasses many of the favorable, as well as unfavorable, characteristics associated with the broader class of transition-metal oxide photoelectrodes.¹⁰ In comparison to other metal oxide photoelectrodes, this material possesses a moderate band gap, energetically favorable band edge positions, and relatively long minority carrier diffusion lengths.¹⁰ Advanced methods of doping,^{11–14} mesostructuring,^{15–17} and selective contacting¹⁵ have enabled outstanding advances in PEC performance characteristics, with current densities under anodic bias that are beginning to reach theoretical light-limited values (Figure 1).¹⁵ On the other hand, the material also suffers from strong carrier localization,¹⁸ degradation via photocorrosion,¹⁹ and inadequately characterized defect properties. Indeed, despite the large photocurrent densities obtained under applied anodic bias, overall performance suffers from relatively low fill factors and nonideal photovoltages considering the band gap. Such properties are only now beginning to be addressed, and significant opportunity lies in improving understanding and establishing control of electronic structure, photocarrier dynamics, defect physics, and chemical interactions.

The fundamental limitation of BiVO_4 is that its band gap is too wide to achieve the solar-to-fuel conversion efficiencies that are considered to be necessary for a practical technology.^{5,20,21} While this critique is valid, it is important to not dismiss the material on that basis but rather recognize its utility for elucidating complex phenomena in multinary oxide light absorbers. With this in mind, we show a generalizable approach to detailed study of mechanisms in transition-metal oxides,

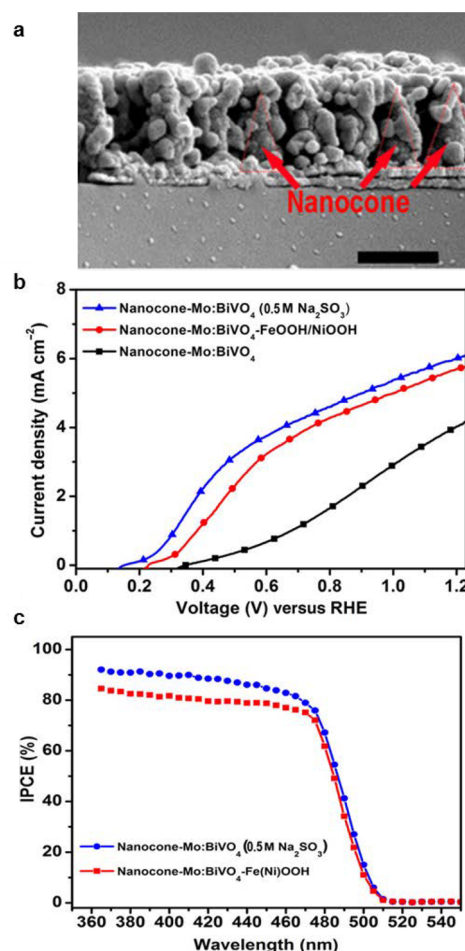


Figure 1. (a) Scanning electron micrograph from mesoporous Mo-incorporated BiVO_4 (Mo:BiVO_4) assembled on a $\text{SiO}_2/\text{Pt}/\text{SnO}_2$ conductive nanocone substrate reported by Qiu et al. Regions of partially exposed nanocones are indicated in the figure, and the scale bar is 500 nm. (b) Photoelectrochemical J - E characteristics from a nanocone/ Mo:BiVO_4 film measured in phosphate buffer with (blue) and without (black) 0.5 M Na_2SO_3 as a sacrificial hole acceptor, compared to a nanocone/ Mo:BiVO_4 with Fe(Ni)OOH oxygen evolution reaction catalyst on its surface, measured in phosphate buffer (red). (c) Incident photon-to-electron conversion efficiency (IPCE) at an applied anodic bias of 1.23 V vs RHE for the nanocone/ Mo:BiVO_4 in phosphate buffer containing 0.5 M Na_2SO_3 sacrificial hole acceptor (blue) compared to the nanocone/ Mo:BiVO_4 with Fe(Ni)OOH in phosphate buffer (red). (From ref 15. This work is licensed under CC BY-NC (<http://creativecommons.org/licenses/by-nc/4.0/>).)

using BiVO_4 as a case example. In doing so, we describe how the development of design rules for accelerated discovery of stable and efficient semiconductors requires careful consideration of the following factors:

- the basic electronic structure, which is the foundation for optoelectronic processes and chemical interactions;
- photocarrier transport and dynamics, including the important role of self-trapped polaronic states in transition-metal oxides;
- intrinsic and extrinsic defects, which can dramatically impact function in the bulk and at interfaces; and
- chemical and photochemical stability, which is directly affected by charge localization and orbital energetics, combined with kinetic effects.

In addition, we provide an example of how mechanistic insights gained from study of BiVO_4 can be used for predictive material design. At the same time, predictions need to be translated to functional systems. As such, we highlight the importance of developing new synthetic strategies to access complex metal oxides in a wide compositional and morphological range.

Not only is BiVO_4 a useful compound for demonstrating a generalized approach to understanding function, it is becoming apparent that it is representative of the broader class of vanadates, among which a variety of narrow band gap semiconductors have been identified. For example, complex vanadates— $\text{Mn}_2\text{V}_2\text{O}_7$,²² $\text{Cu}_3\text{V}_2\text{O}_8$,²³ Cu_3VO_4 ,²⁴ Ag_3VO_4 ,²⁵ NiV_2O_6 ,²⁶ $\text{Fe}_2\text{V}_4\text{O}_{13}$,²⁷ Ni_2FeVO_6 ,²⁸ BiCu_2VO_6 ,²⁹ and BiZn_2VO_6 ^{30,31}—have emerged as an interesting class of materials for light capture and conversion. Compounds with near-ideal band gaps for solar-fuels applications have been identified within the Mn–V–O and Cu–V–O compositional spaces, with, for example, $\beta\text{-Mn}_2\text{V}_2\text{O}_7$ and $\text{Cu}_3\text{V}_2\text{O}_8$ possessing band gaps of 1.75 and 1.8 eV, respectively.^{22,23} Indeed, Zhou et al. explored the complex pseudobinary $\text{CuO-V}_2\text{O}_5$ composition space and identified multiple photoactive phases (Figure 2).³² However, photocurrents generated from nearly all of these materials are at least 1 order of magnitude lower than the theoretical values for their respective band gaps. For newly discovered and emerging compounds, such a deviation from ideality is to be expected; little is known about structure–function relationships, bulk and interface defects and their

properties, or other factors governing charge extraction efficiencies, such as contact and junction characteristics. Furthermore, flexible synthetic routes to selectivity targeting specific phases, stoichiometries, doping, and morphologies are limited. While each material will possess its own properties and challenges, systematic application of sophisticated methods for synthesis and characterization, developed through intensive investigation of BiVO_4 as a related vanadate, is expected to greatly accelerate evaluation of the viability of potentially promising materials within this class.

Electronic Structure and Optical Properties. The electronic structure of any material plays a central role in defining its

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interactions with light, charge transport characteristics, (photo)chemical reactivity, and equilibrium with contacting phases. Predictive theory, in the form of ab initio electronic structure calculations, is an essential tool for accelerating discovery of new materials. However, the power of density functional theory (DFT) is fully realized when combined with experimental studies.

With this in mind, we recently undertook a comprehensive study of the near band-edge electronic structure of BiVO_4 , including direct comparison of DFT calculations with experimental electronic structure data.³³ Monoclinic scheelite BiVO_4 is composed of Bi^{3+} and V^{5+} coordinated with O^{2-} in distorted BiO_8 dodecahedra and VO_4 tetrahedra, respectively.³⁴ Despite the well-characterized structure and phase stability of monoclinic BiVO_4 , standard DFT methods (e.g., PBE) find the tetragonal phase to be the ground-state structure.³⁵ Identifying why DFT predicts the wrong structure and what refinements can be applied to improve accuracy is important for reliably understanding electronic processes in this material. More broadly, such information may aid in calculations of the emerging class of vanadates mentioned above, where vanadium is typically also four-coordinate but does not express perfect tetrahedral symmetry.

Synchrotron X-ray methods, including X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES), which sample unoccupied and occupied electronic states, respectively, provide unique access to electronic structure with elemental specificity. In addition, resonant inelastic X-ray scattering (RIXS), a powerful variant of XES, allows characterization of orbital contributions to the total densities of states, d-manifold splitting energetics, charge-transfer excitations, and more.³⁶ Important for emerging classes of transition-metal oxides, it also enables determination of the nature of charge transfer and Mott–Hubbard insulators.^{36,37}

A summary of the results from our combined experimental and theoretical study of the electronic structure of BiVO_4 is presented in Figure 3, which shows the major orbital contributions to the conduction band (CB) and valence band (VB) densities of states. Complementary photoelectron spectroscopy (PES) allowed these data to be placed on an absolute energy scale, revealing monoclinic scheelite BiVO_4 to

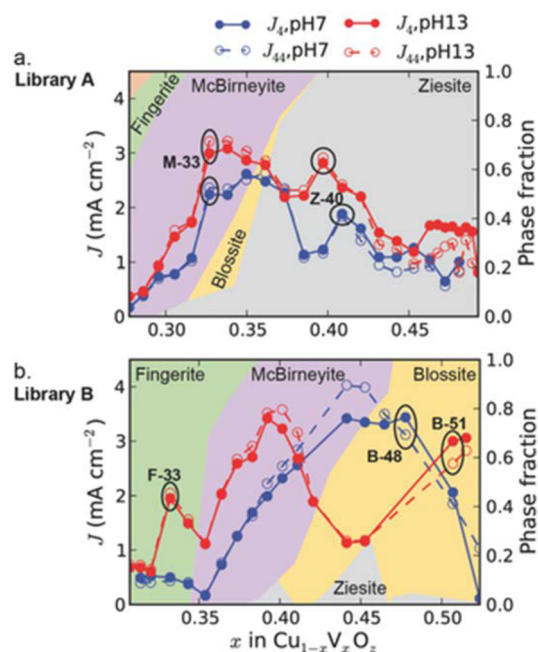


Figure 2. Summary of results from high-throughput exploration of the $\text{CuO-V}_2\text{O}_5$ phase space for photoactive semiconductors. The left axis shows the saturation photocurrent density, and the right axis shows the phase fraction as a function of the V content, x , in $\text{Cu}_{1-x}\text{V}_x\text{O}_2$. The material was formed by annealing at (a) 550 °C and (b) 610 °C, resulting in different phase distributions. Multiple photoactive phases were discovered, as determined through photoelectrochemical measurements at pH 7 (blue) and pH 13 (red). Solid (open) points represent the photocurrent after 4 s (44 s) of photoelectrochemical testing. (Reprinted with permission from ref 32. Copyright 2015 John Wiley and Sons.)

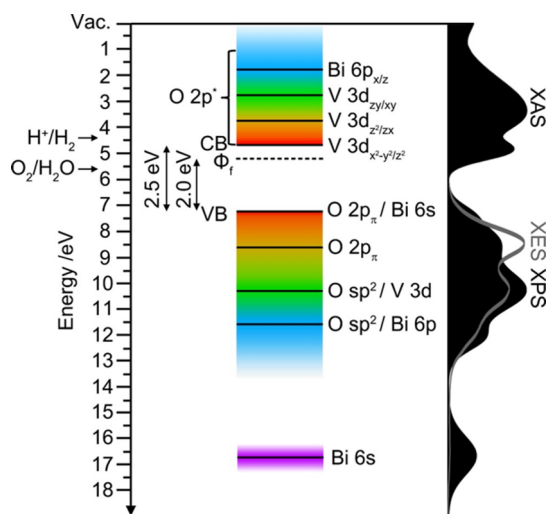


Figure 3. Energy level diagram summarizing the findings of our combined theoretical and experimental study of the electronic structure of BiVO_4 . The dominant orbital character in each region is represented with respect to the vacuum level. Experimental X-ray absorption spectra (conduction band) and X-ray emission and photoelectron spectra (valence band) are presented at the right. The Fermi energy position at the surface of the material, determined by photoelectron spectroscopy, is specific to the analyzed thin film because it is a function of doping and surface band bending. (Reprinted from ref 33. Copyright 2014 American Chemical Society.)

have an electron affinity of approximately 4.79 eV.³³ XAS indicated triplet d-orbital splitting of the hybridized V 3d/O 2p orbitals comprising the CB. This finding is in good agreement with the reduced symmetry of distorted VO_4 tetrahedra described above. Importantly, the V 3d contribution to the partial density of states at the CB minimum (CBM) is primarily of $d_{x^2-y^2}$ and d_{z^2} character, with poor orbital overlap between atomic sites.³³ This finding suggests undesired localization of electrons at the CBM, which would be expected to result in poor electronic mobility. In fact, the situation is far worse than implied by the CB electronic structure; as described below, this orbital character favors localization of electrons as small polarons,³⁸ resulting in mobilities that are orders of magnitude lower than those expected by the extended band structure.

The orbital composition of the VB was experimentally established using a combination of RIXS and PES. Critically, the electronic structure in the VB is intimately tied to the physical structure of the material; the monoclinic distortion that yields the ground-state phase of BiVO_4 is believed to arise from mixing of Bi 6p states with hybridized Bi 6s/O 2p lone pair states, which reduces antibonding destabilization.^{35,39,40} Reliable characterization of these orbitals is the key to assessing shortcomings of theory. Although O 2p/Bi 6s mixing at the VBM could not be directly measured because of spectral broadening, O 2p/V 3d orbitals in the middle of the VB and O 2p/Bi 6p hybrids deep within the VB were resolved, as were energetically deeper isolated Bi 6s states. The VBM was found to be dominated by O 2p states, in good agreement with prior work identifying only minor Bi 6s contributions there. While these measurements revealed relatively good qualitative agreement with standard electronic structure calculations (DFT-PBE), important quantitative differences were observed. In particular, both the mixed O 2p/Bi 6p and isolated Bi 6s

orbitals were found to lie approximately ~ 2.5 eV deeper below the VBM than predicted.³³

Comparison of our experimental data with the calculations from Kweon et al. reveals that hybrid DFT more accurately captures the experimentally resolved electronic structure, with best agreement appearing with 50% Hartree–Fock (HF) exchange.³⁵ Importantly, the authors also found that at 50% HF exchange the monoclinic phase was energetically stabilized. However, agreement between theory and experiment is not perfect. The same work showed that 25% HF exchange described local VO_4 distortions most accurately. Nevertheless, application of hybrid DFT offers significant improvement over standard methods, which is expected to be particularly important for more accurately describing localization associated with defects, polarons, and highly correlated materials, as well as for predicting new materials. At the same time, this level of theory is computationally expensive. In another approach, Ma and Wang systematically varied the Bi 6s energy to match our experimental results.⁴¹ This work verified the importance of capturing the Bi 6s level for accurately describing s–p coupling and, in turn, the physical and electronic structure of the material.

In addition to constructing a portrait of the orbital characteristics of the VB and CB, describing the functional properties of semiconductor photoelectrodes relies on establishing the nature of optical transitions between these states and across the band gap. Despite the attention BiVO_4 has received, its basic optoelectronic properties were not, at the time of our work, well-established.⁴² One striking example of this uncertainty was that the fundamental nature of the band gap, either direct or indirect, and its magnitude were inconsistently assigned in the literature.^{40,41,43–45} To resolve this controversy, we applied a combination of RIXS, ultraviolet–visible absorption, and variable angle spectroscopic ellipsometry (VASE), which together conclusively revealed that BiVO_4 is an indirect band gap semiconductor.⁴² This work was aided by the availability of highly planar BiVO_4 thin films, which were nearly ideal for optical characterization with minimal scattering. VASE allowed for construction of a model of the complex dielectric function and, in turn, the optical constants of BiVO_4 . These data are important for modeling of solar fuels component and device characteristics^{46,47} and therefore are provided in the [Supporting Information](#). Tauc analysis confirmed that BiVO_4 possesses a fundamental indirect band gap of 2.5 eV. However, we also found that a direct transition is present just 200 meV above this indirect band gap. This observation helps to explain the origin of prior confusion regarding the nature of the band gap and, more importantly, reveals that BiVO_4 is a strong visible light absorber, despite being an indirect band gap semiconductor. As new light capture materials emerge, rigorous characterization of basic optical properties should be undertaken from the outset so that function can be accurately described without ambiguity and thermodynamic limits to efficiency can be established as performance targets.

Charge Localization and Polaron Formation. Electron and hole self-trapping via small polaron formation in some semiconductors, especially transition-metal oxides, can severely reduce mobilities,^{18,38,48–50} thereby limiting the PEC conversion efficiencies of otherwise promising materials. Small polarons are characterized by strong localization of carriers at individual lattice ions, resulting in change of the formal oxidation state at that site, distortion of the surrounding lattice,

and slow transport via thermally activated hopping.⁵⁰ Furthermore, because small polarons exist as deep level states within the band gap, they can also introduce additional recombination channels.⁴⁹ Thus, identifying polaronic conduction and understanding its implications is essential for evaluating materials and developing approaches for improving their efficiencies. This is particularly true for indirect band gap semiconductors, in which absorption of light can occur deep below the surface and charge must be extracted over long distances.

The propensity of photoexcited carriers to form small polarons is intimately related to the basic electronic structure of the host material. The barrier to formation is typically small when the orbital in which the polaron localizes has a high density of states near the band edge, and the relaxation energy associated with this localization is large when this state forms bonding or antibonding orbitals with ligand states.³⁸ For the case of electrons in BiVO₄, both conditions are well met. As described above, the CBM comprises hybridized V 3d/O 2p antibonding states, and strong orbital localization leads to weak band dispersion with a high density of electronic states at the band edge,³³ thus favoring self-trapping to create small electron polarons.⁵¹

Recently, Rettie and co-workers reported detailed charge transport measurements in single crystals of doped BiVO₄ and discovered thermally activated transport that is indicative of electron small polaron conduction, with an activation energy of 300 meV (Figure 4).^{18,52,53} Their measurements yielded a

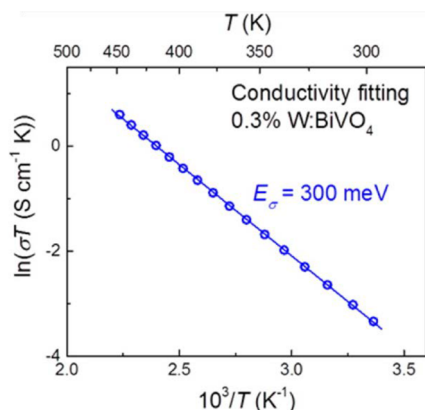


Figure 4. Temperature-dependent transport in single crystalline W-doped BiVO₄ is well-described by a model for the drift mobility associated with small-polaron hopping in the high-temperature adiabatic regime. An activation barrier for hopping of 300 meV is obtained from this analysis. (Reprinted from ref 18. Copyright 2016 American Chemical Society.)

room-temperature drift mobility of $\sim 10^{-4}$ cm²/V·s, in agreement with the findings of Abdi and co-workers obtained using microwave photoconductivity.^{18,54} Building on our X-ray spectroscopic work, Jovic et al. applied a combination of RIXS and resonant PES to study Mo- and W-doped BiVO₄.⁵⁵ Spectral features and assignments from undoped material were in excellent agreement with our own, but important new components, including an energy loss feature in RIXS and midgap state in resonant PES, provided the first spectroscopic indications of states associated with doping and small electron polarons within the band gap of BiVO₄.⁵⁵

Despite strong experimental evidence for majority electron small polaron formation, probing the properties of minority

carriers has been significantly more challenging. Adding to this knowledge gap, theoretical studies have yet to reach consensus on the nature of minority carrier transport. Liu et al. applied DFT+*U* and predicted hole localization as small polarons when a sufficiently large *U* was used.⁵⁶ In a different approach, Kweon and Hwang used hybrid DFT with 25% HF,⁵⁷ which described well the monoclinic structure and, as more recent examination shows, also provides improved agreement with our electronic structure measurements.^{33,35} This work suggested weak hole localization and no small polaron formation in the monoclinic phase of BiVO₄.⁵⁷ Understanding localization, or lack thereof, of minority carrier holes in BiVO₄ is of critical importance because these are the photogenerated charge carriers that must be collected for driving oxidative chemistry at the surface.

Recently, Zhang and co-workers explored the temperature-dependent PEC characteristics of Mo-doped BiVO₄ electrodes and found evidence for minority carrier transport via a thermally activated hopping process with an activation energy of ~ 180 meV.⁵⁸ At present, it is unclear if this is a consequence of small hole polaron transport, defect-related trapping, or other processes.⁵⁸ Indeed, it is important to note that this experimental study was based on analysis of temperature-dependent photocurrents in doped material, whereas theory has been applied to isolated positive charges on the pristine lattice.^{56,57} Future theoretical treatment of mechanisms relevant to photoexcited material, including interactions between oppositely charged polarons, properties of self-trapped excitons, and defect interactions, is needed. Regardless of mechanism, the experimental work by Zhang and co-workers leads to the important finding that, in contrast to traditional pictures of photovoltaic and photoelectrochemical energy conversion, increasing temperature can lead to increasing energy conversion efficiencies in materials characterized by minority carrier localization. In such cases, improved carrier collection efficiencies at elevated temperature can outweigh relatively minor photovoltage losses.⁵⁸

Addressing Charge Localization. An important consideration associated with doping of polaronic materials is the interaction of the localized carrier with the impurity core, as well as other defects within the material. Such interactions can lead to strong polaron binding, even for the case of dopants with otherwise small ionization energies.⁵⁰ For BiVO₄, as well as many other oxide semiconductors envisioned for use in PEC systems, little information exists on polaron binding energies, and there is a pressing need for applying both theoretical and experimental approaches to understanding how photogenerated charge carriers interact with the lattice, with defects, and with one another.

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Recognition of the important role of carrier localization reveals the need to reevaluate approaches to electronic doping and defect passivation. Oxygen vacancies (O_{vac}) tend to be electronically active in transition-metal oxides, most commonly acting as donors, including in BiVO₄.^{59–61} However, signifi-

cantly improved PEC characteristics have been obtained by intentional n-type doping with high valent transition-metal cations, such as W and Mo.^{11–14} Interestingly, it has been found that very high concentrations of these impurities must be incorporated.^{11–14} In effect, the semiconductor must be alloyed, often in the few atomic percent range, to achieve optimal photocurrent response. Despite the effectiveness of this strategy, there remain open questions about the mechanism by which these high doping concentrations positively affect PEC performance.

While it is commonly assumed that improved current densities with doping are due to increased conductivity, this argument is incomplete. Increased dark conductivity, due solely to higher carrier concentrations, would reduce resistance losses within the photoelectrode and increase fill factor but have only minimal impact on the saturation photocurrent density. In contrast, increased doping can significantly increase photo-carrier trapping rates^{54,62} and reduce the width of the charge separating depletion region.⁶³ Thus, given that optimal doping levels in BiVO₄ lie in the range of a few atomic percent,^{11–14} where space charge widths can be as small as a few nanometers, the significant performance enhancements with doping are somewhat surprising. A potential resolution to this discrepancy could come from the recognition that heavy extrinsic doping can reduce the energy barrier to hopping conduction, thereby increasing the electron mobility and allowing photogenerated electrons to be more effectively extracted.¹³ While additional recent evidence for this effect has been observed in N-incorporated BiVO₄,⁶⁰ mechanisms by which the barrier to hopping is reduced must be examined in greater detail. Nevertheless, it appears that design rules for doping and alloying of photoelectrodes will depend sensitively on the nature of charge carriers. For materials exhibiting strong majority carrier localization, such as BiVO₄, alloying with impurities that reduce barriers to hopping conduction may be favored. In contrast, for semiconductors governed by transport of band-edge carriers, lighter doping will ensure formation of spatially extended depletion regions that can aid charge separation. Gradient doping, in which high doping concentrations are used but internal electric fields are generated from the doping profile, represents a hybrid approach that has proven to be effective at balancing these considerations.¹¹

Within the context of polaronic transition-metal oxides, there is precedent for hydrogen impurities acting as donors that bind small electron polarons much more weakly than, for example, O_{vac} defects.⁶⁴ Considering the experimentally measured electron affinity of BiVO₄ and the universal hydrogen level proposed by van de Walle and Neugebauer,^{33,65} hydrogen is expected to be an effective donor in the material. Indeed, in 2013, Wang and co-workers demonstrated experimentally that annealing in H₂ can significantly increase the performance characteristics of BiVO₄ photoanodes.⁶⁶ Complementary theory suggested that hydrogen impurities could be low formation energy donors, but experimental validation was not possible at that time.⁶⁶ Therefore, we recently undertook a study of the role of hydrogen in defining the electronic character of BiVO₄ photoanodes.⁶⁷ Using a suite of experimental tools, together with theory, we found that hydrogen is an electronically active donor and that it can incorporate at both substitutional and interstitial sites. In doing so, it serves a dual role in improving performance of BiVO₄ photoanodes by donating electrons and passivating recombination centers (Figure 5). The result is a near complete

elimination of majority carrier transport limitations, even for the case of mesoporous structures.

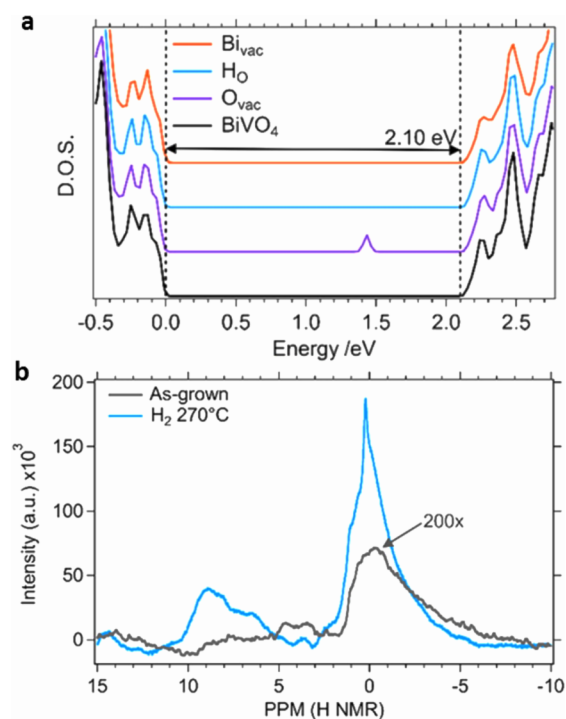


Figure 5. (a) Total density of states calculated by DFT-PBE for pristine BiVO₄ (black) and with oxygen vacancy (purple), substitutional hydrogen on an oxygen vacancy site (blue), and bismuth vacancy (orange) defects. Oxygen vacancies introduce electronic states into the band gap, but hydrogen serves to eliminate these states. Radiative recombination at midgap states is observed by photoluminescence spectroscopy and is quenched by hydrogen treatment, consistent with the theoretical picture of hydrogen passivation of oxygen vacancy defects. (b) ¹H NMR of BiVO₄ powder as-grown (gray) and after hydrogen annealing at 270 °C (blue). The resonance at ~7–10 ppm was assigned to interstitial hydrogen, and the resonance at ~0 ppm was assigned to substitutional hydrogen on oxygen sites. The spectrum from as-grown material reveals residual hydrogen is present from the synthesis. (Adapted from ref 67. Copyright 2016 American Chemical Society.)

While intentional impurity incorporation has led to significant advances in the functional performance of photoelectrodes, basic questions about the nature and role of point defects remain. For example, although the n-type character of BiVO₄ is the essential property that defines the semiconductor as a photoanode, the basic origin of its conductivity had not, until recently, been addressed in detail. In fact, theory predicted that BiVO₄ formed under typical experimental conditions should exhibit p-type conductivity because equilibration of O_{vac} donors and Bi_{vac} acceptors was expected to pin the Fermi level ~550 meV above the VBM.⁶¹ In contrast, BiVO₄ is observed to be n-type, regardless of how it is synthesized.³⁴ This contradiction may be resolved by our recent observation of a background concentration of hydrogen in as-synthesized BiVO₄ (Figure 5b).⁶⁷ This result suggests that unintentional incorporation of hydrogen donors could play a crucial role in defining the n-type character. Indeed, hydrogen is a ubiquitous, yet difficult to detect, impurity that can come from decomposition of precursors during synthesis or from ambient

water vapor during annealing.⁶⁸ Beyond BiVO₄, this finding highlights the need to carefully consider the properties of native and impurity defects, both intentionally and unintentionally introduced, in semiconductor photoelectrodes. This is especially true for material discovery efforts, where poorly understood and controlled defects can define unanticipated functional characteristics.

Chemical Interactions and Stability. Semiconductor discovery efforts target materials that are not only efficient but also stable. For this reason, intensive research into new photoanodes has been devoted to thin-film metal oxides because they are expected to have improved photochemical stability under the oxidative conditions required for evolving oxygen from water.⁶³ However, oxides are not universally stable under reaction conditions. Stability against dissolution is given by the chemical potentials of elemental constituents of solid-state materials relative to corresponding ions in solution as a function of electrochemical potential and pH, as represented in Pourbaix diagrams. In practice, experimental Pourbaix diagrams are rarely available for advanced photoelectrode materials. To address this gap, the Materials Project provides open access to an extensive database of computed Pourbaix diagrams,⁶⁹ thus serving as a valuable guide for initial assessments of which materials might be stable under which conditions. However, for PEC applications, stability under illumination must also be considered. Recently, Chen and Wang reported a computational survey of semiconductors to assess their propensity to undergo photocorrosion.⁷⁰ In that work, they compared the oxidation and reduction potentials of the semiconductor to those of water and considered that stability under illumination requires that it be energetically favorable for holes (electrons) to oxidize (reduce) water rather than the material itself. While this represents an important criterion for assessing photocorrosion processes, it may not be a sufficient condition to ensure long-term durability. In particular, if a photoanode possesses an oxidation potential that resides between the VBM and the water oxidation potential, both oxidation processes would be energetically accessible to photogenerated holes in the VB. The chemical stability of the resulting oxidized state must also be considered; in the absence of lattice destabilization and/or dissolution, such a state would potentially serve as a recombination center but not as a source of physical degradation.

The mechanisms by which materials degrade are often not clear, and a rigorous methodology to determine corrosion

The mechanisms by which materials degrade are often not clear, and a rigorous methodology to determine corrosion pathways is necessary.

pathways is necessary. As a demonstration of a generalizable approach to understanding stability, we recently applied a combination of experimental and computational tools to probe chemical and photochemical degradation processes on BiVO₄ photoanodes.¹⁹ Figure 6a–f shows electron micrographs obtained before and after stability testing, with signs of degradation in both near-neutral and alkaline environments. The computed Pourbaix diagram for BiVO₄, shown in Figure 6g, suggests that BiVO₄ is unstable against V dissolution but that stable Bi oxide phases should form on its surface, thus passivating the material against further chemical attack, under

typical operating conditions.¹⁹ In contrast, we observed bulk dissolution of BiVO₄ thin films, with loss of both cations to solution. This behavior can be understood by considering that, following initial V loss, significant structural reorganization would be required to form chemically stable Bi oxide phases. As materials discovery efforts target complex oxides, it is expected that such a kinetic limitation to self-passivation may be observed more generally because of increasing demands for structural reorganization following near-surface chemical transformations.

Illumination of BiVO₄ was found to dramatically accelerate degradation.¹⁹ Based on prior calculations, the oxidation potential of the material is nearly equivalent to that of water, suggesting questionable resilience against photocorrosion according to the criterion of Chen and Wang.⁷⁰ On the other hand, oxidation of BiVO₄, an already highly oxidized compound, does not immediately imply chemical instability. To address this point, it is necessary to consider the specific nature of photogenerated holes at the surface. As described above, bulk theoretical predictions of hole states in monoclinic BiVO₄ are currently inconclusive regarding polaron formation.^{56,57} However, the case is different at the surface. Calculations of the surface structure and its impact on hole localization predicted the presence of trapped holes, with charge density residing primarily on distorted BiO₈ dodecahedra.⁷¹ In our work, we find that such hole localization destabilizes the lattice against oxygen loss and could promote chemical attack.¹⁹ Thus, the basic electronic structure of the material, together with the nature of photogenerated charge carriers at the surface, plays a vital role in defining chemical interactions with the surroundings. In general, developing strategies for overcoming (photo)chemical instabilities requires mechanistic understanding of these processes. For the case of BiVO₄, integration of a catalyst onto the surface to rapidly extract holes can mitigate photocorrosion.^{11,16} However, the ability to either physically isolate the semiconductor from the electrolyte^{72,73} or to slow V loss to the point that chemically passivating Bi oxides are kinetically accessible will determine long-term durability of the system.

Toward Predictive Materials Discovery. Recognition of the importance of isolated Bi 6s states and s–p coupling in defining the band gap and structure of BiVO₄, enabled by improved quantification with experimental electronic structure data, allowed the prediction of new semiconductor compositions with narrower band gaps for PEC applications. In particular, Ma and Wang proposed substitutional incorporation of Sb on Bi sites of BiVO₄ to form Bi_{1–x}Sb_xVO₄.⁴¹ This simple approach was intended to take advantage of the energetically higher position of Sb 5s states relative to Bi 6s states to enhance s–p coupling. A 200 meV, reduction of the band gap was predicted with an Sb fraction of $x = 12.5\%$. Based on this prediction, a range of conventional synthetic approaches, including sol–gel, physical vapor deposition, and spray pyrolysis were used, but all failed to yield this compound and resulted in phase segregation of the constituent oxides. This result motivates the need for diverse synthetic approaches, including those well-adapted to accessing potentially nonequilibrium phases, in order to more rapidly advance material discovery efforts.

Among the myriad physical and chemical approaches for forming semiconductor compounds, colloidal synthesis is appealing for materials discovery because it is a kinetically driven wet-chemistry approach that allows for tunability of size, shape, composition, and crystalline phases, including those that

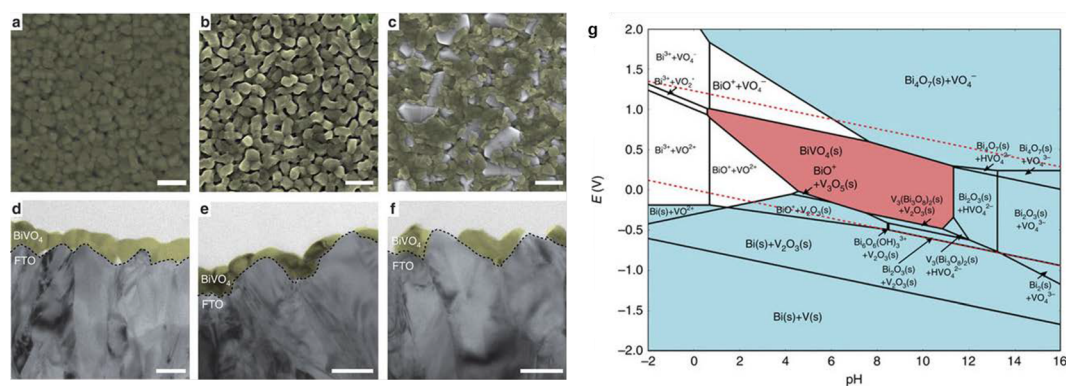


Figure 6. Plan view scanning electron micrographs (scale bar, 500 nm) and cross sectional transmission electron micrographs (scale bar, 100 nm) of pristine (a, d), degraded at pH 6.8 for 60 min (b, e), and degraded at pH 12.3 for 30 min (c, f) BiVO_4 thin films. False coloring of the F-doped tin oxide (transparent blue) and BiVO_4 (transparent yellow) was used for clarity. (g) Calculated Pourbaix diagram for BiVO_4 , obtained from the Materials Project for a 50–50% Bi–V system in aqueous solution, reveals that there is a driving force for V dissolution under normal operating conditions. However, a stable bismuth oxide would be expected to form on the surface and passivate the underlying semiconductor. As highlighted by the micrographs, such a self-passivation effect is not observed, which is attributed to kinetic limitations to the considerable structural reorganization that would be required for formation of a stable bismuth oxide phase. (Reprinted with permission from ref 19. Copyright 2016 Nature Publishing Group.)

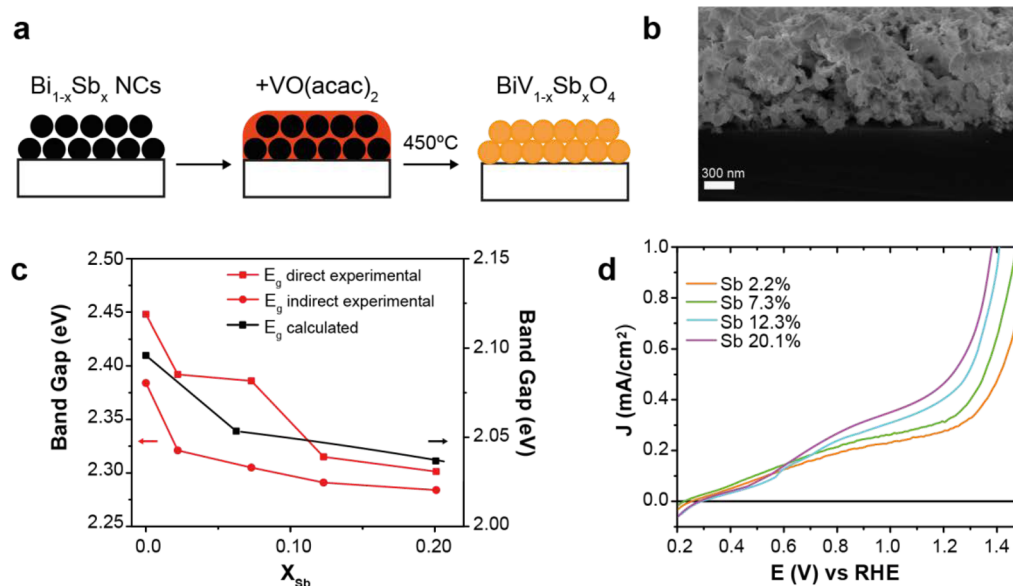


Figure 7. (a) Schematic representation of nanocrystal-based growth process in which $\text{Bi}_{1-x}\text{Sb}_x$ NC seeds were converted to Sb-BiVO_4 films. (b) Representative scanning electron micrograph of a nanoporous film of $\text{BiSb}_x\text{V}_{1-x}\text{O}_4$. (c) The band gap is experimentally observed to decrease with increasing Sb content in $\text{BiSb}_x\text{V}_{1-x}\text{O}_4$, which is due to lattice strain that increases s–p coupling in the material. (d) Photoelectrochemical characterization reveals that the photocurrent density increases with decreasing band gap. While obtained photocurrents are low, optimization of function for newly discovered compounds requires significant research into bulk and surface defects, morphology, and interfaces with contacting phases. (Adapted with permission from ref 75. Copyright 2015 John Wiley and Sons.)

are inaccessible by many other synthetic techniques.⁷⁴ With this in mind, we have developed a nanocrystal-seeded growth process, in which nanocrystals of tunable composition are used as a precursor and serve as seeds for nucleation of ternary and quaternary light-absorbing oxides (Figure 7a).⁷⁵ Using this approach to access compositional complexity in metal oxides, we succeeded in producing phase-pure materials in the Bi–Sb–V–O compositional space.⁷⁵ While the monoclinic phase was preserved up to 20% Sb atomic content, X-ray characterization revealed it to be energetically favorable for Sb^{3+} to substitutionally incorporate at V^{5+} lattice sites. Therefore, in contrast to the original theoretical prediction of $\text{Bi}_{1-x}\text{Sb}_x\text{VO}_4$, $\text{BiSb}_x\text{V}_{1-x}\text{O}_4$ thin films (Figure 7b) were formed. Nevertheless, we found a

100 meV decrease in the fundamental band gap going from 0 to 20 at % Sb (Figure 7c), along with corresponding increases of photocurrent densities from films constructed of these materials (Figure 7d). Based on experimental results, revised DFT calculations showed that a decrease of the Bi–O bond length resulting from the introduction of Sb beneficially enhances O 2p/Bi 6s coupling, thus leading to VB lifting and band gap decrease.⁷⁵ Although the originally predicted compound was not realized, this work revealed an alternative strategy for reducing the band gap by introducing lattice strain. From an electronic structure perspective, the design principle is the same: to reduce the band gap by enhancing s–p coupling in monoclinic vanadates.

Summary and Outlook. Basic studies of semiconductor properties and mechanisms associated with solar energy transduction are enabled by the availability of well-defined material. Indeed, our work has been advanced by simultaneous development of thin films deposited by reactive cosputtering,^{76,77} spin coating,⁷⁸ and chemical vapor deposition,⁷⁹ with high reproducibility and precise control over composition. Nevertheless, it must be noted that these are polycrystalline thin films, in which heterogeneity, disorder, and substrate interactions are present; macroscopic measurements performed on such films represent the characteristics of an ensemble. Furthermore, reliable in-plane electrical transport measurements from such films are confounded by grain boundaries. These limitations can be overcome with single crystalline material, either in the form of heteroepitaxial thin films⁴⁵ or bulk crystals.^{52,53} This is exemplified by the insightful transport studies by Rettie et al.,^{52,53} who conclusively established the characteristics of small electron polaron transport in BiVO₄ using precisely doped single crystals. As new materials emerge, understanding basic properties and mechanisms of function will rely on intensive parallel efforts dedicated to formation of high-quality samples. In addition, development of advanced in situ and operando characterization techniques, which allow for understanding of how chemical, morphological, and energetic heterogeneity in polycrystalline materials affects functionality, will help to establish structure–property relationships and pave the way toward next-generation photoelectrodes.

At the same time, translating mechanistic insights and materials predictions into high-performance photoelectrodes often requires construction of compositionally complex structures with defined features at the nano- and mesoscale. While chemical vapor deposition,⁸⁰ electrodeposition,¹⁶ and top-down fabrication approaches^{15,81} have been used with great success, colloidal chemistry represents a powerful, yet underexplored, tool for materials discovery and development in the field of artificial photosynthesis.⁷⁴ From a thermodynamic perspective, colloidal nanocrystals can be trapped in metastable crystalline phases thanks to the size-dependence of phase transformations.⁷⁴ In addition, colloidal synthesis routes provide the possibility for kinetic stabilization and tuning the chemical potential of the reaction mixture by simply changing reactant concentration, temperature, precursors, and surfactants. As described above for the example of BiSb_xV_{1-x}O₄,⁷⁵ these approaches can allow access to compositions and phases that are difficult to achieve with other methods. Indeed, the nanocrystal-seeded growth approach can be easily generalized to form a range of complex oxides.⁷⁵ Likewise, chemical routes can be used for precise placement of dopants and impurities at the atomic scale⁸² and modular approaches to assembly allow fabrication of heterostructured nanocomposites containing complex oxides.⁸³ Such structures can promote charge extraction across interfaces, thereby providing an alternative to doping in overcoming localization of charge, while also reducing recombination via creation of charge-separated states within the assembly.⁸³

Colloidal chemistry represents a powerful, yet underexplored, tool for materials discovery and development in the field of artificial photosynthesis.

Ultimately, there is a pressing need to expand the database of viable photoanodes capable of supporting efficient and stable PEC energy conversion. Exploration of increasingly complex multinary metal oxides, using both computational and experimental approaches, may provide a route to achieving the combination of properties demanded for artificial photosynthesis. Insights gained, experimental methodologies established, and synthetic approaches developed through ongoing study of best-available materials such as BiVO₄ are expected to accelerate progress toward a next generation of systems capable of supporting solar fuels production with high efficiency and long-term durability. Though BiVO₄ may not be the photoelectrode material of the future, it might help to discover one that is.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acsenergylett.6b00586](https://doi.org/10.1021/acsenergylett.6b00586).

Data file containing optical constants of BiVO₄ obtained via variable angle spectroscopic ellipsometry (XLSX)

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