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Perspective—Multinary Oxide Semiconductors for Solar Fuels Generation: Closing the Performance Gap between Theory and Practice

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This Perspective addresses the current state-of-the-art with the development of multinary oxides—a family of compounds that has long interested Prof. John B. Goodenough. Specifically, here we focus on their use as photoelectrodes for solar fuels generation. Using optical data and assuming an idealized 100% incident photon-to-electron conversion efficiency, it is possible to project the maximum short circuit photocurrent efficiency to be expected for a given oxide semiconductor. The performance gap between this theoretical value and that realized experimentally, is shown to be sizable for all but a couple of candidates. The technical issues underlying this gap and strategies for closing it are presented below.

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While the breadth and scope of John B. Goodenough's contributions to solid state chemistry and energy conversion are truly mindboggling, his early career was studded with accomplishments in the understanding of electron transport and chemical bonding in transition metal oxides including ternary oxides of the perovskite type.¹ This Perspective deals with such compounds developed for possible applicability in the storage of solar energy via chemical bonds and fuels (e.g., hydrogen). Indeed, it is worth noting that Prof. Goodenough also made pioneering contributions in this area during his tenure at Oxford University in the 1980s.^{2–6}

Transition metal oxides have played a prominent role in the photoelectrochemical (PEC) application of solar energy conversion and John's early work focused on both binary and ternary oxides, for example: TiO_2 and $SrTiO_3$.^{2–6} (Much of this body of work has been eloquently described in Andrew Hamnett's article² in this focus issue). As discussed elsewhere,⁷ both *n*- and *p*-type oxide semiconductors can be used for this purpose; however, the combination of properties required of the photoelectrode material is daunting indeed. Specifically, solid state, surface (catalytic), optical and electrochemical attributes must match the requirements of the material being both a champion photovoltaic converter as well as an excellent electrocatalyst for water splitting.⁷ As if these requirements are not stringent enough, the component elements and the photoelectrode material must be durable, Earth abundant, and non-toxic.

The net result is that the continued search for a photoelectrode candidate that meets all these criteria, while vigorous and worldwide, has still not resulted in a 'magic bullet.' We will now examine where the PEC solar fuels community is poised in the area of multinary oxide semiconductors. We will focus below on the solidstate aspects and defer a discussion of the electrochemical and durability issues to another venue. Eight ternary and one quaternary compound are considered below. The choice of these compounds reflects mostly the collective experience of our respective research groups; nonetheless, they offer a reasonable representation of the possibilities with multinary oxides for this particular application, i.e. solar fuels generation. It is noted that efficiency and durability represent the twin pillars of performance evaluation of any given photoelectrode material for the solar fuels application. To keep this discussion to a reasonable length, however, the latter aspect is not addressed below. Nor are aspects related to practical photoelectrode material preparation details specifically addressed below. The interested reader may wish to consult the original literature cited for such details.

Current Status

Any device for converting the photon energy from the Sun to electrical or chemical energy, whether it is a solid-state photovoltaic device or a PEC cell (considered here), has the three process components depicted in Fig. 1. Each of the three steps has to be optimized for an efficient end device. A BiVO₄ photoactive layer is considered specifically in Fig. 1 but the three process steps are completely general for any of the materials discussed below. For the overall water splitting process to be efficient, all three steps in Fig. 1 must be efficient. Otherwise, many of the photogenerated carriers will be lost via recombination and will not be available for the allimportant redox reaction at the photoelectrode/electrolyte interface. Other parasitic losses include those associated with high resistance, overpotentials etc; these are not explicitly considered in what follows. The percent of the carriers collected to the number photogenerated, represents the incident photon-to-electron conversion efficiency (IPCE) and is ideally 100%.

Figure 2 and accompanying Table I summarize the compounds considered in this Perspective. Note that both *n*- as well as *p*-type semiconductors are being considered. The theoretical maximum solar photocurrent was determined by integrating the AM1.5 G solar spectrum from 280 nm to the wavelength corresponding to the bandgap energy of the semiconductor. The theoretical maximum assumes that: (a) Every photon with energy greater than or equal to the bandgap is absorbed and produces an exciton. (b) There is no charge carrier recombination. (c) There is no back reaction of the photogenerated products or intermediates. The optical properties of the compounds also span a wide range, with the optical band gap energies (*E*_g) ranging from ~2.6 eV for copper(I) tantalate to ~1.6 eV for tin(II) titanate. Correspondingly, the short-circuit photocurrent improves, with the projected value approaching ~25 mA cm⁻² for tin(II) titanate.

Before we examine each of these compounds in more detail, some clarifying remarks are needed as to what experimental result(s)





Figure 1. The three basic process components of a solar photoanode (an *n*-type bismuth vanadate film as an example) for converting photon energy contained in the Sun to chemical energy. The latter is used to instigate redox processes at the photoanode surface to oxidize water to molecular oxygen as shown in the third frame. See text for details.



Figure 2. Projected short-circuit photocurrent density values as a function of excitation wavelength for the nine semiconductors considered in this study. Further details of these compounds may be found in Table I. The shaded bars show the measured photocurrents culled from the literature (see also Table I).

are to be compared with the projected performance for each compound. Specifically, what figure-of-merit was to be utilized from among the array of information contained in the literature data? In this context, we note many prior discussions (e.g., Refs. 17–19) on computation of process efficiencies for solar water splitting. The ideal metric is derived from two-terminal devices where parameters such as the open-circuit voltage, short-circuit current etc can be readily measured like for any solid-state photovoltaic cell in response to strictly defined solar excitation (e.g., AM1.5 G). Unfortunately, much of the experimental data are based on three-electrode measurements, and there is wide variability in the conditions used, e.g., electrolyte pH, applied bias potential, redox composition etc.

Given these constraints, the photocurrent density was used as a figure-of-merit and every attempt was made to specify the underlying variables in each study so that the reader can assess the degree to which each compound's photoactivity met the theoretical (i.e., the idealized) performance metric in Fig. 2 and Table I. Bolstering our use of the photocurrent figure-of-merit is the fact (as pointed out elsewhere, Ref. 20) that this parameter is the only experimental variable in a solar-to-hydrogen (STH) efficiency calculation. (An ideal figure-of-merit for use in Fig. 2 and Table I would have been the STH efficiency; unfortunately, this is rarely ever reported in the studies that were consulted here (see below).

In using Table I, it is worth noting that every attempt was made to quote, as much as was feasible, only measured photocurrent values (sixth column) that could be evaluated on a comparative basis. Thus, for the *n*-type compounds, these values were measured at 1.23 V (vs RHE) (lone exception: Ref. 11 for CuV_2O_6 where the photocurrent is shown for 1.74 V vs RHE). Similarly, for the *p*-type semiconductors, a potential of -0.6 V (vs RHE) was used. The excitation source in all the cases was the visible output of a Xe arc lamp, invariably fitted with an AM1.5 G filter. However, not all the measured photocurrents in Table I pertain to the oxygen evolution reaction (for *n*-type) (cf, Fig. 1) or the hydrogen evolution reaction (for *p*-type). In fact, rarely ever, are the gases evolved (or their relative stoichiometry) explicitly identified. At least, in a couple of instances (e.g., Refs. 10 and 13), H₂O₂ and sulfite were added as electron or hole scavengers so that water splitting is short-circuited.

Copper(I) tantalates.—These compounds are *p*-type semiconductors owing to the facile oxidation of Cu(I) to Cu(II), and are thus employed as photocathodes. ^{15,16,21} Two compounds that have shown promise are Cu₅Ta₁₁O₃₀ and Cu₃Ta₇O₁₉. Both compounds have visible light bandgaps of ~2.6 eV and ~2.5 eV, respectively, and lead to theoretical maximum solar photocurrents of ~5.0 and ~6.2 mA cm⁻² (Fig. 2 and Table I). Compared to binary oxides such as Ta₂O₅, the visible light bandgaps of Cu₅Ta₁₁O₃₀ and Cu₃Ta₇O₁₉ are derived from negatively shifted valence band edges which are composed of filled Cu *3d*¹⁰ states.^{15,21} As a result, the valence band maximum (VBM) is at higher energy than the Cu *3d*¹⁰ configuration,²² which facilitates hole doping; Cu vacancies are

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Semiconductor	Bandgap energy (eV)	Threshold wavelength (nm)	Semiconductor type	Theoretical max. solar photocurrent $(mA \ cm^{-2})$	Measured photocurrent $(mA \ cm^{-2})$	Reference
Sn ₂ TiO ₄	1.6	775	п	25.4	0.11	8 ^a
BaNbO ₂ N	1.7	720	n	21.8	5.2	9 ^b
CuBi ₂ O ₄	1.8	689	р	19.6	2.8	$10^{\rm c}$
CuV ₂ O ₆	1.9	653	n	17	0.75	11 ^d
$Cu_2V_2O_7$	2.2	620	п	14.6	0.41	12 ^e
CuWO ₄	2.3	539	п	8.9	1.0	13 ^f
$BiVO_4$	2.4	517	n	7.5	4.3	14 ^g
Cu ₃ Ta ₇ O ₁₉	2.5	496	р	6.2	1.5	15 ^h
Cu5Ta11O30	2.6	477	р	5.0	0.6	16 ⁱ

Table I. Optoelectronic Properties and the Performance Gap for the Nine Semiconductors in Fig. 2, in order of increasing band gap.

a) pH = 9.0; oxide surface modified with CoOx catalyst. b) pH = 13; photoelectrode surface modified with Co(OH)₂-FeO_x dual catalyst. c) $pH = \sim 7$; electron scavenger added; see text. d) pH = 9.2. e) pH = 7.5. f) $pH = \sim 7$. g) pH = 10. After a pre-soak of the photoanode under the light source. h) $pH = \sim 6.3$. After thermal oxidation; see original reference. i) The oxide was doped with niobium.

usually responsible for the *p*-type character. The Ta 5*d* contributions to the conduction band make the conduction band minimum (CBM) relatively more delocalized and contribute to the higher band gap of $Cu_5Ta_{11}O_{30}$ of 2.6 eV. A similar effect of Ta on the CBM and band gap was found in another group of tantalates.²³

The density of states (DOS) plot in Ref. 24 further showed that for the pristine $Cu_5Ta_{11}O_{30}$, the photoexcitation of electrons stems from transitions between the 3d to 5d bands. Upon the formation of Cu vacancies, the VBM showed a significant contribution from O 2p forming shallow defect levels above the band edge. The resulting O 2p to Ta 5d photoexcitation of electrons will be relatively stronger than the pristine one. On the other hand, a hybrid DFT calculated DOS showed²⁵ that at the Fermi level, DOS with a smaller peak with Cu 3d character separated from the rest of the valence band; in addition, it reported a smaller, indirect fundamental gap of 2.1 eV and a direct gap of 2.6 eV. The UV–vis diffuse reflectance spectra confirmed these gaps.

Both Cu₅Ta₁₁O₃₀ and Cu₃Ta₇O₁₉ have shown promise as photocathodes for proton reduction (or hydrogen evolution reaction or HER) owing to their *p*-type conductivity. Photocurrents for Cu₃Ta₇O₁₉ and Cu₅Ta₁₁O₃₀, however, only represent ~25%-30% of their theoretical maximum. Thus, both compounds have yet to practically attain their full potential. A central issue for both Cu₅Ta₁₁O₃₀ and Cu₃Ta₇O₁₉ is poor charge separation leading to high rates of charge recombination. The poor charge separation in these compounds is attributed to both the anisotropic carrier mobilities as a consequence of their respective crystal structures as well as the lower degree of band dispersion leading to relatively higher carrier effective masses.

These issues can be partially mitigated by the partial oxidation of either compound, which leads to the formation of CuO nanosized islands on the surface with a type-II band offset. These features serve to collect the photogenerated electrons and thereby enhance charge separation.²⁴ For example, films of Cu₅Ta₁₁O₃₀ irradiated with visible light resulted in photocurrents of $\sim 0.2 \text{ mA cm}^{-2}$; however, after partial oxidation to form CuO nanoislands the photocurrent increased ten-fold to $\sim 2.5 \text{ mA cm}^{-2.24}$ Similar results were found for Cu₃Ta₇O₁₉, where the presence of CuO nanoislands led to an increase of the photocathodic current from $\sim 0.1 \text{ mA cm}^{-2}$ $\sim 0.9 \text{ mA cm}^{-2.21}$ Niobium doping has been studied to Niobium doping has been studied for $Cu_5Ta_{11}O_{30}^{16}$ with the results shown in Table I. In general, the values quoted for the photocurrents for these compounds above and in Table I, must be regarded as only representative of what have been achieved to date. An additional beneficial feature of these compounds is that they are highly defect tolerant, with defect energies that typically fall within the valence band, and thus reduces the potential number of recombination centers that can drastically reduce photocurrents.^{24,21}

Bismuth and copper vanadates.—Among the oxides considered here, it is safe to conclude that BiVO₄ has received the most attention.²⁶ Theoretically, BiVO₄ can reach a STH conversion efficiency of ~9%;²⁷ however, until now, a maximum STH conversion efficiency of only ~1.1% has been achieved. On the other hand, the performance gap from a simple photocurrent perspective shows this compound to be the champion performer among the candidates considered here (Fig. 2 and Table I). Electronhole recombination is the significant bottleneck to achieving even better performance with BiVO₄, especially from a STH efficiency perspective.

BiVO₄ has a significant contribution from the V 3*d* band in the CBM, which contributes to the higher effective mass for the photoexcited electrons. Our previous study by DFT showed that selective Nb substitutional doping in BiVO₄ reduces the effective mass of electrons significantly.²⁸ It has been shown that in BiVO₄, V⁴⁺ states are found in conjunction with oxygen vacancies.²⁹ The V⁴⁺ state is situated at a lower energy from the CBM, and hence can act as a shallow charge recombination center. The V⁴⁺ state can also be modeled as an electron polaron localized on a V-site.^{30,31} The presence of polaron states is one of the major causes behind the lower photoconduction and reduced photoactivity in $BiVO_4$.³² A comprehensive first-principles study of self-doping in $BiVO_4$ showed³³ that O vacancies and Bi vacancies could create shallow donor and acceptor levels, respectively; however, they do not lead to significant *n*-type or *p*-type conductivity.

Among the ternary copper vanadate family, α -CuV₂O₆ and β -Cu₂V₂O₇ have been the most photoelectrochemically-active oxides.¹¹ Even though copper vanadates generally exhibit spin ordered magnetic states, the calculated exchange energy showed a very weak magnetic coupling. Thus, at room temperature, α -CuV₂O₆ would be in a paramagnetic state. The calculated DOS plot showed unoccupied mid-gap states comprised of Cu 3d and O 2p bands. The mid-gap states are situated about 0.4 eV above the VBM. The CBM is of V 3d band character, whereas at the VBM, the presence of either Cu 3d or V 3d is minimal; the VBM is mostly O 2p. Given the band configuration, it is likely that O vacancies impart *n*-type semiconductor type to the parent compound. On the other hand, the mid-gap states can act as recombination centers.

The β -Cu₂V₂O₇ compound has a monoclinic structure with space group C2/c. The DFT calculations also predict a paramagnetic state at room temperature for this Cu vanadate phase. Electronic structure calculations showed similar features as α -CuV₂O₆, except for the mid-gap states.³⁴ The mid-gaps are close to the conduction band continuum and have Cu and V *3d* contributions. Even though the experimental results showed *n*-type behavior for β -Cu₂V₂O₇, the electronic origin is not very clear. For example, O vacancies would create occupied defect levels near the CBM, and then the mid-gap states would couple with defect levels. For instance, it was reported that O vacancies would be present on Cu₂V₂O₇ and would place Cu⁺ defect states within the band gap.³⁵ There is no defect study, either by experiment or DFT, available to elaborate the mechanism of *n*type doping in β -Cu₂V₂O₇.

Copper tungstate and bismuthate.—Copper tungstate, CuWO₄ is an *n*-type semiconductor that crystallizes in an anisotropic triclinic structure with symmetry $P\bar{1}$. It has an indirect band gap of 2.3 eV. For CuWO₄, DFT calculations without spin polarization predict it to behave electronically as a metal; however, with an antiferromagnetic (AFM) configuration, it is shown to have a band gap of about 2 eV by DFT+U theory.³⁶ The optical absorption calculations showed an onset of absorption slightly above 2 eV; however, a significant increase of excitation occurred above 3 eV.³⁷ Given the localized nature of the VBM and CBM, the photocurrent should be rather low; indeed, it is (Fig. 2). In addition, like BiVO₄,³⁸ the CBM of CuWO₄ does not straddle the H₂O reduction potential.³⁹ To enhance the performance of CuWO₄, Co₃O₄ was proposed as a 'co-catalyst'.¹³

CuBi₂O₄ is a promising semiconductor photoabsorber candidate due to its optimal band gap and low-cost fabrication. Its crystal structure belongs to the tetragonal P4/*ncc* (space group130). It is a *p*type semiconductor with an optical gap of 1.75 eV. The DFT calculated direct band gap of pristine CuBi₂O₄ was found to be 1.90 eV, slightly higher than the experimentally observed one.⁴⁰ From the calculated DOS plot, a strong contribution of the Cu 3*d* band was seen at the CBM and a dominant O 2*p* at the VBM. Near the VBM, anti-bonding Bi 6*s* contribution was also found, similar to that in BiVO₄⁴¹ or Bi₂WO₃.⁴² The position of the Bi 6*s* band near the VBM indicates the stereochemical activity of the lone-pair 6*s* electrons. Recent hybrid-DFT calculations report the Bi 6*s* DOS peak to be a few tenths of an eV below what was found in an earlier report.⁴³

Several defect formation probabilities within CuBi_2O_4 were calculated; among them, Cu vacancies were found to be the most probable one at oxygen-rich single-phase growth conditions.⁴⁰ Due to the Cu vacancies in CuBi_2O_4 , the O 2p defect bands just above the VBM reduce the band gap closer to the experimental optical gap of 1.75 eV. In addition, due to the dominant presence of Cu 3d band at the CBM of CuBi_2O_4 with Cu vacancy, the photoexcited electron will be excited to the Cu 3d band, irrespective of the presence of a Bi

 δs band near the VBM. It has been claimed that the source of photocurrent in CuBi₂O₄ is due to photo-corrosion, rather than from water reduction.⁴⁴

Tin(II) titanate.—The crystal structure of Sn_2TiO_4 is isostructural to 'red lead' Pb_3O_4 ($Pb^{2+}_2Pb^{4+}O_4$). The presence of Sn(II) and Ti(IV) cations in a single oxide can facilitate the coexistence of *p*-type and *n*-type conductivity with a relatively low optical band gap. From DFT calculations with PBE Sol and HSE06 functionals,⁴⁵ the band structure for Sn_2TiO_4 showed relatively dispersed bands near the VBM and the CBM. Band offset calculations showed that Sn_2TiO_4 has a higher VBM and a lower CBM compared to TiO₂, implying a shallower donor state is possible in Sn_2TiO_4 . An experimental study showed the oxide to have *n*-type character (see also Fig. 2 and Table I),⁴⁶ though the mechanism for the *n*-type character was not presented.

From a structural point of view, a possible *p*-type conduction mechanism is the facile oxidation of Sn(II) to Sn(IV), and the formation of a local surface SnO₂-type structure. A SnO to SnO₂ transition is known to occur near room temperature in air,⁴³ and local lattice distortions can induce such transitions in Sn₂TiO₄. However, the *n*-type conductivity can be rationalized by the mechanism could be due to O-vacancies. The dominant presence of Ti *3d* bands near the CBM implies that the O vacancy defect-state will be of *3d* character and can create a very localized energy level, as is usually found in TiO₂ with O vacancy.⁴⁷

The small bandgap value of this oxide is attributed to the presence of Sn(II) cations, which interact with O 2p states in the valence band and leads to a significantly negatively shifted (higher energy) valence band as compared to most metal oxides.^{45,46} Additionally, a conduction band consisting of low-lying Ti 3d states leads to a conduction band energy that is only slightly greater than the thermodynamic proton reduction potential. Taken together, Sn₂TiO₄ is one of only a few known compounds which not only has a small bandgap that is capable of absorbing a large fraction of the solar spectrum but also maintains suitable band edge energies for overall water-splitting.

In practice, films of Sn_2TiO_4 so far have failed to deliver a performance close to its theoretical potential (see Table I). The underlying factors are still in need of further investigation, but have so far been attributed to large crystallographic anisotropies leading to highly anisotropic carrier mobilities and carrier recombination.⁴⁷ The structure of Sn_2TiO_4 consists of 1-dimensional chains of SnO_3 and TiO_6 polyhedra with no extended connectivity in the other two dimensions. So, while the effective masses are low for photogenerated electrons and holes along the chain direction, the values along the other crystallographic directions are significantly higher.⁴⁶ In any case, films of Sn_2TiO_4 have been shown to generate relatively stable photocurrents at 810 nm (0.8% efficiency).⁴⁷

Barium niobium oxynitride.-BaNbO2N, which forms in the perovskite structure, is a highly promising *n*-type semiconductor for water oxidation. Unlike the other compounds discussed so far, the valence band of BaNbO₂N is not formed from oxygen, but rather, N 2p orbitals. The higher energy N 2p orbitals lead to a more negatively shifted valence band edge for oxynitrides as compared to most oxide semiconductors. The higher energy valence band, combined with a low energy conduction band formed via empty Nb 4d states, leads to a small bandgap of \sim 1.7 eV that is ideal for solar absorption.⁴⁸ Indeed, the small bandgap value leads to a high theoretical maximum solar photocurrent of $\sim 21.8 \text{ mA cm}^{-2}$. Not only does BaNbO₂N have a high theoretical maximum photocurrent, in practice, BaNbO2N also shows some of the highest reported experimental photocurrents for water oxidation under AM 1.5 G. As shown in Fig. 2 and Table I above, films of BaNbO₂N have reached $5.2 \text{ mA cm}^{-2.9}$ While the experimental photocurrent of BaNbO₂N is the largest of any of the compounds discussed here, there is clearly still room for further improvement as the 5.2 mA cm^{-2} only represents $\sim 24\%$ of the theoretical maximum (Fig. 2).

The *n*-type conduction in BaNbO₂N arises from the partial reduction of Nb⁺⁵ to Nb⁺⁴ during the synthesis of the oxynitride, which typically employs ammonia gas as the nitriding agent. Due to the strong reducing potential of ammonia, every known nitride/oxynitride has been found to have *n*-type conductivity. As such, nitrides/oxynitrides have primarily been investigated as photoanodes. Furthermore, the presence of reduced niobium species leads to the formation of deep trap states that have been shown to be highly deleterious for charge separation. There have been several investigations which have attempted to reduce the presence of these trap states via the doping of lower valent transition metals such as Zr⁺⁴ as a means of suppressing the formation of reduced niobium, and in turn, mitigating their impact on charge separation.

Future Needs and Prospects

The preceding section, while summarizing the current status, has also served to identify the voids that currently exist in our understanding of multinary oxides. The defect structures and origins of nor *p*-type conductivity seem rather poorly understood at present. The situation with tin titanate is a case in point. In general, it can be stated that information on the solid-state electronic aspects of multinary oxides, especially of the types considered in this Perspective, is largely outdated and/or is completely lacking. New such studies motivated by the applicability of these materials to solar fuels generation are critically needed. Further studies on impurity doping, both from a predictive theory and experimental validation perspectives, are sorely needed to close the performance gaps in Fig. 2 and Table I. For example, in the case of BiVO₄, we now know that for securing high conductivity, impurity doping is necessary. Conditions prescribed for better *p*-type conductivity include Br, Ca, Na, or K substitutional doping on the Bi site under oxygen-rich growth conditions and for better n-type doping, Mo or W substitutional doping on the V site under an oxygen-poor growth condition.

While initial studies of Sn_2TiO_4 have shown promise as summarized above, further investigations are necessary. In particular, methods to prepare oriented films along the crystallographic directions of high carrier mobility, with an ultimate aim to improve charge transport to the film surface, will be critical for Sn_2TiO_4 realizing its full potential. On the other hand, the highly localized band structure may induce polaron conduction in this material, which could lead to a very small photocurrent, unless dopants can be found analogous to the BiVO₄ case. To test these opposing scenarios, further experimental and theoretical studies are warranted.

Recent work on Sn(II) containing perovskite solid-solutions of composition $(Ba_{1-x}Sn_x)(Zr_{1-y}Ti_y)O_3$ have shown promisingly small bandgaps and have demonstrated photocatalytic activities as suspended powders for water oxidation from visible light with quantum yields of ~0.39%.⁵⁰ However, films of these compounds have yet to be fabricated and thus there are currently no data on their use as photoelectrodes.

It is worth recalling that the theoretical maximum performance for any given material in Fig. 2 and Table I above was computed on the basis of zero recombination anywhere between the point of photogeneration of the electron-hole pairs and their ultimate collection (cf. Fig. 1).

In this context, two paradigms, little or only peripherally addressed here, may be mentioned. The first is the notion of improving carrier separation by mating the oxide nanoparticles considered here with other complementary electron-acceptor components such as graphene. The resultant nanocomposites have the potential to minimize charge carrier recombination via vectorial separation of the photogenerated electron-hole pairs. Indeed, this approach takes a leaf out of Nature's playbook wherein intricately assembled systems consisting of components with complementary functions work together in concert.³⁹

The second paradigm exploits the possibilities with chemically modifying the anion sublattice⁵¹ in the multinary oxide. Thus, in the

eight compounds addressed here, the cation sublattice was modified while in the case of BaNbO2N, both the cation and anion sub-lattices of the perovskite structure, were simultaneously modified to explore the optoelectronic consequences. Will this chemical architecture modification improve carrier separation and collection as well? Much remains to be learnt on these and related structure-property correlations and the possibilities are intriguing.

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