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On the successes and opportunities for discovery of metal oxide photoanodes for solar fuels generators

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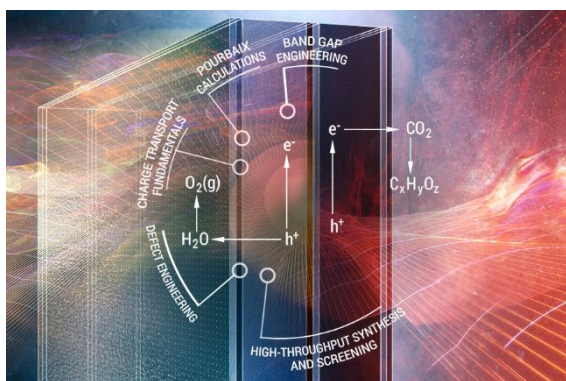
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ABSTRACT: The importance of metal oxide photoanodes in solar fuels technology has garnered concerted efforts in photoanode discovery in recent decades, which complement parallel efforts in

development of analytical techniques and optimization strategies using standard photoanodes such as TiO_2 , Fe_2O_3 and BiVO_4 . Theoretical guidance of high throughput experiments has been particularly effective in dramatically increasing the portfolio of metal oxide photoanodes, motivating a new era of photoanode development where the characterization and optimization techniques developed on traditional materials are applied to nascent photoanodes that exhibit visible light photoresponse. The compendium of metal oxide photoanodes presented in the present work can also serve as the basis for further technique development, with a primary goal to establish workflows for discovery of materials that perform better against the critical criteria of operational stability, visible light photoresponse, and photovoltage suitable for tandem absorber architectures.

TOC GRAPHICS



The generation of chemicals and fuels from CO_2 , N_2 , and H_2O in photoelectrochemical reactors would enable sustainable energy infrastructure with decreased reliance on photovoltaic and battery technologies that pose challenges for energy storage and transport.¹ The source chemical CO_2 is used for generation of C-containing chemicals such as CO and formate as well as higher-order fuels such as liquid hydrocarbons and alcohols that could displace fossil-based liquid fuels while leveraging existing infrastructure.² The source chemical N_2 is used for generation of NH_3 and less

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3 often N_2H_4 , which may serve as fuels but can serve a more pressing need of sustainable fertilizer
4 production.³ These families of reactions involve electrochemical reduction of the source
5 chemicals, generally referred to as CO_2 reduction reactions (CO_2RR) and N_2 reduction reactions
6 (N_2RR), respectively. These reduction reactions require protons and electrons, and liberation of
7 those reactants from H_2O via the O_2 evolution reaction (OER) has been adopted as the primary
8 strategy for establishing broadly-deployable solar fuels technologies. The H_2 evolution reaction
9 (HER) can also be coupled to the OER without CO_2 or N_2 reactants, making solar
10 photoelectrocatalysis of the OER a cross-cutting technology for generation of H_2 , C-containing,
11 and N-containing fuels. Metal oxide photoanodes can also be used for anodic reactions other than
12 the OER, resulting in synthesis of other chemicals,⁴ although the present work considers solar fuels
13 photoanodes to be photoelectrocatalysts for the OER in aqueous electrolyte.

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15 While photoelectrocatalysis of the HER and OER can occur with a single wide-gap
16 semiconductor, as demonstrated in the seminal water splitting work utilizing TiO_2 ,⁵ the broad
17 consensus, supported by multi-physics device modelling,⁶ is that efficient utilization of the solar
18 spectrum requires tandem light absorbers with band gap energies in the visible spectrum. While a
19 number of device architectures utilizing a pair of visible-gap semiconductors have been proposed,
20 a grand challenge of the solar fuels community has been the identification of a suitable solar fuels
21 photoanode, i.e. a semiconductor that can utilize visible light to effect photoelectrocatalysis of the
22 OER and circumvent a broad range of deactivation processes such as corrosion.

23
24 Photovoltaic-grade semiconductors, most notably III-V semiconductors, have enabled a variety
25 of high efficiency solar water splitting demonstrations.⁷ While protective coating⁸ of photovoltaic
26 semiconductors has been effective in increasing operational stability from minutes to over 100
27 hours,⁷ semiconductors that don't self-passivate under operational conditions will always be

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3 susceptible to device failure upon damage in the protective coating(s). This type of single point
4 failure is difficult to circumvent in systems engineering and can render the technology untenable
5 for deployment. Intrinsic stability of the semiconductors is the most reliable way to achieve a
6 durable solar fuels generator, which has motivated the persistent and continuing effort to
7 understand metal oxide semiconductors and identify those that can serve as solar fuels
8 photoanodes. No fundamental limit on the efficiency of metal oxide photoanodes has been
9 established beyond those dictated by the thermodynamics of solar energy conversion, and BiVO₄-
10 based devices with ca. 5% efficiency are approaching these limits given its 2.4 eV band gap.⁹
11 Photoanode band gap energies no larger than 2 eV are required to realize the 15%-20% solar to
12 fuel conversion efficiencies, the target range per techno-economic and device models,^{6, 10} requiring
13 the community to pursue a combination of low band gap energy and high radiative efficiency that
14 has yet to be approached by metal oxide photoanodes.
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30 To establish the outlook for this grand challenge, we first summarize the progress to date. Recent
31 reviews have highlighted a broad portfolio of materials, techniques and devices. Abdi and
32 Berglund¹¹ recently reviewed metal oxide photoanodes with focus on the optimization of BiVO₄
33 and its implementation into water splitting devices, along with summary of several other V, W and
34 Fe-based oxide photoanodes, covering in total 9 metal oxide photoanode phases. Chu et al.¹²
35 focused more on classes of materials and the integration of photoelectrodes into devices. He et
36 al.¹³ compiled a more detailed survey of metal oxide photoanodes with 33 phases discussed and
37 critical analysis of several topics including the electronic character of the conduction and valence
38 bands and other electronic structure considerations. Our literature survey, summarized in Fig. 1
39 and detailed in the SI, identified 109 OER metal oxide photoanode phases, including recent
40 discoveries from our labs. Of these, we find 70 visible light-active phases, corresponding to
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3 photoanodes demonstrated to be photoactive with only sub-3 eV illumination.[§] The breadth of
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5 elements utilized in photoanode studies is rapidly expanding, and the number of visible light-active
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7 metal oxide photoanodes has increased 5-fold in the past 20 years, an acceleration in discovery
8
9 driven by the concerted efforts in the community, including our high throughput discovery
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11 program in the Joint Center for Artificial Photosynthesis (JCAP). During these 20 years, there has
12
13 also been substantial effort to develop and deploy the present champion visible-gap metal oxide
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15 photoanode, BiVO₄.^{11, 14} These parallel community efforts in discovery of new metal oxide
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17 photoanodes and in optimization and understanding of BiVO₄, both of which have been
18
19 remarkably successful, provide the framework for the future of the field.
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24 BiVO₄ is an exemplar of a complex metal-oxide, visible-light photoanode whose study has
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26 established the basis for accelerating development of metal oxide photoanodes.¹⁵ In addition to
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28 optimization schemes such as defect engineering for charge transport and selective carrier
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30 extraction,¹⁶ research on BiVO₄ has resulted in development of a broad range of materials and
31
32 device-level solar fuels characterization techniques.¹⁷ A recent review of strategies for enhancing
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34 the photocurrent, photovoltage, and stability of photoelectrodes highlights the breadth and
35
36 effectiveness of feedback between synthesis and characterization of device-relevant parameters to
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38 optimize materials, as illustrated in Fig. 2.¹⁷ The breadth of these materials development strategies
39
40 far exceeds the breadth of candidate photoanodes for which they have been deployed. The general
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42 bias in scientific research towards continued investigation of well-researched materials is both
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44 broadly known and recently evaluated as a limitation on creativity and discovery,¹⁸ motivating our
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46 effort in the present work to establish the set of known visible light-active photoanodes and discuss
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48 opportunities for improving performance both within this set of materials and beyond, via new
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50 materials discovery strategies.
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3 Of the 70 visible light-active metal oxide photoanodes, historically Fe_2O_3 and more recently
4 BiVO_4 are arguably the only materials for which the community has deeply invested in detailed
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6 understanding and optimization, motivating further study on the other 68 phases, or some
7
8 principled selection of a subset thereof. Some notable efforts in this area include detailed
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10 experimental investigation of $\alpha\text{-SnWO}_4$,¹⁹ Fe_2WO_6 ,²⁰ copper vanadates such as $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ and $\gamma\text{-}$
11
12 $\text{Cu}_3\text{V}_2\text{O}_8$,²¹ and computational investigation of $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ ²² to elucidate performance-limiting
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14 properties. Of these, only the copper vanadates exhibit a photon energy onset of photoactivity near
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16 2 eV, the desired upper-limit described above. Fig. 3 summarizes the photon energy onset for 49
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18 metal oxide photoanodes that exhibit external quantum efficiency (EQE) in excess of 0.01% in our
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20 experiments. Two notable phases with photoactivity at 2.1 eV (but insufficient to meet the EQE
21
22 threshold) are $\text{VCrO}_4\text{-orth}$ ²³ and $\text{V}_2\text{CoO}_6\text{-tri}$.²⁴ The 4 phases that exceed the threshold at 2.1 eV
23
24 are FeBiO_3 , discovered by Chen et al.,²⁵ as well as FeWO_4 ,²⁶ $\gamma\text{-V}_2\text{Cu}_3\text{O}_8$,²⁷ and $\text{Y}_3\text{Fe}_5\text{O}_{12}$,²⁴
25
26 highlighting the challenge of identifying metal oxide photoanodes with broad spectral response. A
27
28 chopped illumination voltage sweep is shown for each of these 4 phases, demonstrating that the
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30 photocurrent decreases quickly with decreasing bias for most phases. Anecdotal examples
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32 demonstrating improvement in operational photovoltage, i.e. beyond that exhibited in this figure,
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34 include the observation of a turn on potential (lowest potential with observed photocurrent) near
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36 0.6 V vs RHE for FeBiO_3 ²⁵ and near 0.4 V vs RHE for Bi-alloyed FeWO_4 .²⁶ More detailed
37
38 understanding of the semiconductor-liquid junctions and band energy alignment are needed to
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40 elucidate the limiting photovoltage and associated efficiency of each photoanode, as discussed
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42 further below.
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51 With regards to the opportunity space for further discovery, it is interesting to consider the
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53 fraction of the metal oxide search space that has been explored. The 70 visible light photoanodes
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3 utilize 25 cation elements from the periodic table. Considering only ternary metal oxides, which
4 account for all but 6 of these phases, only 34 of the 300 pairwise combinations of these cations
5 have been reported. While some may have been explored without discovery, most remain
6 uncharted territory. High Throughput (HiTp) experimental screening of OER photoanodes,
7 pioneered by Parkinson²⁸ and McFarland²⁹ and advanced by others,³⁰ accelerates exploration of
8 this broad class of photoanode candidates, although the search space remains too large to be
9 comprehensively searched with brute force screening. Our research has, thus, focused on guidance
10 of high throughput experiments via theory-based identification of promising materials systems for
11 photoanode discovery.

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24 The photoanodes identified by our high throughput screening (see SI) include 4 copper vanadates
25 that were identified simultaneously by HiTp theory and experiment.²³ These initial discoveries
26 motivated theory screening of Materials Project entries³¹ based on electronic structure and stability,
27 leading to experimental demonstration of photoanodic activity in 8 additional ternary metal
28 vanadates³² and 5 ternary metal manganates.²⁷ Experimental screening in composition spaces
29 related to these theory predictions resulted in the identification of an additional 29 photoanode
30 phases.^{24, 33} Perhaps the most important lesson from this work is that computational screening not
31 only identifies target phases but also promising composition regions that are sufficiently specific
32 to enable exploration by HiTp experiments, which are in turn sufficiently broad in scope to identify
33 materials beyond the computational search.

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47 The fringe cases in these photoanode discovery campaigns offer insights for guiding future
48 discovery efforts. FeWO₄ was identified through combinatorial investigation of non-equilibrium
49 synthesis conditions.²⁶ This Fe⁺²-containing metal oxide is stabilized against oxidation by a self-
50 passivation surface layer that includes Fe⁺³, highlighting the role of self-passivation in enabling
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3 stable operation of thermodynamically unstable photoanodes. Self-passivation was also observed
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5 in copper vanadates, where the degradation in photocurrent was found to depend on the thickness
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7 of the developed passivating film.³⁴ Passive surface films are of intense interest in the metals and
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9 alloy industry and provide a fruitful research area in themselves as their formation and
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11 functionality are still not entirely understood.³⁵ A range of phenomenological models have been
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13 developed to explain the evolution of passivation layers, which display varying morphology, short-
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15 range order and chemical constitution depending on the growth process and chemical
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17 environment.³⁶ The stability of a passivating surface film, and hence that of the underlying bulk
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19 material, is explicitly linked to ionic transport through the film which in turn depends critically on
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21 the film morphology. Establishing thermodynamic and kinetic criteria for classifying a photoanode
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23 as being operationally stable and supporting photoelectrocatalysis is a key area for designing the
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25 next-generation of photoanode screening. In previous work,^{34, 37} we have found that well-
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27 benchmarked Pourbaix diagrams³⁸ can provide a qualitative guide as to the likely formation of, as
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29 well as general chemical composition of, a passive surface film. Furthermore, first-principles
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31 methods have been shown to provide quantitative estimates for the relative Gibbs free energy and
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33 corresponding aqueous regimes where a candidate photoanode material may form inert passivating
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35 films, or steadily corrode to aqueous species.³⁷ Detailed understanding of the growth process,
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37 evolution, and structure of these complex, self-passivation films is presently lacking, motivating
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39 development of new computational and experimental techniques that lead to a predictive model
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41 for how the near-surface of a given material will evolve under operational conditions.
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49 The heterogeneous composition and structure of the photoanode as a function of depth from the
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51 electrolyte surface complicates the already complex model of semiconductor-liquid junctions, as
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53 the effect on these surface layers on band alignment and carrier transport have been insufficiently
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3 studied to date. The standard thermodynamic requirement of band alignment, i.e. the vacuum
4 energy of the photoanode's valence band being sufficiently negative such that the photo-generated
5 holes are sufficiently oxidizing to drive the OER, is complicated by electrolyte pH-dependent
6 surface dipoles.³⁹ The polar surfaces of metal oxides introduce the additional complications of
7 facet and termination-dependent dipoles that alter this band alignment, as exemplified by
8 BiMn_2O_5 ⁴⁰ where band level calculations for each of 6 low-energy surfaces indicate more than 1.4
9 eV variation in work function, making the assessment of band alignment with respect to OER as
10 much of a property of the surface as it is of the bulk electronic structure. Further study of facet-
11 dependent and interfacial layer-dependent properties are likely to identify optimal photoanode
12 surfaces and guide synthesis and device implementation by designating desirable and undesirable
13 facets at the electrolyte interface. Initial demonstrations of this concept include facet-dependent
14 charge separation in BiVO_4 ⁴¹ and SrTiO_3 .⁴²

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31 This aforementioned BiMn_2O_5 ,⁴⁰ as well as $\beta\text{-Mn}_2\text{V}_2\text{O}_7$,⁴³ provide additional opportunity to
32 investigate performance-limiting attributes of metal oxide photoanodes. The 1.8 eV direct gap of
33 each phase is ideal with respect to solar absorption, but they have yet to be demonstrated as OER
34 photoanodes. While operational stability is a prime suspect for a lack of photoactivity, these are
35 among the most electrochemically stable low-gap metal oxides, with Pourbaix-stable regions in
36 the approximate ranges 0.3-0.7 and 0.3-1.2 V vs RHE, respectively. Despite these desirable
37 attributes, these phases are not classified as photoanodes in the present work due to their
38 photoactivity only in the presence of sacrificial hole acceptors. The modest photoactivity obtained
39 with sacrificial hole acceptors also indicates that the photoanode performance limitations extend
40 beyond poor OER catalysis. From an electronic structure point of view, these are exemplary
41 photoanode candidates, motivating detailed inspection as to whether materials optimization can
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3 confer higher photoactivity, and/or identification of fundamental properties that limit photoactivity
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5 with commensurate design of associated screening techniques.
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8 Ternary manganate phases also illustrate the challenges of treating high-temperature or
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10 disordered magnetic states in electronic structure calculations. For these ternary manganates, zero-
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12 temperature calculations with judiciously-chosen magnetic configurations were required to gauge
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14 the possible electronic structure of each phase's ambient temperature paramagnetic state;^{40, 43}
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16 paramagnetic states, in which the local magnetic moments on each open-shell cation are nonzero
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18 but their configurational average is zero, are not trivially-compatible with periodic supercells.
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20 Typically, high-throughput computational screening employs a computationally less expensive
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22 model of the magnetic state, e.g. the ferromagnetic configuration, which can induce significant
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24 changes to the electronic structure⁴⁴ of the material compared to the paramagnetic state. In our
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26 experience, this approximation can lead to exclusion of promising low-gap metal oxides that
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28 exhibit a metallic character in their ferromagnetic state. Antiferromagnetic (AF) ordering is
29
30 typically a better approximation of the paramagnetic state, and currently the Materials Project is
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32 pursuing a large computational survey of the magnetic state of its materials including at least one
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34 AF ordering for each transition metal oxide.⁴⁴ Other approaches for computational modelling of
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36 paramagnetic materials have been introduced in the literature,⁴⁵ creating an opportunity to evaluate
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38 the electronic structure of photoanode materials at relevant operating temperatures.
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45 The compendium of photoanode phases described in the SI offers various opportunities for
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47 identifying trends and descriptors for photoactivity. A seldom-discussed materials property that is
48
49 well characterized by our combinatorial experiments is cation off-stoichiometry of metal oxide
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51 photoanodes. Fig. 4 shows the EQE under 3.2 eV illumination for 55 $A_{1-x}B_x$ oxide phases, where
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53 B is taken to be the higher valent cation produced by the Materials Project oxidation state
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3 interpreter, and each phase is plotted by the difference in x between XRF measurements of thin
4 film composition and that of the formula unit (FU). In addition to showing the considerable
5 variation in EQE over the collection of metal oxide photoanodes, the observation of appreciable
6 EQE at substantial composition deviations is quite striking. There are 5 phases with composition
7 deviation more than 0.18 from the composition of the prototype structure. With this level of
8 composition deviation, nanocrystalline secondary phases (not detected by XRD) may be present,
9 although such composition differences often occur with a multi-valent cation such that the host
10 structure can support substantial alloying. For example, the phases with an excess of the higher
11 valent cation include formal valences A^{+2} ($A = \text{Ca}$ or Mg) and either Mn^{+3} or Mn^{+4} , where excess
12 Mn appears to alloy as Mn^{+2} on the A^{+2} site. There are also cases where the structure of interest is
13 only observed in off-stoichiometric conditions, such as $\text{V}_2\text{Ag}_{0.33}\text{O}_5$ where an excess of Ag is
14 needed to form the structure under our synthesis conditions, likely resulting in some metallic Ag
15 in the thin film sample. This level of off-stoichiometry in solar energy conversion materials has
16 been most extensively studied with Cu-based p-type semiconductors such as $\text{Cu}(\text{In,Ga})\text{Se}_2$,⁴⁶
17 $\text{Cu}_2\text{SnZnS}_4$,⁴⁷ and CuBi_2O_4 ⁴⁸ where alloyed variants improve phase stability with respect to
18 competing phases and/or alter the electronic structure. These phenomena underlie the composition
19 variations of photoanodes in Fig. 4, where alloying can additionally optimize a catalytic activity
20 and/or electrochemical passivation.
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44 The uncertainty in the XRF compositions is nominally 5 at.%, so phases appearing outside the
45 ± 0.06 window are confidently off-stoichiometric, bringing into question whether traditional
46 methods would discover these photoanodes. Of the 23 such phases, 7 are also photoactive within
47 the ± 0.06 window, so discovery may have been possible with synthesis at a composition matching
48 the target FU. The remaining 16 phases required composition deviation to be discovered in our
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3 experiments, highlighting the utility of composition libraries in photoanode discovery and
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5 motivating further study of how substantial alloying optimizes photoanode performance.
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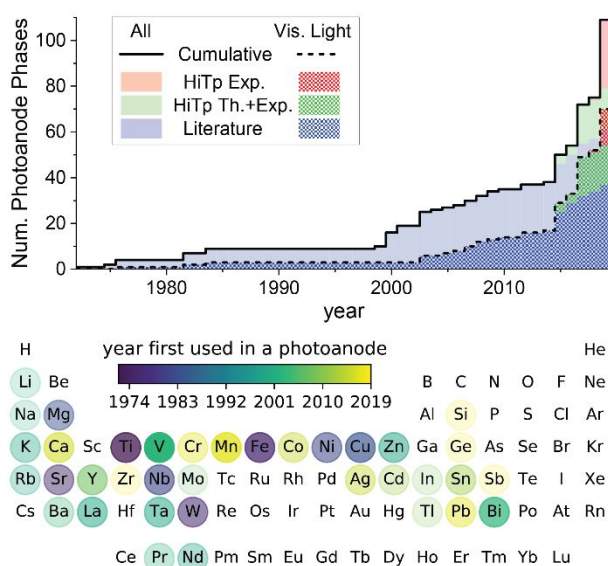
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8 Intertwined with the cation off-stoichiometry is the oxygen stoichiometry, or oxygen vacancy
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10 concentration, which is not amenable to high throughput characterization, resulting in a lack of
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12 observable trends over the set of known photoanodes. Recent work on BiVO₄ has demonstrated
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14 that over various time scales, the sub-band-gap states created by oxygen vacancies trap holes and
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16 electrons, ultimately requiring thermal de-trapping to produce photoactivity.⁴⁹ These results
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18 highlight the complexity of carrier transport in metal oxide photoanodes, which often involves
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20 small polaron hopping⁵⁰ and may additionally involve more complex phenomena over a range of
21
22 time scales. An opportunity arising from these recent advances is determination of the extent to
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24 which the observed conduction mechanisms of BiVO₄ are universal to ternary vanadates and other
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26 metal oxide photoanodes, and if the electronic structure contributions of oxygen vacancies, for
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28 example, can be used as a functional descriptor of metal oxide photoanodes. Our HiTp screening
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30 work includes a concerted exploration of ternary vanadates where we demonstrated tuning of band
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32 gap energies across the visible range through band edge hybridization with various open-d-shell
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34 cations.²³ These are specific examples of a general property of metal oxide photoanodes: nontrivial
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36 orbital character (particularly d orbital character) at band edges creates opportunities for tuning the
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38 band-edge electronic structure in new ways, potentially leading to electron and hole conductivities
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40 that are not well described by semi-classical, Boltzmann-based band transport theory.
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47 Traditional semiconductor characterization of conductivity or effective carrier mobility is
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49 necessary but insufficient for specific identification of the transport-limiting phenomenon. Recent
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51 developments in ultrafast spectroscopy have demonstrated direct observation of polaron
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53 formation,⁵¹ and application of such techniques to a broader class of photoanodes will help
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3 establish trends in the roles of defects, excited states, etc. in metal oxide semiconductor transport.
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5 Disentangling the transport mechanisms can also be facilitated by theory, although the highly-
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7 localized and strongly correlated electronic states (e.g. states with d orbital character) typically
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9 require rigorous treatment beyond that of standard theories and computational methods. Metal
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11 oxides often exhibit such electronic states, and as noted above, photoanodes of interest often
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13 encompass additional structural and chemical complexity that may alter transport properties and
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15 may require treatment of many-atom systems, creating substantial computational expense.
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17 Although DFT calculations are often used to compute band structures in practice, rigorous
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19 calculations of spectroscopic properties of metal oxide photoanode candidates require formalisms
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21 beyond the ground-state, time-independent DFT. In materials physics, the formalism of choice for
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23 quantitative prediction of the band structure and optical properties is *ab initio* many-body
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25 perturbation theory (MBPT).⁵² MBPT has been historically computationally prohibitive for
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27 complex materials, but it is beginning to be applied to complex systems, such as the metal oxide
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29 photoanodes BiVO₄ and β -Cu₂V₂O₇,^{22, 53} and interfaces involving photoanode materials and
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31 water.⁵⁴ Additionally, detailed *ab initio* calculations of photoexcited carrier dynamics, limited by
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33 phonon scattering, are now possible for simple semiconductors,⁵⁵ and have more recently been
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35 extended to oxides.⁵⁶ A growing number of recent methodologies are being proposed for more
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37 rigorous calculations of polaron formation energies.⁵⁷ Collectively, advances in these methods
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39 promise a significantly deeper and richer understanding and assessment of photogenerated carrier
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41 phenomena in existing candidate photoanodes, which will also lead to new descriptors for
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43 discovery of photoelectrode materials.
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51 Solar fuels photoanodes pose substantial challenges for materials discovery due to the combined
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53 needs of solar absorption, charge carrier separation and transport, chemical and electrochemical
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3 stability under operating conditions, as well as catalytic activity for the OER. The recent increase
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5 in chemical diversity of metal oxide photoanodes presents both challenges, for example
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7 determining which phases are amenable to optimization and integration into solar fuels generators,
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9 and opportunities, for example developing new theory and experiment campaigns to better
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11 understand fundamental properties that give rise to photoanodic activity. Despite the prolific
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13 photoanode discovery efforts of the last 20 years, solar fuels photoanodes are still rare compared
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15 to other types of functional materials, motivating continued identification of such materials to
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17 formulate models that relate fundamental materials properties to photoanode performance,
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19 enhancing scientific understanding as well as development of deployable solar fuels materials. The
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21 photoactivity of off-stoichiometric variants of phases is notable, motivating application of defect
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23 and transport characterization techniques, which have been recently developed via study of Fe_2O_3
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25 and BiVO_4 , to a broader set of metal oxide phases. Combining the recent proliferation of both
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27 photoanode discoveries and advanced characterization techniques will advance fundamental
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29 understanding of metal oxide photoelectrocatalysts and the design of next-generation photoanodes.
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53 Figure 1: (top) Summary of OER photoanodes from literature (blue), as well as our previous
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55 reports integrating HiTp theory and experiment (green) and additional HiTp experiment
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discoveries (red). (bottom) Using all photoanodes, the year in which each element was first used in a photoanode is shown on the periodic table, with the saturation of each circle corresponding to the number of times the element appears in the list of 109 photoanodes.

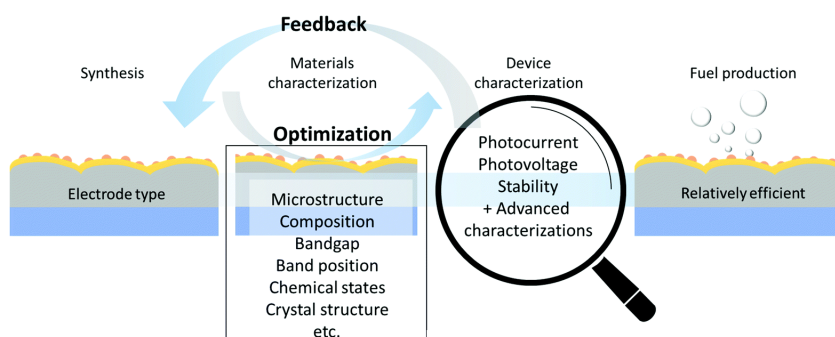


Figure 2: Illustration of synthesis and processing-based optimization of a library of materials properties, with feedback provided by an ever-expanding suite of materials and device-level characterizations. Adapted from Ref. ¹⁷ with permission.

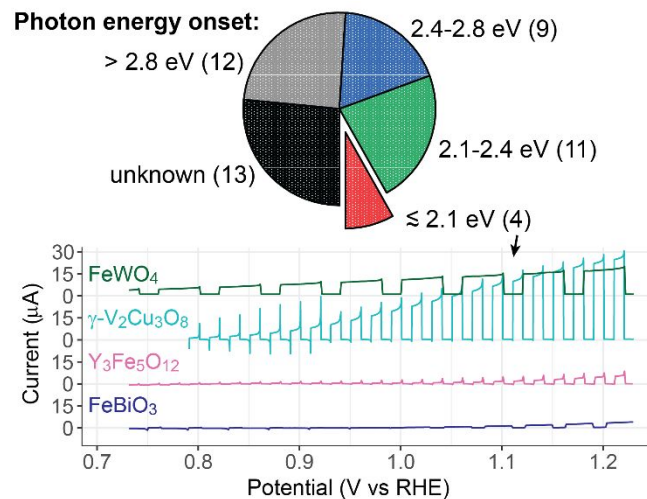


Figure 3: The pie chart shows the distribution of photon energy onset for photoactivity, for 49 metal oxide photoanode phases from combinatorial libraries with EQE in excess of 0.01% (see SI). The photon energy onset is determined via photoelectrochemistry at 1.23 V vs RHE with a

series of light emitting diodes, and due to their spectral breadth the boundaries between the 4 ranges have ca. ± 0.1 eV uncertainty. For the 4 photoanodes with photoactivity at 2.1 eV, the cathodic sweep from a cyclic voltammogram is shown with toggled 3.2 eV illumination (variable illumination intensity, see SI). These data were acquired in pH 13 (0.1 M NaOH) for γ - $V_2Cu_3O_8$ and $Y_3Fe_5O_{12}$ and borate-buffered pH 9.3 electrolyte for $FeWO_4$ and $FeBiO_3$, as reported previously.^{24, 26-27}

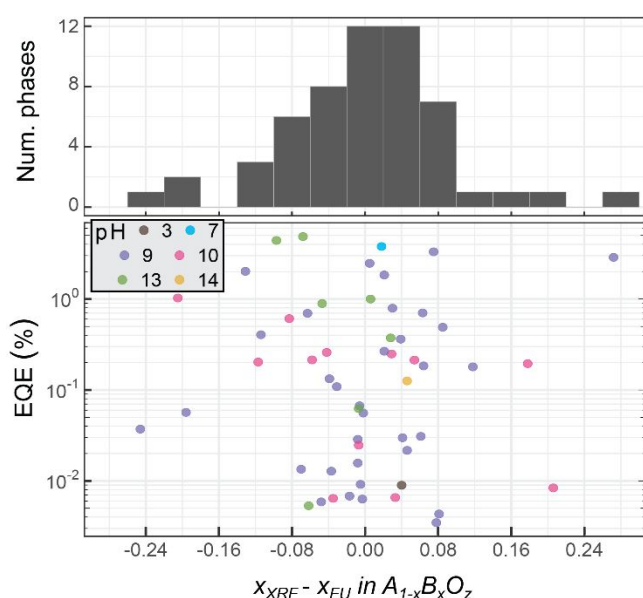


Figure 4: Summary of 55 photoanode phases from combinatorial libraries with available XRF measurement of composition. For each identified ternary oxide, the cation stoichiometry x is taken as $A_{1-x}B_xO_z$ where B is generally the higher valent cation. The quantity $x_{XRF} - x_{FU}$ is the difference in x between the composition of the most photoactive sample and that of the formula unit. The EQE at 3.2 eV is shown as the metric for photoactivity as this is the only illumination source used for all photoanode samples.

ASSOCIATED CONTENT

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3 **Supporting Information.** Table of 109 metal oxide photoanodes from the literature survey
4 summarized in Fig. 1. Table of HiTp composition and photoelectrochemical data for 58 phases
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6 measured in our labs.
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17 **Notes**
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20 The authors declare no competing financial interest.
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23 § In the literature survey, photoactivity under white light illumination combined with optical
24 identification of a sub-2.8 eV band gap was considered to be sufficient evidence for a visible
25 light photoanode.
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43 Experimentation group at Caltech, which accelerates scientific discovery by automating critical
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45 components of materials research workflows, from synthesis to data interpretation.
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52 **ACKNOWLEDGMENT**
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QUOTES TO HIGHLIGHT

Theoretical guidance of high throughput experiments has been particularly effective in dramatically increasing the portfolio of metal oxide photoanodes, motivating a new era of photoanode development where the characterization and optimization techniques developed on traditional materials are applied to nascent photoanodes that exhibit visible light photoresponse.

Computational screening not only identifies target phases but also promising composition regions that are sufficiently specific to enable exploration by high throughput experiments, which are in turn sufficiently broad in scope to identify materials beyond the computational search.

The photoactivity of off-stoichiometric variants of phases is notable, motivating application of defect and transport characterization techniques, which have been recently developed via study of Fe_2O_3 and BiVO_4 , to a broader set of metal oxide phases.

Combining the recent proliferation of both photoanode discoveries and advanced characterization techniques will advance fundamental understanding of metal oxide photoelectrocatalysts and the design of next-generation photoanodes.

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