

In Search of the “Perfect” Inorganic Semiconductor/Liquid Interface for Solar Water Splitting

by Krishnan Rajeshwar, Paul A. Maggard, and Shaun O'Donnell

Introduction

Arguably, one would be hard-pressed to envision a more ideal renewable energy conversion system than the solar splitting of water. The energy-rich product, hydrogen, may be stored and used later on-demand for generating power either via combustion or in a fuel cell. In scenarios where dioxygen is needed for respiration (e.g., space travel), CO₂ may be used instead of water as the reactant feed. Both these applications require a photon absorber for capturing sunlight, and an inorganic semiconductor fulfills this function. Therefore, a photoelectrochemical (PEC) system may be devised based on an *n*- or *p*-type semiconductor electrode in contact with the reactant fluid. On bandgap excitation of the photoelectrode, the generated holes or electrons respectively are used to drive the oxidation or reduction of the reactant species. In the case of water splitting, these are the OH[•] or H₃O⁺ ions, respectively. In a CO₂ photoreduction system, the corresponding species are OH[•] and (dissolved) CO₂. In both cases, the analogy with a plant photosynthesis system is direct.

This article reviews design criteria for the choice of the semiconductor photoelectrode and the underlying challenges.^{1,2} The present discussion is confined to solar water splitting rather than CO₂ reduction. Our focus here is on electrodes rather than the related photocatalytic strategy involving semiconductor nanoparticle suspensions. While considerable progress has been made on tandem photovoltaic-PEC cell combinations, the discussion below centers on integrated assemblies wherein the semiconductor electrode(s) fulfill(s) both the photovoltaic (PV) and electrochemical functions, shown in Fig. 1. This inevitably complicates the materials' design, but the potential technology payoff justifies the R&D endeavor involved. Dye-sensitized PEC designs are also not considered herein; i.e., in all the cases below, the inorganic semiconductor (instead of a dye) functions as the photoabsorber. New-generation PV materials such as organic perovskites are also beyond the scope of this discussion that is focused on oxide semiconductors.

Single or Dual Photoelectrode Designs?

The PEC cell may be designed with a single *n*- or *p*-type photoelectrode and a dark counterelectrode where either the proton reduction or water oxidation respectively occurs. Alternatively, the plant photosynthesis system may be mimicked via a two-photon approach (e.g., a so-called Z-scheme) using an *n*- and *p*-type semiconductor photoelectrode in concert. The maximum theoretical efficiencies have been computed for both approaches.³ The dual-photoelectrode cell design is complicated by the need for carefully matching the photocurrents at both terminals.

Design Criteria

In discussing the semiconductor photoelectrode material prerequisites, it is expedient to consider the photocurrent density J_{ph} as a figure of merit and consider its component parameters:⁴

$$J_{ph} = q\phi\eta_{LH}\eta_{CS}\eta_{CT} \quad (1)$$

Here, ϕ is the photon flux and the third, fourth, and fifth η terms represent the efficiency terms for light-harvesting (LH), charge (i.e., electron-hole) separation and transport to the surface (CS), and charge transfer (CT) across the interface, respectively. Of these three η terms, the first two impact the photovoltaic (PV) performance of the material, while the last term encompasses its electrochemical (EC) activity. A “perfect” PEC photoelectrode is a perfect PV and EC material; herein lies the challenge.

What might be considered to constitute a perfect EC material? Given that electrochemical processes are surface-confined, the material has to have excellent catalytic attributes. The kinetic constraints are even more drastic for the four-electron water oxidation process (oxygen evolution reaction or OER) relative to the two-electron hydrogen evolution reaction (HER). Unfortunately, inorganic semiconductor surfaces are typically only poorly catalytic, and as such, co-catalysts are needed to drive the multielectron water-splitting reactions. These catalysts should ideally be derived from Earth-abundant and non-toxic elements when the PEC water-splitting system is scaled up. Recall also that any solar energy conversion system requires large active areas for the photon-harvesting component, although this constraint impacts PV and PEC devices alike.

As if the above criteria are not stringent enough, the need for photoelectrode stability (minimum 10-year lifetime) is an added complexity (relative to a PV device counterpart) in the PEC system. This is much less of a concern with a PV system in that the device is all solid state, i.e., containing no electrolytes with corrosive or

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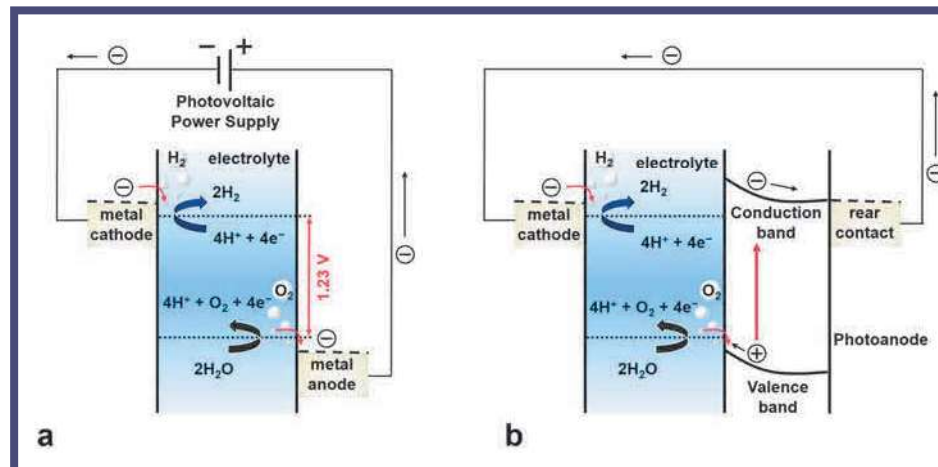


FIG. 1. Schematic diagrams of the functional operation of water-splitting semiconductor systems that are (a) photovoltaic driven with a coupled electrolyzer unit or (b) photoelectrochemically driven with a light absorbing photoanode and a metal cathode.

complexing component species. The PEC stability includes preservation of surface chemical fidelity both in the dark and under bandgap irradiation of the photoelectrode. Note that efficiency and stability are intertwined in the sense that if the last term in Eq. 1 above is not optimal, charge carriers will accumulate at the surface and will attack the semiconductor itself.

Also, note that the foregoing discussion (and Eq. 1) apply equally well to PEC interfaces derived from *n*- or *p*-type semiconductors. The distinction is that the photocurrent is anodic for *n*-type, e.g., Fig. 1b, and cathodic for *p*-type semiconductors, and the relevant minority carriers that feed into Eq. 1 are holes and electrons, respectively, for the two semiconductor types. Table 1 captures the essential combination of attributes sought for a PEC semiconductor electrode.

The threshold voltage for water splitting at 298 K is 1.23 V; to this thermodynamic value must be added kinetic (overpotential) and other electrical (e.g., iR drop) losses. Thus, the net critical voltage amounts to ~ 1.7 V. If the open circuit photovoltage is set to ~70 % of the semiconductor bandgap, it becomes immediately obvious that Si (with a bandgap of 1.1 eV) can be ruled out. In fact, it is quite unlikely that a single semiconductor will fulfill the energy requirements for unassisted (zero bias) water splitting. A sequence of two semiconductors with bandgaps of ~ 1.9 eV and ~1.3 eV has been proposed to attain the requisite voltage to split water.⁵ Further, the semiconductor energy levels in this combination must be such that the conduction band edge lies at a potential more negative than the HER potential. The valence band edge must be more positive than the OER potential. In this manner, the photogenerated electrons and holes will have sufficient potential to reduce protons and oxidize water, respectively, without the need for an external bias potential.

Unfortunately, the state-of-the-art synthetic routes do not yet enable one to simply dial in the attributes listed in Table 1 and secure the “ideal” semiconductor photoelectrode. Given this roadblock, there is no alternative to the painstaking synthesis-characterization-optimization loop. Combinatorial approaches suggest a potential way out of this impasse; note that the water-splitting community shares a similar challenge with the pharmaceutical enterprise in this regard.⁶ However, at this writing, there is, unfortunately, no magic bullet semiconductor that fulfills all the criteria listed above.

Photoelectrode Semiconductor Candidates

The progress with the PEC materials genome for solar water splitting has been thoroughly reviewed such that only a snapshot

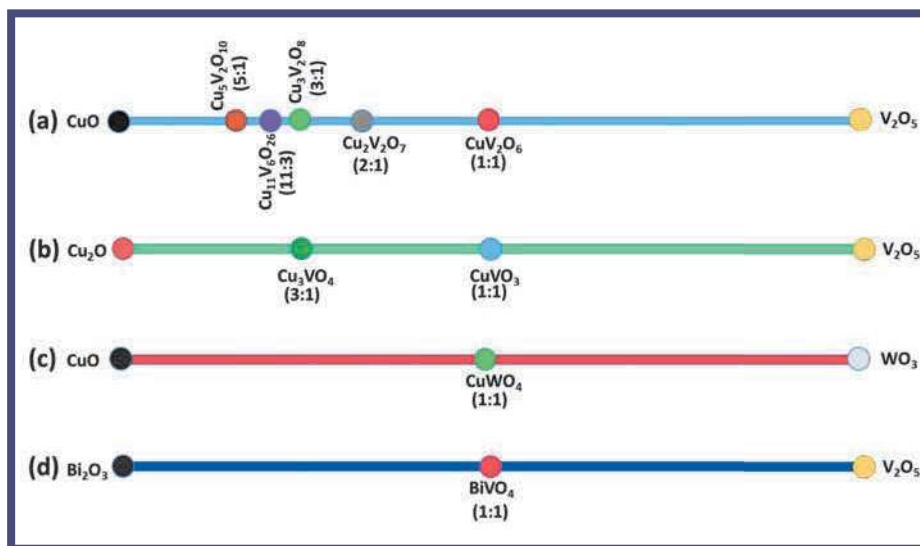


Fig. 2. Composition line diagrams (see also Ref. 1) for various stoichiometric oxides in the (a) $MO-V_2O_5$, (b) $M_2O-V_2O_5$, (c) $MO-WO_3$, and (d) $M_2O_5-V_2O_5$ compound families. $M = Cu$ or Bi .

needs to be given here.^{1,7-9} As in the PV case, the search has progressed beyond elemental semiconductors to binary compounds, to ternary compounds and beyond. For solid state PV devices (where corrosion stability is not an overriding concern as in the PEC counterparts), Si, CdTe, and ternary (and multinary) chalcogenides (e.g., copper indium gallium selenide or CIGS) have emerged as promising candidates.¹⁰ In the PEC case, oxide semiconductors have been intensely studied since they appear to at least partly meet the stringent requirements discussed above. However, these materials have exhibited rather low device efficiencies for water splitting relative to other candidates such as group III-V semiconductors. Nonetheless, the community continues to pursue the search for an optimal oxide in the hope that good corrosion stability can be combined with high charge transfer efficiency.

In this vein, the remainder of this article focuses on oxide semiconductors. While ternary oxides (e.g., $SrTiO_3$) featured fairly early on in the history of PEC water splitting, the vast majority of the studies focused on binary oxides, of which TiO_2 , Fe_2O_3 , WO_3 , and Cu_2O are worthy of mention.¹¹⁻¹⁶ Of these, both Fe_2O_3 and Cu_2O have the optical advantage of a low bandgap. However, Cu_2O is not stable in aqueous solutions; Fe_2O_3 , while stable, has rather poor charge transport properties. These findings have prompted researchers (including the present authors) to pursue ternary oxides, such as many derived from Cu_2O ,¹⁷⁻²² in the hope that the otherwise excellent PEC performance can be combined with enhanced stability via the incorporation of a second metal cation. In this regard, ternary compositions based on another copper oxide, namely CuO , have also been considered. (See Fig. 1c.)

Table 1. Characteristics of an ideal PEC semiconductor electrode for solar water splitting.

PV Properties	Electrochemical Properties	Other Criteria
High absorption coefficient	High catalytic activity for OER and HER	Earth abundance and non-toxicity of component elements
Optimal bandgap	High corrosion stability in the dark and under irradiation	Ease of synthesis and scale-up
Large minority carrier diffusion length		
Negligible bulk recombination		
Negligible surface and space charge layer recombination		
Negligible bulk resistance		

Ternary and Multinary Oxides

In exploring the myriad compositions to be considered in the discovery phase, ternary or higher multinary oxides may be considered as derivatives of their binary oxide components. Consider, for now, the ternary oxides that may be derived from combinations of Cu_xO ($x = 1$ or 2), WO_3 , and V_2O_5 . The chemical compositions may be expressed in a line diagram bounded by the two end-members (binary oxides) and the position of the ternary compound on the line dictates its stoichiometry. This is illustrated in Fig. 2 for several examples that have been most heavily investigated for their PEC performance as photoelectrodes.

The Cu-V-O system in Figs. 2a and b, for example, features a rich array of compounds with varying stoichiometry and the A cation (Cu) in two different oxidation states. This has enabled an examination of their PEC properties as a function of the Cu:V ratio in the compound.^{23,24} The activity toward OER has been found to improve with decreasing Cu:V ratio. In general, while the bandgaps of these compounds are in the right range (1.8–2.0 eV), their PEC properties have much room for improvement. In this vein, alloying of +2 cations (e.g., Sr) onto the Cu site has been found to enhance the PEC activity. With *The Materials Project* database currently listing ~30 distinct structures in this system,²⁵ these compounds represent the tip of the iceberg in regard to possible structures and compositions.

In the related Cu-W-O system, CuWO_4 (Fig. 2c) repairs two handicaps associated with the use of WO_3 as a photoanode for solar water splitting: (a) it harvests longer wavelengths of the solar spectrum owing to its smaller bandgap; (b) it does not degrade under long-term irradiation in electrolytes with neutral pH as long as complexing ions (e.g., phosphate) are not present. Water photooxidation, however, is hindered by a large charge transfer resistance such that J_{ph} is limited to only fractions of an mA/cm^2 .²⁶ (See Table 1.) Nonetheless, the nearly quantitative Faradaic efficiency reported for OER bodes well for further optimization, and the improvement over WO_3 constitutes a step in the right direction. While only CuWO_4 is listed on this diagram, and which has been the focus in recent investigations, the predicted existence of 10 or more new compositions in this system portends a promising future path to tuning the CuO and WO_3 components and understanding their relative impacts on the charge transfer resistance.^{25,26}

Of all the ternary oxide photoelectrode material candidates explored to date, BiVO_4 (Fig. 2d) has garnered the most attention. Initial studies revealed its surface to have very poor hole transfer efficiency, but this handicap has been partly remediated with the use of co-catalysts such as cobalt phosphate, FeOOH , or MnO_x .²⁷

Nonetheless, surface recombination is still a problem that must be further tackled with this material. (See Table 1.) Surface modification may prove to be a way out of this difficulty; for example, J_{ph} has been boosted to ~2.7 mA/cm^2 by chloride modification.²⁸ Photocorrosion of BiVO_4 is another concern; in-operando strategies for understanding and remediating photocorrosion pathways offer hope for the future.

The foregoing discussion was only meant to provide a capsule summary of the promise offered by ternary and multinary oxide semiconductors. Other than the candidates identified here, there are many other families of ternary oxides (e.g., delafossite ABO_2 , perovskite ABO_3) that are promising.¹⁸ We next turn to more fundamental solid state aspects associated with the materials in Fig. 2. In the subsequent section, the roles of the AO_x and BO_x components are analyzed from a solid state perspective.

Solid State Aspects of Ternary and Multinary Oxides

The PEC properties of semiconducting oxides are fundamentally determined by their crystalline structures and chemical compositions. The crystalline structure is, in turn, dictated by local and extended bonding configurations of the constituent components, such as for the AO_x and BO_x within an ABO_{2x} composition. Thus, the choice of the different metal cations, as well as their relative molar ratios, has a significant influence on their PEC properties through concomitant changes in their crystalline and electronic structures. As discussed above, the many underlying and interdependent factors (e.g., atomic orbital energies, ionic radii, oxidation states) make it virtually impossible to dial in an optimal set of semiconductor PEC properties. Yet, much progress towards a deeper understanding of the key structure-property relationships is emerging.

For example, the relative stoichiometric ratios of the AO_x and BO_x components generally influence whether the structure forms with either isolated AO_x/BO_x units or extended $[\text{A-O-A-O}]_n$ (n = repeating unit) and $[\text{B-O-B-O}]_n$ bonding, shown in Fig. 3. While the former leads to localization and trapping of the charge carriers, the extended bonding in the latter can yield the desired high majority carrier diffusion lengths in more delocalized band states owing to their greater dispersion. As a test case, in the Cu-V-O chemical system, the higher molar concentration of the V_2O_5 component in CuV_2O_6 (i.e., 1:1) leads to extended two-dimensional $[\text{V-O-V-O}]_n$ sheets, Fig. 3 (left). By comparison in $\text{Cu}_5\text{V}_2\text{O}_{10}$, Fig. 3 (right), the higher CuO: V_2O_5 molar ratio of 5:1 gives a structure with only isolated VO_4 tetrahedra but extended $[\text{Cu-O-Cu-O}]_n$ layers. Intermediate compositions nearer to a 1:1 metal ratio are more optimal for finding structures with extended bonding for both metal cations, such as is the case for

CuWO_4 , Fig. 3 (middle). In this example, a wide band dispersion can occur in both the valence and conduction bands owing to the extended bonding of both $[\text{Cu-O-Cu-O}]_n$ and $[\text{W-O-W-O}]_n$ components that form as chains. This is one potential key to efficient charge separation of excited electrons and holes and transport over separate structural components.

Many other solid state principles have also been discovered that demonstrate how the choice of multiple different metal cations, and thus the AO_x and BO_x components, can yield semiconductors with smaller bandgaps, greater band dispersion and charge carrier mobility, energetic tuning of deep versus shallow trap states, as well as tuning between n -type and p -type semiconducting behavior. An archetype oxide example results from the combination of two metal cations with a sum of oxidation states of +6 and having the ABO_3 composition. The choice

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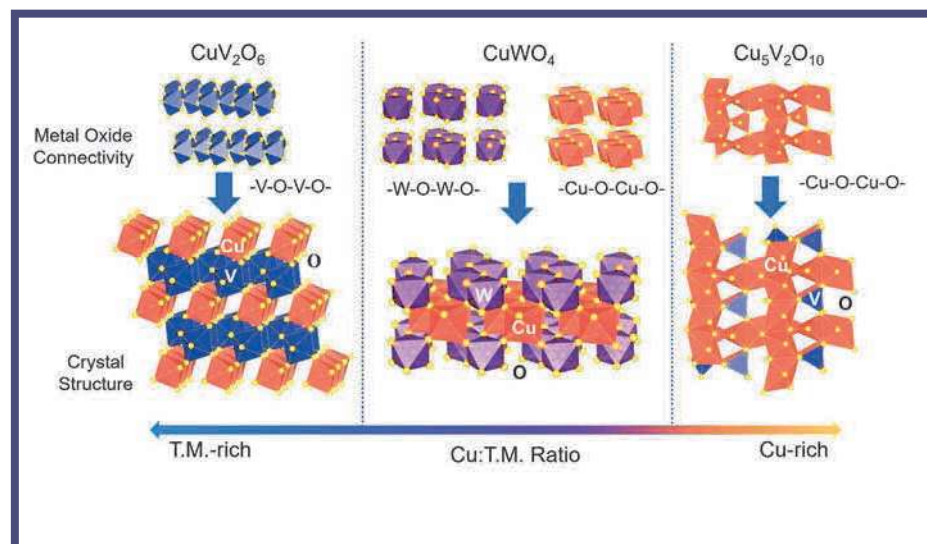


FIG. 3. Crystalline structures with varying Cu: T.M. (T.M. = transition metal) atomic ratios and metal-oxide connectivity, including with extended vanadate layers in CuV_2O_6 (1:1; left), cuprate layers in $\text{Cu}_5\text{V}_2\text{O}_{10}$ (5:1; right), and with both tungstate and cuprate chains in CuWO_4 (middle).

of two metal cations with compatible ionic radii (i.e., satisfying the Goldschmidt tolerance factor) can result in the ubiquitous perovskite-type structure, such as in highly studied *n*-type SrTiO₃ films. Alternately, the combination of one transition metal with a *d⁰*-electron configuration (e.g., Ti(IV), V(V)) and another with a *d¹⁰*/*d⁰**s*²-electron configuration (e.g., Cu(I), Pb(II)) can yield a small bandgap, as found in CuNbO₃ and PbTiO₃ with bandgaps of ~2.0 eV and ~2.7 eV, respectively.^{29,30} Multiple metal cations can thus be used advantageously to satisfy many of the desired semiconductor PEC properties listed in Table 1.

The challenging side of this approach is that semiconductors containing a combination of multiple metal cations can suffer from a high degree of both crystallographic anisotropy and order/disorder issues, shown in Fig. 4. Frequently, a low degree of symmetry is enforced upon the crystalline structure because of the disparate coordination preferences and connectivity of the separate AO_x and BO_x components. This is the case for the connectivity of the titanate and stannate chains in Sn₂TiO₄, illustrated in Fig. 4, as a result of the Ti(IV) and Sn(II) cations having dissimilar ionic radii and coordination preferences. The net consequences are large differences in charge carrier mobility and absorptivity with crystal orientation, e.g., such as only down the one-dimensional chains. Thus, highly anisotropic structures necessitate a favorable alignment of the directions of high carrier mobility within the photoelectrode film so that the majority and minority carriers can efficiently transport to the back contact and outer film surfaces, respectively.

At the opposite extreme, completely disordered structures also occur, e.g., as solid solutions, when the multiple metal cations are sufficiently similar in chemistry. A representative example is Sn(Zr_{1-x}Ti_x)O₃, Fig. 4 (right), with the Zr(IV) and Ti(IV) cations completely disordered over the same crystallographic sites of the perovskite structure because of their similar ionic radii and

coordination preferences. A significant amount of trapping and scattering of charge carriers would be expected in this case with high atomic-site disorder. Surprisingly, several solid-solution semiconductors show promisingly high photocurrents and photocatalytic activity, i.e., such as for BaTa(O₂N) and (Ba_{1-x}Sn_x)(Zr_{1-x}Ti_x)O₃,^{31,32} with mixed anion and cation sites, respectively. This counterintuitive property emerges when the percolation thresholds of their bonding networks have been exceeded. Many such fundamental relationships remain to be discovered in these more complex systems.

Outlook and Prospects

The preceding discussion ought to make it abundantly clear that fascinating solid state chemistry lurks within the search spaces encompassing the elusive “perfect” inorganic semiconductor photoelectrode. While only the future holds the answer to whether we will ultimately succeed in this search, much progress would have been made regardless in our fundamental understanding of the structure-optoelectronic property correlations in solid state inorganic frameworks. Solid state sciences undeniably contributed handily to the search for high-temperature superconductivity and energy storage devices (e.g., Li ion batteries). It will not be a stretch to imagine a similar outcome in the area of solar water splitting. The ingenuity of the human mind and the inspiration derived from the rich history of scientific and technologic advances will surely drive future progress toward the goal of efficiently and persistently splitting water using sunlight.

Acknowledgement

Paul A. Maggard gratefully acknowledges the support of this work from the National Science Foundation (DMR-2004455).

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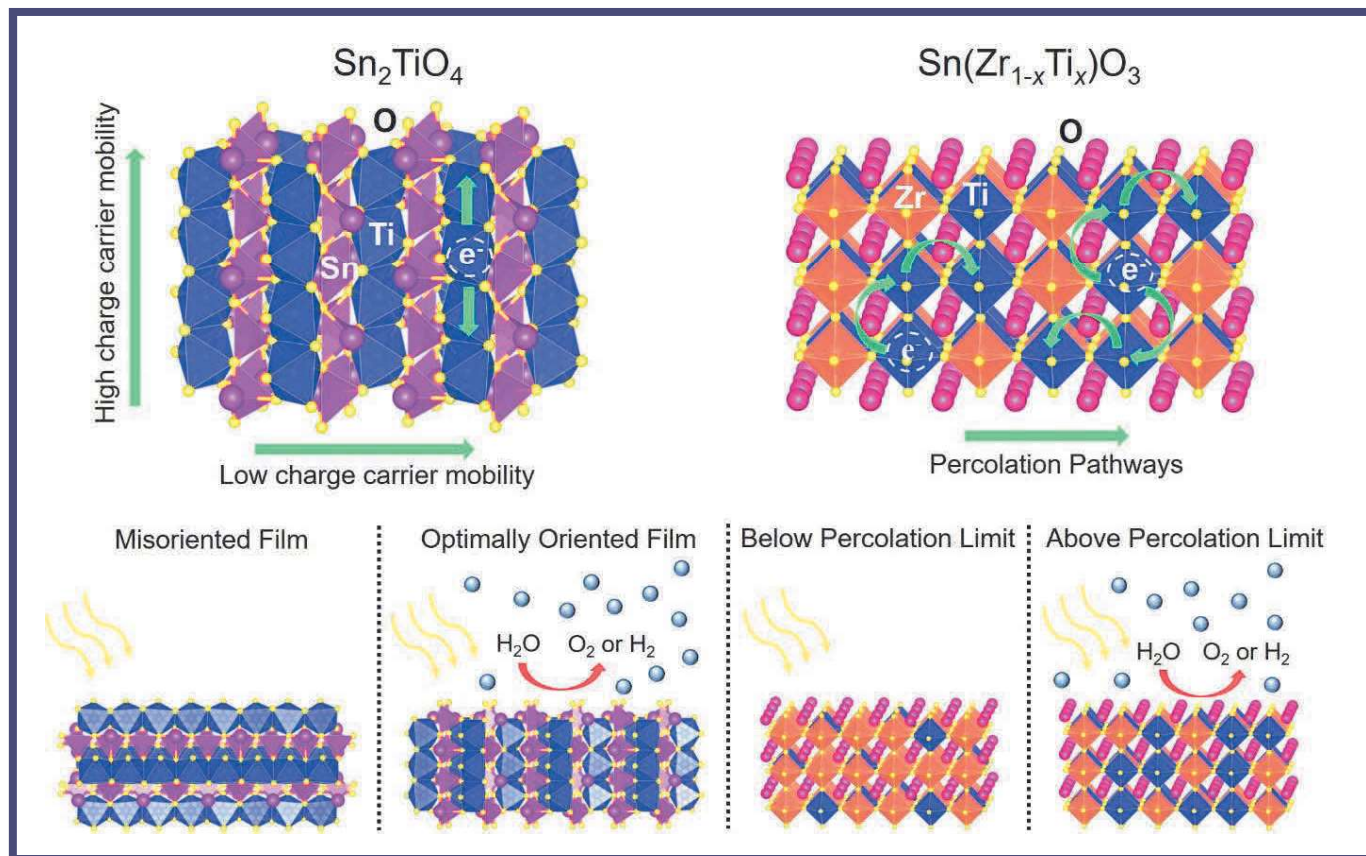


FIG. 4. Comparison of the ordered structure of Sn₂TiO₄ with significant crystallographic anisotropy (i.e., one-dimensional), left, and the disordered structure of Sn(Zr_{1-x}Ti_x)O₃ with percolation thresholds for site-to-site charge carrier diffusion, right.

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