

Narrowing the search for potential hydrogen-generating photocatalysts

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Cationic lone pairs may point the way towards low band-gap metal oxides for solar-driven hydrogen production.

The sun offers an immense amount of free and clean power, which we have not yet begun to seriously exploit. In addition to directly converting sunlight to electrical energy, we could also generate storable chemical energy, to be used at a time of our choosing. The photoelectrochemical (PEC) decomposition of water to form hydrogen and oxygen is ideal for this purpose, since hydrogen can be generated, stored, and later converted to emission-free electricity using fuel cell technologies. The missing link in this idealized cycle is the first step: an efficient and affordable way to generate hydrogen from water and sunlight. The challenge is to find a low band-gap semiconductor that is stable in solution, catalytically active, and has high overall solar-to-hydrogen conversion efficiency.

Metal oxides are ideal candidate photocatalysts because of their low cost and high stability in aqueous solutions.¹ Unfortunately their optical band-gaps generally lie outside the visible range ($> 3\text{eV}$), making them good for transparent electronics,² but bad for solar applications. Despite immense effort, attempts to reduce the band-gaps of catalytically active oxides such as TiO_2 through doping or co-doping have not produced a promising material. We must therefore find new avenues of oxide design.

Millions of potential multi-ternary oxides exist, but researchers need a strategy to identify the most likely material classes. The valence bands of most oxides generally lie well below the water oxidation potential, while the conduction bands straddle the hydrogen reduction potential. Thus, the task requires raising the valence band, not lowering the conduction band. One approach could harness low binding energy cations with an nd^{10} electron configuration, such as Cu and Ag. Alternatively, scientists could use low binding energy ns^2 cations such

as Sn(II), Sb(III), Pb(II), Bi(III). We are currently focusing on the latter.

Typical metal oxides such as MgO and ZnO have band edges formed from occupied O $2p$ and unoccupied cation s orbitals, respectively. Heavier post-transition metal cations are unique because the binding energy of the cation s orbital increases, giving rise to two accessible oxidation states. These orbitals are either nominally filled or empty, such as Sn(II)O/Sn(IV)O₂ and Sb(III)₂O₃/Sb(V)₂O₅. The filled orbitals were historically thought chemically inert, but stereochemically active. However, we recently showed that cation s – anion p hybridization dominates in these systems and second order cation p coupling with the antibonding cation s – anion p states occurs towards the top of the valence band.^{3–7} We also verified this theoretical understanding with hard x-ray photoemission spectroscopy.⁸

Bismuth vanadate (BiVO_4) is a ternary oxide combining Bi(III) $6s^2$ and V(V) $3d^0$ cations, as shown in Figure 1. It has a well-demonstrated potential for water photodecomposition with the presence of both a low band-gap (2.4eV) and reasonable catalytic activity.¹ We used density functional theory to analyze its electronic structure and explain its unusual properties.⁹ BiVO_4 has a direct fundamental band-gap, with the Bi $6s$ states helping to raise the valence band by 0.4eV, while the conduction band remains low because of the V $3d$ states. Both the electron and hole effective masses are relatively light, indicating the potential for both p and n -type conductivity.

The combination of ns^2 and nd^0 cations generally results in unique crystal structures because the ns^2 ones have a strong preference for disordered coordination that varies with the cation s binding energy. This is demonstrated by BiVO_4 , which has distorted 2D stacking of Bi–O–V layers with C_{2h}^6 symmetry. The generality of this cation combination is apparent from a recent optical evaluation of ternary tungstenates by

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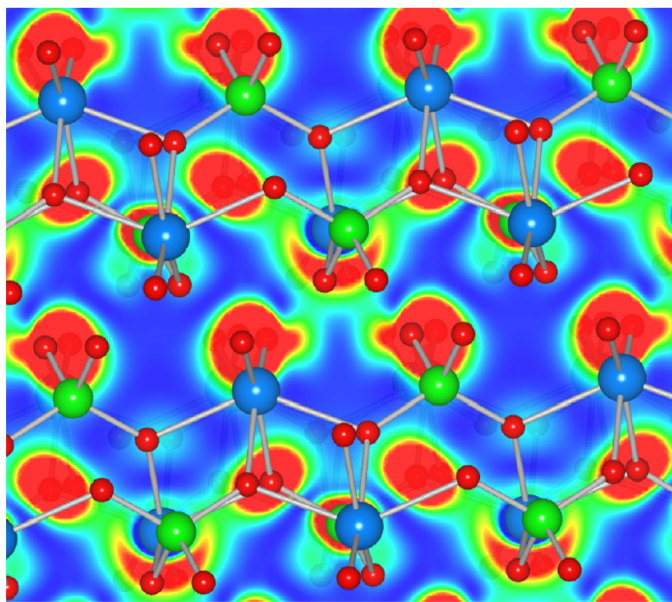
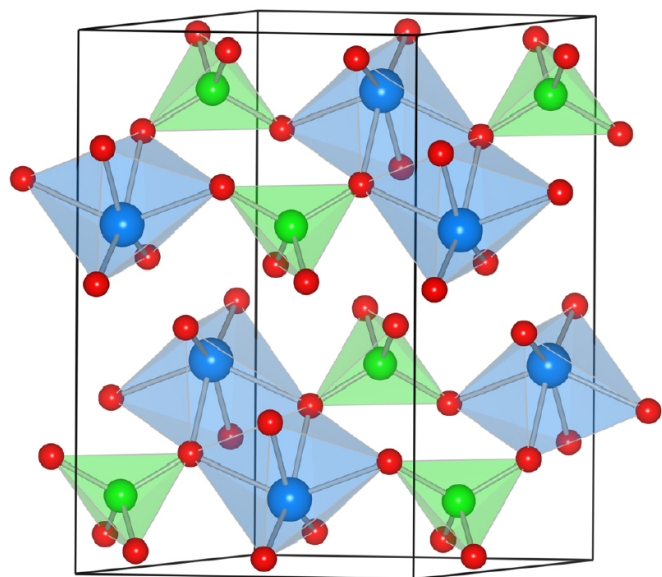


Figure 1. Crystal structure representation (top) and a 2D valence electron density slice of BiVO₄ (bottom). The bismuth atoms are colored blue, with green vanadium and red oxygen.

Lacombe-Perales et al.¹⁰ They found Sn(II)WO₄ to have a remarkably low band-gap of 2.5 eV. Both the increase in valence band energy and the added band dispersion of the ns² cations are highly beneficial characteristics, which can be coupled with the well-established catalytic activity of nd⁰ cations, such as TiO₂, WO₃.

We are also exploring another route for lowering metal oxide band-gaps for PEC applications (see Figure 2), forming ternary

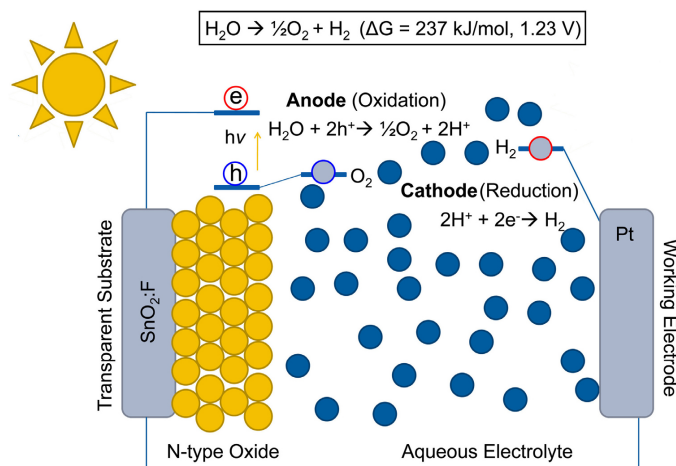


Figure 2. Light impacts the oxide electrode and generates an electron-hole pair, which separate. This causes the formation of oxygen gas at the metal oxide surface and hydrogen gas at the working electrode surface.

systems that combine transition metal 3dⁿ and ns⁰ cations to produce Co_{3-x}Al_xO₄ and related compounds.^{11,12} This homologous series of spinel compounds offers great flexibility in the optical band-gap through substitution on the spinel octahedral sites. For example, the band-gap decreases as you move down group 13 from Al to In. Unfortunately, in experiments, such low gap systems have poor transport properties, due to the high localization of the transition metal 3d states and subsequent small polaron-dominated carrier mobility.¹³ This route seems more problematic than using low binding energy nd¹⁰ or ns² cations.

Commercialization of solar-driven hydrogen production hinges on the discovery of a cheap, stable, and photoactive semiconductor. Chemical intuition can help narrow the search. Taking metal oxides as a target system, we argue that the combination of ns² and nd⁰ cations offer a viable route, combining the high valence band produced by the first with the catalytic activity of the second. Possible combinations can be drawn from (Sn, Sb, Pb, Bi)_x(Ti, V, Nb, Mo, Ta, W)_yO_z. We are currently exploring this avenue through theoretical modeling, which will be complemented by experimental synthesis and characterization when promising candidate materials are identified.

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Aron Walsh obtained his BA and PhD in chemistry from Trinity College, Dublin in 2003 and 2006. For his thesis work, under G. W. Watson, he received the Royal Irish Academy Prize for Young Chemists in 2006. His present work with Su-Huai Wei concerns the application of electronic structure theory to photoelectrochemical hydrogen production, solid-state lighting, and photovoltaic materials. He has been awarded a (European Union) Marie Curie Fellowship to work with C. Richard A. Catlow of the University College, London starting this summer.

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