TORICAL REVIEW

Designing catalysts for water splitting based on electronic structure considerations

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Keywords: photocatalyst, band alignment, electronic structure, water splitting, hard x-ray photoelectron spectroscopy

Abstract

The disproportionation of H2O into solar fuels H2 and O2, or water splitting, is a promising strategy for clean energy harvesting and storage but requires the concerted action of absorption of photons, separation of excitons, charge diffusion to catalytic sites and catalysis of redox processes. It is increasingly evident that the rational design of photocatalysts for efficient water splitting must employ hybrid systems, where the different components perform light harvesting, charge separation and catalysis in tandem. In this topical review, we report on the recent development of a new class of hybrid photocatalysts that employs MxV2O5 (M = p-block cation) nanowires in order to engineer efficient charge transfer from the photoactive chalcogenide quantum dots (QDs) to the water-splitting and hydrogen evolving catalysts. Herein, we summarize the oxygen-mediated lone pair mechanism used to modulate the energy level and orbital character of mid-gap states in the MxV2O5 nanowires. The electronic structure of MxV2O5 is discussed in terms of density functional theory and hard x-ray photoelectron spectroscopy (HAXPES) measurements. The principles of HAXPES are explained within the context of its unique sensitivity to metal 5(6)s orbitals and ability to non-destructively study buried interface alignments of quantum dot decorated nanowires i.e., MxV2O5/CdX (X = S, Se, Te). We illustrate with examples how the MxV2O5/CdX band alignments can be rationally engineered for ultra-fast charge-transfer of photogenerated holes from the quantum dot to the nanowires; thereby suppressing anodic photo-corrosion in the CdX QDs and enabling efficacious hydrogen evolution.

1. Introduction

One of the most critical challenges for today’s world is to meet its ever-increasing energy demands. For years, mankind has heavily relied on limited natural resources, such as fossil fuels and natural gas to meet its indispensable energy needs. Transportation is the single largest source of fuel consumption worldwide and consumes $1.7 \times 10^{19}$ J of energy per year from gasoline in the U.S. alone [1]. This has led to increased CO2 emissions and posed existential threats, such as climate changes [2, 3]. Developing alternative renewable energy resources which are clean and abundant, has therefore, become more urgent than ever before. Hydrogen is regarded as one of the cleaner alternatives to fossil fuels since it does not emit CO2 upon combustion. The U.S. Energy Information Administration anticipates growth of the energy contribution from hydrogen from $2.6 \times 10^{16}$ J per year to $5.0 \times 10^{18}$ J per year by 2050 [1]. In order to make hydrogen economically competitive
with the conventional fuels, the U.S. Department of Energy has supported the pursuit of low cost methods of hydrogen production with a targeted end user cost of $4/gasoline gallon equivalent [4]. The photoelectrochemical (PEC) splitting of water into hydrogen and oxygen gas in the presence of sunlight (equation (1)), presents a low cost and renewable method of large scale hydrogen production using water and sunlight: [5–9]

\[ \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2 \]  

(1)

1.1. Photolysis of water: basic principles

Figure 1(a) summarizes the principles of water splitting, involving the (i) generation of photo-generated excitons; (ii) charge separation of the exciton is required to avoid the their recombination and facilitate the (iii) transport of the electrons and holes to the hydrogen and oxygen evolving half reaction sites, respectively. The generation of hydrogen and oxygen from water splitting requires a thermodynamic potential of 1.23 eV. However, recombination of the photo-generated charge carriers and other energy losses increases this value to \( \sim 1.8 \) eV. For this reason, direct sunlight-driven water splitting cannot be accomplished due to the insufficient energy of the solar spectrum [10]. Semiconductor photocatalysts are thereby required to absorb solar energy and catalyze water splitting. Typical photocatalysts function by absorbing photons with energy higher than their band gap energy \( (E_g) \) and excite photoelectrons into the conduction band and holes into the valence band. The photo-generated electrons and holes then become available for photocatalytic oxidation of adsorbed water molecules and reduction of protons producing gaseous oxygen (equation (2)) and hydrogen, respectively (equation (3)) [11]. A single semiconductor is inefficient in performing the full water splitting process due to the issue of recombination and the need for spatial separation of the two half reactions.

oxidation: \( \text{H}_2\text{O} + 2h^+ \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2 \)  
reduction: \( 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \)  

(2)  
(3)

Figure 1(b) demonstrates a schematic of the photoelectrochemical cell derived from the original demonstration of water photolysis of water using a semiconductor electrode by Fujishima and Honda in 1972 [5]. The photoelectrochemical cell contains two main electrodes: a semiconductor (n- or p-type) working electrode (WE) and a platinum (Pt) counter electrode (CE). Often, a third reference electrode (RE) is used to measure or set the potential of the working electrode. For n-type semiconductors, the photogenerated holes oxidize the adsorbed water molecules to produce oxygen gas (equation (2)), while the electrons are transferred to the counter electrode, where they reduce \( \text{H}^+ \) into \( \text{H}_2 \) gas (equation (3)). In contrast, \( \text{H}_2 \) evolution occurs on the catalyst when a p-type semiconductor catalyst is employed, while \( \text{O}_2 \) evolution occurs at the (dark) counter electrode [7]. The selection of the n- and p-type semiconductor catalysts is furthermore determined by the precise positioning of the conduction band and valence band edges. For example, a wide band gap oxide, TiO\(_2\), which absorbs in the UV regime was employed in the seminal work by Fujishima and Honda [5]. The valence band edge of TiO\(_2\) is derived from the filled O 2p shell and is situated at a very negative potential compared to the oxidation potential of water, therefore requiring a highly undesirable \( \sim 2 \) V over-potential. For efficient visible light photolysis of water, the employed semiconductor electrode should have a band gap of \( \sim 2 \) eV, with the conduction band minimum higher than the proton reduction potential and valence band maximum lower than the oxidation potential of water [12].

1.2. Practicalities of photoelectrochemistry

For semiconductors that are deemed suitable for photocatalytic water splitting, figure 2 summarizes schematically the photoelectrochemical studies need to be performed in order to systematically and reproducibly
Figure 2. (Right) The development of photocatalysts begins with materials design. Important benchmarks include, optical and electrical properties; incident photon-to-current (IPCE) and solar-to-hydrogen (STH) efficiencies; and, photocatalytic stability. Traditionally, these benchmarks are used to provide feedback to optimize the materials selection/design and synthesis but can be considerably time consuming and lead to minor alterations to the original design. (Left) An accelerated rational design approach focuses on the materials design by considering the electronic structure of the active materials and the interfaces they form. This approach can result in a paradigm shift in the design of the photocatalyst where initial promising but sub-optimal candidates can be engineered for photocatalysis by high-throughput screening and chemical analysis. Reaction scheme modified and reprinted with permission from [13]. Copyright (2018) American Chemical Society.

quantify H₂ generation. For materials exhibiting a favorable band gap and band offsets, the first step would be to determine the conductivity and flat band potential (V_{FB}) of photoelectrodes. The illuminated open circuit potential (OCP) is the simplest way of determining the V_{FB} [14]. When illuminated under an applied electric field, the photogenerated electron–hole pairs are separated. A field opposing the applied electric field is generated by majority carriers, while the minority carriers move towards the semiconductor/electrolyte interface. When the applied field becomes equal to the opposing electric field, the voltage between the reference electrode and semiconductor approximates the V_{FB}. The OCP can also help determine the type of conductivity observed in the material. For a given material, if the OCP moves towards anodic potentials under illumination (positive direction), the material is p-type, and vice versa. Alternatively, the Mott–Schottky relationship can also be used to determine the V_{FB}. Practically, this is achieved by measuring the capacitance of the space charge layer of the semiconductor electrode as a function of the applied potential (V). A third method that can be employed is three-electrode cyclic voltammetry (CV), wherein the onset of photocurrent is measured under photoillumination and in darkness [15]. However, the estimation of V_{FB} using the CV method is generally not accurate due to corrosion of the photoelectrode. CV method is also used to measure the saturated photocurrent density in order to determine the hydrogen production rate [16]. The next step delineated in figure 2 is to evaluate the materials’ innate ability to convert incident photons to collected (i.e., as measured by an external circuit) electrons over a specific range of photon energy. This is achieved by measuring the incident photon-to-current efficiency (IPCE), which is also equal to the external quantum efficiency (EQE). IPCE (equation (4)) describes the photocurrent collected per incident photon flux (j_{ph}) as a function of illumination wavelength (λ). The efficiency is derived simply as a function of electrons out per photons in and is expressed mathematically as the ratio of photocurrent measured in a chronoamperometry experiment using a monochromatic light source to the wavelength-dependent rate of incident photons. This method can also be used to determine band gap, with some limitations [16].

\[
\text{IPCE} = \text{EQE} = \left[ \frac{|j_{ph}(\text{mA cm}^{-2})| \times 1240(V \times \text{nm})}{P_{\text{mono}}(\text{mW cm}^{-2}) \times \lambda(\text{nm})} \right] \quad (4)
\]

where 1240 V × nm refers to a multiplication of h (Plank’s constant) and c (the speed of light), P_{mono} is the power intensity in (mW cm⁻²).
The solar-to-hydrogen efficiency (STH) is another important parameter which describes the overall efficiency of PEC water splitting device under broadband solar irradiation (AM 1.5 G) without applying voltage between the WE and CE. For direct STH measurements, the WE and CE are immersed in solutions with same pH. For accurate determination of STH values, the electrolyte employed should not contain any sacrificial acceptors or donors. STH efficiency is defined as chemical energy produced per unit solar energy input as given by equation (5).

\[
\text{STH} = \frac{\text{(mmolH}_2\text{/s)} \times (237 \text{kJ mol}^{-1})}{P_{\text{total}}(\text{mW/cm}^2) \times \text{area(cm}^2)_{\text{AM1.5G}}}
\]

where the chemical energy produced is defined by the product of the rate of hydrogen production (mmol H\textsubscript{2}/s) and the known change in Gibbs free energy per mol of H\textsubscript{2} at room temperature (\(\Delta G = 237 \text{kJ mol}^{-1}\)) and the solar energy is defined as the product of the incident illumination power density (\(P_{\text{total}}\)) and the illuminated electrode area.

If the short circuit photocurrent of the material is significant, the next step is to measure the Faradaic efficiency of water splitting by performing a mass spectrometry or gas chromatography experiment in order to quantify O\textsubscript{2} and H\textsubscript{2}. Finally, the stability of material should be studied for reasonable duration of time (typically 200 h in laboratory settings but 5000 h for industrial benchmarking) [16].

### 1.3. Rational development of PEC materials: electronic perspective

Any development of photocatalysts for water splitting should include the aforementioned steps, since the band gap and band alignment with the water redox levels alone cannot guarantee photolysis. Kinetics of the various charge-transfer processes dictate water-splitting efficiency. However, it is clear that the initial step of materials design is critical to the advancement of efficient visible light photolysis of water for hydrogen generation. The traditional approach to developing PEC materials relies on both chemical modification (e.g., chemical doping/substitution) of existing photocatalysts, such as TiO\textsubscript{2}, or replacement of TiO\textsubscript{2} with smaller band gap semiconductor candidates. The efficiency of such an approach is necessarily dependent on the successful integration of a high throughput synthesis method with PEC measurements to accelerate the iterative approach to system optimization [17–20].

A modern combinatorial approach involves the accelerated screening of candidate materials for ideal band gaps and offsets for the semiconductor. This approach has been more broadly employed since 1995 in order to develop semiconducting materials [21]. Improvements in density functional theory (DFT) computations over the last decade have enabled computational screening of candidate materials based on thermodynamic considerations to predict the bulk properties, including overcoming some of the issues associated with underestimating band gap energies within DFT [22, 23]. These advances have included hybrid functionals that go beyond the local density approximation (LDA) and generalized gradient approximation (GGA) in the Kohn Sham equation by incorporating a portion of the exact exchange from Hartree Fock theory derived from considering full Schrödinger solutions of molecules e.g., B3LYP, PBE0 and HSE [24–26]. In this manner, DFT calculations can be employed to accurately predict bulk properties of new semiconducting candidates [27]. The increased computational cost associated with hybrid functionals limits their use for high-throughput screening and often a GGA level calculation is employed for initial evaluation, where further improvement without significant cost is usually done by GGA + U [28]. On-site Coulomb interactions are neglected in band theory and the +U correction is used to account for the strong on-site Coulomb interactions of localized d and f electrons [29, 30]. Nevertheless, opensource databases such as the Materials Project based on DFT + U provide researchers with cost-effective, data-driven avenues for materials design [31]. Using this accelerated approach one can identify new compounds to synthesize in order replace the original TiO\textsubscript{2} semiconductor electrode. However, it is important to note that hybrid DFT and even DFT + U calculations do not explicitly consider on-site Coulomb interactions sufficiently and may not be suitable for considering mixed 3d cation oxides. A recent example is the band gap of ZnTM\textsuperscript{III}O\textsubscript{4} spinels where experimental verification of the electronic structure from x-ray spectroscopy methods was ultimately required to explain the band gap evolution [32]. As a result, experimental verification of screened candidates from high throughput screening methods is still integral to materials discovery.

There is growing recognition that heterojunctions are necessary for achieving effective separation of photo-generated excitons. Accelerated materials design for efficient water splitting photocatalysts necessitates consideration of hybrid systems, where the different components perform light harvesting, charge separation and catalysis. The synergy between the different components must be considered in the design in order to achieve overall optimization. This has led to the development of bilayered systems [33, 34], which comprise of two closely-interfaced semiconductor photocatalysts. Bilayered systems soften the stringent materials property...
requirements (i.e., alignment of the band edges of a single material with both the water oxidation and hydrogen reduction potentials) since these requirements can be independently satisfied by two different materials (figure 3(b)). High-throughput computing can again screen candidates for the hydrogen and oxygen evolving catalysts, but these calculations are usually limited to bulk considerations that most often do not incorporate interfacial effects that impact charge separation. The reduced symmetry of the interfaces makes them computationally much more challenging to address using DFT. Computational predictions of interface band alignment for electrochemical systems have been successful in some specific cases [23], but is not at the same stage of high throughput screening as for bulk materials discovery. As a result, a rational design approach incorporating techniques sensitive to the thermodynamics (i.e. band offsets) and kinetics (i.e. transfer rates) of the heterojunction must be employed in concert with high throughput synthesis and modeling. This approach can be further adapted to new designs employing an efficient quantum dot light harvester interfaced with an engineered semiconductor, where hole-induced photo-corrosion in the QD is circumvented by engineering efficient charge separation and transfer at energies closer to the desired redox levels (figure 3(c)).

In this topical review, we summarize the development of visible light semiconductor photocatalysts from an electronic structure perspective emphasizing the critical role of interfaces. We focus on the development of nano-engineered nanowire (NW)/quantum dot (QD) heterostructures that have recently demonstrated to be viable photocatalytic architectures capable of efficacious hydrogen evolution [13, 35–37]. The topological synthesis of ternary M₅V₂O₅ nanowires, where M is a lone pair active (N − 2)s² ion, presents a new class of charge-separation components where improved band alignment with the H₂O/O₂ redox can be engineered. The electronic structure of the ternary hole acceptor materials can be modulated through the selective intercalation of post-transition metal ions into crystallographically distinct sites in the interstices of the V₂O₅ structure. Bonding between the inserted ions (M) and the V₂O₅ structure induces oxygen mediated lone pair states, these ‘mid-gap states’ are extended in nature since they originate for atoms in well-defined crystallographic sites. These lone pair induced ‘mid-gap’ states allow for band engineering of the interfacial alignment between the nanowire and QD valence band edges; thereby promotes hole transfer from the photoexcited QD to the nanowire for water oxidation catalyst at energies close to the H₂O/O₂ redox level. The measured electronic structure of post-transition lone pair active metal oxides can be adequately described using DFT at the GGA level when spin–orbit coupling (SO) is included [38, 39]. This topical review examines the underlying measured and computed electronic structure of the ternary M₅V₂O₅ nanowires and the experimentally-verified band alignments after decorating the nanowire with the light harvesting quantum dots. Hard x-ray photoelectron spectroscopy (HAXPES) is highlighted as an important tool for engineering photcatalysts from an electronic structure perspective. HAXPES can both validate materials screening of ternary M₅V₂O₅ due to its sensitivity to the metal s-derived lone pair states and determine the valence band offsets of engineered NW/QD heterojunctions due to its increased effective probing depth (compared to traditional XPS). The photo-electrochemical performance of engineered NW/QD photocatalysts is explained in terms of the electronic structure of the heterojunction formed.
2. Electronic configurations of photocatalysts

Metal oxide semiconductors are amongst the most investigated materials for photocatalytic applications due to their low cost, high chemical stability, robust photostability, and ease of fabrication [40]. TiO$_2$ was the first metal oxide semiconductor used for photocatalytic water splitting applications [5, 41]. TiO$_2$ exists in three polymorphs: anatase($\beta$-TiO$_2$, I$_4$/amd), rutile ($\alpha$-TiO$_2$, P4$_2$/mmn), and brookite ($\gamma$-TiO$_2$, Pbca), of which rutile is the thermodynamically-stable phase at room temperature and atmospheric pressure. The rutile and brookite phases each have a direct band gap, while the anatase has an indirect gap. For photocatalytic applications, the anatase phase is preferred, because the indirect band gap increases the lifetime of the photogenerated electrons and holes by hindering the transition of electrons from the conduction band to the valence band. In addition, the effective mass of the photogenerated electrons in the anatase phase is lighter than in the rutile phase, which facilitates the migration of photogenerated electrons and holes from bulk to the surface of TiO$_2$, resulting in lowering the recombination rate [42]. Recently, the ionization potential of the anatase phase was revealed to be higher than rutile phase demonstrating the need to incorporate electronic structure studies even in ‘traditional’ semiconductors [43].

A cocatalyst plays an important role in facilitating charge transfer, enhancing light harvesting and decreasing overpotential [44]. Compared to other metals, Pt is the most efficient cocatalyst, acting as an electron sink due to its work function and lower overpotential for the hydrogen evolution reaction [45]. The more positive work function of Pt in comparison to the conduction band of TiO$_2$ favors electron transfer from TiO$_2$ to Pt. While TiO$_2$ is cost effective and stable photocatalyst, its band gap (3.2 eV) is 2 eV larger than the redox potential of water [46]. Although nanostructuring of TiO$_2$ materials has been shown to increase the number of reaction sites, the large band gap limits the water splitting under UV light irradiation, which constitutes only \(\sim 2\%–3\%\) of sunlight [47]. The inefficient harvesting of the solar spectrum thus limits the applicability of TiO$_2$ as a commercial photocatalyst [48]. One approach to improving the performance of TiO$_2$ materials involves reducing the band gap by doping with main group elements such as nitrogen and carbon. Doping can either lower the conduction band (CB), raise the valence band (VB), or create ‘in-gap’ defect states, all of which lead to a reduced band gap. Nitrogen-doping into TiO$_2$ raises the valence band edge through contribution of N 2p states that can hybridize with the O 2p states (figure 4), giving rise to a p-type semiconductor [47, 49]. However, the localized nature of the defect-induced ‘in-gap’ states resulting from doping may also trap the photogenerated charge carriers, giving rise to decreased photocatalytic activity [47].

In order to facilitate increased solar efficiency, it is important to screen metal oxide candidates from an electronic structure or chemical intuition perspective [50]. Both $d^0$ and $d^{10}$ metal oxides have a deep O 2p derived valence band which results in a wide band gap with good CB alignment with the hydrogen evolving redox potential but poor VB alignment with the oxygen redox potential, as shown in figure 4. Post-transition metal oxides provide robust properties, for example ZnO is a stable photocatalyst in an aqueous electrolyte [51]. However, due to a large band gap of 3.4 eV of these oxides (figure 4), these oxides can absorb only in the UV region of the solar, which is \(\sim 2\%–3\%\) of sunlight [47]. The inefficient harvesting of the solar spectrum thus limits the applicability of TiO$_2$ as a commercial photocatalyst [48]. One approach to improving the performance of TiO$_2$ materials involves reducing the band gap by doping with main group elements such as nitrogen and carbon. Doping can either lower the conduction band (CB), raise the valence band (VB), or create ‘in-gap’ defect states, all of which lead to a reduced band gap. Nitrogen-doping into TiO$_2$ raises the valence band edge through contribution of N 2p states that can hybridize with the O 2p states (figure 4), giving rise to a p-type semiconductor [47, 49]. However, the localized nature of the defect-induced ‘in-gap’ states resulting from doping may also trap the photogenerated charge carriers, giving rise to decreased photocatalytic activity [47].

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Since no single semiconductor can perform the entire water splitting process alone, bilayered systems were developed; two interfaced semiconductors can absorb a larger part of the solar spectrum resulting in improved efficiency as shown in figure 3(b)) [34]. The bilayered system consists of two semiconducting materials; one is hole accepting, while the other is electron accepting, and each is aligned with a single redox level. The interface between the two semiconductors serves as a heterojunction across which charge separation of electrons and holes can occur [56]. The interface reduces the recombination of photogenerated electron–hole pairs by forming an internal electric field at the heterojunction [34]. The semiconductors used in the bilayered systems can include narrower band gap candidates (<1.8 eV) since they do not need to straddle both redox levels (figure 3(b)). Bilayered configurations therefore permit consideration of n-type and p-type metal oxide semiconductors with narrower band gap candidates. In general, the CB alignment with hydrogen evolving redox is not an issue for most n-type post-transition metal oxides. However, p-type conduction is inherently difficult in wide band gap metal oxides, since one is essentially attempting to oxidize oxygen lattice ions. Metal orbital character at the valence band maximum is required to generate mobile holes as demonstrated by the development of p-type Cu delofoisite oxides [57]. From a defect formation energy perspective, the hybridization of metal orbitals is required to reduce the ionization potential (IP, energy difference between the vacuum level and the VBM) to facilitate the formation of holes [58]. As a result, other electronic configurations need to be
Figure 4. The band edges of various metal oxide semiconductors aligned to the standard hydrogen electrode. The redox potentials are illustrated referenced to the standard hydrogen electrode (SHE) at $-4.4 \text{ eV}$ [76], along with the orbital character of the band edges and the nature of their band gap (indirect or direct) of the semiconductors. The lone pair active BiVO$_4$ displays improved valence band alignment with the vexing O$_2$/H$_2$O redox for water oxidation.

considered where the IP can be raised to generate mobile holes at energies closer to the water oxidation redox level.

Variations of the electronic configurations, i.e. d$^n$ with $n$ other than 0 or 10 can result in less than desirable properties. Fe$_2$O$_3$ ($\sim 2.0 \text{ eV}$) is an example of metal oxides with d$^5$ that can absorb light in the visible region [59], but the transport and extraction of the photo-generated carriers is inefficient due to small polaron formation causing low conductivity and high resistivity [60]. Cu$_2$O (d$^{10}$) is an example of a material with a small band gap ($\sim 2.0 \text{ eV}$) that can absorb light in the visible region (figure 4), but it corrodes when dipped in the electrolyte [61]. In addition, the IP is raised such that the VBM is actually higher than the potential of H$_2$O/O$_2$. As a result, Cu$_2$O may be used as a co-catalyst, but not as a single photocatalyst [44]. In addition, not all metal oxides with d$^{10}-n$ can be used as a photocatalyst. For example, VO$_2$ is a transition metal oxide with d$^1$ configuration. There are two phases of VO$_2$: metallic (rutile, ‘R’) and semiconducting (monoclinic, M$_1$). The metallic rutile phase is not useful for photocatalytic applications, and strong V 3d contributions to the bands in the M$_1$ phase result in a band gap of $\sim 0.6 \text{ eV}$ which leads to poor band edge alignment to water redox potentials [62]. Other materials with partially filled d orbitals result in recombination centers which can limit photocatalytic activity [33].

2.1. Revised oxygen mediated lone pair model for post-transition metal oxides

A successful approach for identifying suitable p-type photo-catalysts is incorporating d$^6$ or d$^{10}$ transition metals with s$^2$d$^{10}$ metals [50, 63, 64]. The states derived from the additional p-block s orbitals will contribute to the top of the valence band thereby decreasing the band gap by shifting the band edge to a more negative potential [65]. More specifically, it is important to consider $(N - 2)$ post transition metal oxides, where $N$ is the number of valence electrons.

Metals in group 13–16, such as Sn$^{2+}$ [13, 66–68], Pb$^{2+}$ [36, 66, 69, 70], or Bi$^{3+}$ [66, 71, 72] often have stable $N - 2$ oxidation states leading to electron configurations that retain populated metal s orbitals (i.e., d$^{10}$s$^2$p$^6$). For this reason, metal oxides incorporating these elements can exhibit lone pair distortions in post-transition metal oxides e.g. PbO and SnO [73, 74]. A combined DFT and x-ray spectroscopy study led by Graeme Watson and Russel Egdell in the 2000s determined the underlying electronic origins of the structural distortions i.e., the oxygen mediated lone pair model [38, 75]. The lone pair s$^2$ electrons hybridize with oxygen 2p orbitals to generate the bonding (B) and antibonding (A) states at the bottom and top of the valence band, respectively. The resultant lattice distortions allow for the metal p orbitals to hybridize with the antibonding states, leading to the stabilization of energy levels formed. The choice of post-transition metal will dictate the degree of hybridization and thereby, overall stability of the material. The d$^{10}$s$^2$p$^6$ electronic configuration leads to a lower effective mass of charge carriers, favoring charge transport through materials, and adsorption of visible light. All of these characteristics are important to photocatalysts, which have made this class of materials, oxygen mediated lone pair post transition metal oxides, of interest for photocatalysis [75].

The oxygen mediated lone pair distortion can be illustrated by comparing the difference between Sn(II)O and Sn(VI)O$_2$ [38, 75]. The calculated partial density of states (PDOS) of SnO$_2$, SnO, and Sn$_2$O$_4$ are shown in figure S(a). In case of SnO$_2$, the valence band is predominantly O 2p, while the conduction band is Sn 5s in
character. Furthermore, the conduction band minimum (CBM) of SnO₂ is lower than the hydrogen reduction potential, which makes it unsuitable for water splitting applications since Sn⁴⁺ cannot be oxidized further [77]. In contrast, SnO, a p-type semiconductor with a 5s² 4d¹⁰ electronic configuration, exhibits an upward shift of the VBM due to the states resulting hybridization of Sn 5s and O 2p [78]. The calculated charge density plots in figure 5(b) reveal the spatial distribution of the hybridized orbitals at the bottom (B) and top (A) of the valence band of SnO. Peak B (−13.0 and 11.5 eV) displays strong orbital bonding between the Sn and O atoms due to the overlap of the Sn 5s and O 2p orbitals. Meanwhile, peak A (−6.0 and −4.5 eV) reveals the characteristic asymmetric lobe centered on the Sn atom projected into the interlayer spacing characteristic of the lone pair state [78]. However, the lone pair mechanism for SnO results in a valence band edge above the standard hydrogen electrode (SHE) and is therefore not well suited to water splitting applications [79]. Sn₃O₄, on the other hand, represents an intermediate scenario, where the presence of Sn²⁺ and Sn⁴⁺ gives rise to a smaller band gap than SnO and a more negative valence band edge than SnO. Figure 5(c) summarizes the effect of Sn⁴⁺ and Sn²⁺ on the band structure of SnO₂ and SnO₂−ₓ. Experimental confirmation of the SnO electronic structure and band alignment with SnO₂ summarized here has been confirmed using HAXPES, which is discussed further below [80, 81].

In 2014 Piper et al., demonstrated how the revised oxygen mediated lone pair distortion mechanism could be synthetically controlled by incorporating Pb²⁺ ions into the structure of V₂O₅ nanowires, such that the ionization potential could be raised closer to the H₂O/O₂ redox potential [82]. Chemical considerations would suggest that interfacing the synthetic lone pair active β-PbₓV₂O₅ nanowires with dedicated light harvesting quantum dots would present an opportunity to rationally engineer efficient photo-excited charge separation necessary for photocatalysis [35]. For synthetic lone pair metal oxides such as β-PbₓV₂O₅, the valence band alignment could possibly be modified by chemical substitution of the Pb²⁺ ion with alternate (N − 2) post-transition metal ions [82], significantly altering the resultant thermodynamics and kinetics of the photoexcited carriers and thereby the resulted photocatalysis [13, 36, 37]. In order to engineer the offsets at the nanowire (NW)/quantum dot (QD) to tailor the interfacial electronic structure to promote efficient light-induced charge separation and photocatalytic proton reduction requires a technique sensitive to both the lone pair orbital, and buried band offset alignments to guide computational studies i.e. HAXPES [80, 82, 83].

3. Hard x-ray photoelectron spectroscopy (HAXPES)

X-ray photoelectron spectroscopy (XPS) has proven an invaluable tool for measuring the chemical composition and electronic structure of materials, as recognized the award of Nobel prizes in Physics to Albert Einstein in 1921 for ‘his discovery of the law of the photoelectric effect’ [84], and to Kai Siegbahn in 1981 (shared with Arthur Schawlow and Nicolaas Bloembergen) for ‘his contribution to the development of high-resolution electron spectroscopy’ [85]. The major benefit of XPS has been the ability to directly measure the band structure and density of states of materials. An assumption of no further electron rearrangement following the ejection of a photoelectron (i.e., such that the binding energy of the photoelectron is approximated as the orbital energy in the material i.e. Koopman’s theorem) has enabled direct comparison of XPS with DFT calculations [86]. An exquisite example is the angle-resolved photoemission spectroscopy studies of graphite mapping out the Dirac cone responsible for the ultra-high mobility carriers [87]. The reduced symmetry (i.e. 2D) and thickness...
Figure 6. (a) The increased effective probing depth of HAXPES compared to traditional surface-sensitive XPS enables the chemical and electronic studies of the (b) bulk and (c) buried interfaces.

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(i.e. monolayer) associated with graphene makes it ideal for photoemission studies and facilitates direct comparison with calculated energy–momentum band structure calculations using DFT [88]. XPS is referred to as a surface sensitive technique due to the attenuation of the escaping photoelectrons, with typical laboratory based Al Kα sources (1.4 keV) having effective probing depths on the order of 5 nm. Increasing the kinetic energy of the escaping photoelectrons provides a means of increasing the effective probing depth, enabling greater sensitivity to the bulk properties of the solid; this variant is referred to as HAXPES [89].

The first HAXPES study was reported in 1974 using the Stanford storage ring in a parasitic mode [90], but it was the advent of high-performance commercial spectrometers in the mid-2000s that enabled bona fide HAXPES at dedicated synchrotron facilities with total energy resolution comparable to traditional soft x-ray photoelectron spectroscopy [91, 92]. Over the last decade, various HAXPES studies at synchrotrons have demonstrated the ability to obtain precise chemical and electronic information at previously inaccessible buried regions, making it highly appealing for materials and device characterization [83, 89, 91–98]. The increased probing depth of HAXPES enables non-destructive studies of buried interface band alignment in addition to vertical spatial extent of chemical intermixing within manufactured device architectures at technologically relevant dimensions, as summarized in figure 6. Moreover, it can provide comparable information regarding the interfacial quality of oxide/oxide interfaces that can complement traditional STEM-EELS studies [99, 100]. Meanwhile, the increased probing depth of HAXPES affords non-destructive studies of the band alignment of buried semiconductor interfaces as deep as 20 nm (e.g. CdO/SnTe) [83], along with the sensitivity to chemical intermixing (spatial extent and composition).

HAXPES has been restricted to synchrotron facilities largely because conventional laboratory-based x-ray sources cannot generate sufficient brightness to compensate for the plummeting atomic orbital cross-sections at higher photon energies. As a result, only a small number of lab-based systems have been reported, with a typical maximum photon energy of 5.4 keV (Cr Kα) [92]. In addition, the combination of plummeting cross-sections with the e-beam power density limits of traditional solid anode x-ray sources means that chemical studies using these lab-based sources have been restricted to core-levels. Electronic studies of the important bulk valence band regions have thus been completely restricted to synchrotron facilities due to their exceedingly high brightness. Recently, Scienta Omicron have developed a commercial lab-based HAXPES system capable of valence band studies by combining a new, high brightness Ga metal liquid jet source (hν = 9.25 keV) with advanced monochromating optics and a high resolving power EW4000 hemispherical electron analyzer [101]. This review includes recently obtained HAXPES data of lone pair metal ion incorporated V2O5 nanowires, using the Scienta Omicron laboratory based HAXPES.

4. Natural lone pair metal oxide photoanode: BiVO4

Before discussing the synthetic lone pair system i.e. N – 2, MₓV₂O₅ nanowires, we discuss the electronic structure of the lone pair active photocatalyst BiVO₄ [63], as an illustration of combined DFT and x-ray photoemission studies [50, 102]. BiVO₄ can exhibit three phases dependent on synthesis method and temperature [103, 104]: a zircon-type structure with tetragonal symmetry and a scheelite-type structure with a reversible phase transition between monoclinic or tetragonal symmetries. In both polymorphs, each Bi-ion is coordinated by eight O atoms, while each V-ion is coordinated by four O atoms in a tetrahedral site. In the scheelite structure each Bi ion is surrounded by eight VO₄ tetrahedra, while in the zircon structure each Bi ions is surrounded by six VO₄ tetrahedra [105]. The reduced crystal symmetry of the monoclinic phase gives rise to increased distortions around the Bi and V ions compared to the tetragonal scheelite structure [106]. The zircon structure (kinetically stabilized) is formed by low temperature synthesis, while the monoclinic scheelite structure is favored at high temperatures (thermodynamically stabilized). The electronic structure of two phases of
Figure 7. (a) A molecular orbital diagram with respect to the vacuum energy level of BiVO₄. (b) The corresponding DFT computed PDOS of monoclinic BiVO₄ identifying the oxygen mediated lone pair mechanism i.e. bonding and anti-bonding states. (c) A comparison between measured and simulated valence band spectra, accounting for variations in orbital cross-sections. (d) Orbital cross-section dependence as a function of photon energy, the energies used in x-ray photoemission studies are highlighted (dashed lines).

 scheelite BiVO₄ are similar, with a band gap of 2.34 eV for the tetragonal phase and a band gap of 2.4 eV for the monoclinic phase. Despite these similarities and modest differences, the monoclinic phase seems to be the most advantageous for water splitting under both UV and visible light irradiation [107]. The major difference in the photocatalytic activity of two phases derives from distortions in the local structure. The increased distortions of the Bi-O polyhedra in the monoclinic phase coupled with the Bi 6s² lone pair-mediated hybridization raises the VBM and improves the band alignment for photocatalytic performance [63]. The increased symmetry of the tetragonal phase, on the other hand, gives rise to predominantly O 2p character in the VB and V 3d character in the CB.

The monoclinic BiVO₄ can be synthesized from Bi₂O₃ and V₂O₅ [75]. The orbital diagram of oxygen mediated lone pair mechanism for BiVO₄ is shown in figure 7(a). The PDOS derived from DFT with spin orbital coupling (SO) are displayed in figure 7(b) [75], and reveal the oxygen-mediated bonding and anti-bonding states above and below the O 2p-derived valence band. The band gap of ~2.4 eV agrees well with the published band gap and reflects the energy separation between the occupied lone pair orbital state and unoccupied V 3d derived conduction band [102]. Although BiVO₄ has a direct band gap, it suffers from recombination and poor transport of charge carriers which led to the investigation of quantum dots for improved photocatalytic performance [108]. Quantum confinement effects are believed to result in a negative shift of the conduction band and/or oxygen vacancies, which decreases the activation energy for water splitting reactions. Computational studies have investigated the effects of interactions between quantum-sized BiVO₄ clusters and water molecules. Radial distribution calculations showed that water molecules only interact with the bismuth atoms [108].

While BiVO₄ does show improved water oxidation performance against other metal oxides through the incorporation of lone pair active ions into the structure, there still exists a need to reduce the 2.4 eV bandgap. Additionally, raising the valence band edge higher would further improve the band edge alignment with the water-oxidation potential. Although other polymorphs of BiVO₄ do exist (e.g., the monoclinic structure),
single phase monoclinic epitaxial BiVO₄ grown on (001) yttria-stabilized cubic zirconia substrates by molecular beam epitaxy have not improved the ionization potential further [72]. However, BiVO₄ highlights the potential benefit of lone pair engineering that could be achieved with synthetic lone pair systems, such as Pb²⁺-incorporated V₂O₅ [82].

Core-level x-ray spectroscopy techniques played a critical role in verifying the lone pair mechanism in BiVO₄ [38, 75]; the orbital sensitivity to the oxygen-mediated lone pair states is similarly expected to play a critical role in examining the mechanism in the synthetic systems discussed in the review. Here we illustrate the suitability of HAXPES for determining the electronic structure to evaluate DFT, using BiVO₄ as an illustrative example. The lone pair state is adequately described by the GGA + SO DFT calculations without requiring an additional on-site Coulombic (Uₐeff) correction [38, 75]. This is supported by the excellent agreement observed between the DFT and the valence band measured by photon-energy dependent HAXPES. Figure 7(c) shows the valence band spectra of BiVO₄ measured at 6 keV and 1.5 keV. The valence band has primarily O 2p character from ~2–9 eV. The bonding state with a strong Bi 6s character emerges at the bottom of the valence band at around 11 eV. This feature appears more prominent at higher photon energies compared to contributions from p or d orbitals. Similarly, the antibonding state with Bi 6s character appears at the top of the valence band as a result of hybridization of Bi 6s–O 2p states. This results in a slight decrease in the band gap, as expected from the lone pair mechanism, and reducing the ionization potential. These results demonstrate the increased sensitivity of s orbitals to higher photon energies and highlights the importance of HAXPES in investigating the lone pair active systems.

The calculated valence band region of the total DOS for BiVO₄ is shown in figure 7(c). Increasing the photon energy with HAXPES enables the identification of metal s-orbital character of the bonding and antibonding states, due to the relative variation in the orbital cross-sections with photon energy [82]. The cross-section is element orbital specific and decreases as the photoionization energy increases [109]. The bond intensities vary with photon energy and thus also the probability of ionization [110]. From the relative variation of the metal orbital cross-sections with respect to the O 2p orbital, it is possible to distinguish the orbital character of states relative to the main O 2p derived valence band, refer to figure 7(d). This must be accounted for in DFT calculations. By cross-sectionally weighting the calculated partial density of states for each photon excitation energy, excellent agreement between DFT and XPS/HAXPES is observed, as shown in figure 7(c).

5. Synthetic lone pair metal oxides: MₓV₂O₅

In this section, we examine the ability to synthetically modulate the IP of lone-pair metal oxide nanowires by topochemical synthesis of metastable ternary V₂O₅ nanowires [111]. This approach enables the independent control of polymorph (i.e., vanadium–oxygen framework connectivity), the inserted cation (i.e., incorporated ion, ‘M’), and its stoichiometry. The ability to control these aspects of the composition of these materials makes the MₓV₂O₅ system optimal for high-throughput synthesis, combined with DFT and HAXPES (and transient absorption) studies in order to accelerate materials identification for integration with QDs for further photoelectrochemical inspection as nano-engineered photo-catalysts [13, 35–37].

5.1. Crystalline V₂O₅ polymorphs

British Chemist Sir Henry Enfield Roscoe first reported elemental compositions of the different binary oxides of vanadium in 1867. However, the first established crystallographic data on V₂O₅ was reported in 1936 by Ketelaar, later by Bystrom et al [112], and then by Bachman [113], and solved by Rietveld refinement by Galy et al [114]. The orthorhombic layered structure of V₂O₅ with a space group of Pnma is derived from square pyramidal coordinated vanadium-centered building blocks. Galy suggested that V₂O₅ is best described as [V₂O₅]ₙ layers built up from VO₅ square pyramids sharing edges to form a zig-zag chain along the b-axis and sharing corners along the a-axis [114, 115].

The open layered framework and the facile redox characteristics of the thermodynamically-stable α-V₂O₅ phase made it suitable for different applications ranging from Li-ion batteries, actuators, photodetectors, antifouling films, and catalysts for selective oxidation to electrochromic elements [116, 117]. The only other layered V₂O₅ (γ’-V₂O₅ space group = Pnma) phase can be obtained by de-intercalation of Li ions from the highly lithiated γ-LiV₂O₅ [118]. Recently, another metastable polymorph of V₂O₅ with a quasi-one-dimensional tunnel structure (space group = C2/m) has been stabilized can by hydrothermally de-intercalating Ag⁺ ions from β-Ag₀.₃V₂O₅ using hydrochloric acid. The tunnel framework is stable to temperatures in excess of 600 °C and remains available for chemical or electrochemical re-intercalation of various ions including Mg²⁺ and Li⁺ [111, 119]. These different cations can intercalate into the open tunnel framework by occupying two possible sites (β, and β’) as that are located within tunnels running parallel to the [010] direction. The size and stoichiometry (i.e., ‘x’ in MₓV₂O₅) of the intercalating cation are the main factors
in determining the occupied site. For instance, the preferred site for both Ag$^+$ and Na$^+$ is $\beta$, while Li$^+$ and Cu$^+$ can occupy both sites depending on the stoichiometry [120).

5.2. Electronic structure of V$_2$O$_5$ polymorphs

Certain cations (M) deintercalate from the open tunnel framework of the $\beta$-M$_x$V$_2$O$_5$ structure without inducing significant structural distortions or amorphization of the V–O framework. $\zeta$-V$_2$O$_5$ can be derived from leaching of Ag-ions from $\beta$-Ag$_{0.33}$V$_2$O$_5$ [111, 119], or alternatively by leaching Cu ions from $\beta$’-Cu$_{0.5}$V$_2$O$_5$ [37]. The significant removal of the intercalated cations is verified by studying the oxidation state spectra. The oxidation state of vanadium is investigated by HAXPES in both frameworks (i.e., $\alpha$- and $\zeta$-phases), and both have V$^{5+}$ at $\sim$517 eV. The additional peak of V$^{4+}$ appears in $\zeta$-V$_2$O$_5$ due to some residual Cu/Ag during the synthesis process. The valence band spectrum was measured for both polymorphs and showed a strong contribution of O 2p in the region 2–9 eV.

The electronic structure of both frameworks is also studied by DFT at the GGA level. Figures 8(a) and (b) shows the (partial) density of states (P)DOS of both layered orthorhombic $\alpha$-V$_2$O$_5$ and the tunnel leached structure of $\zeta$-V$_2$O$_5$. For both structures, the valence band is mainly O 2p in origin, whereas the conduction band is largely derived from V 3d states. The calculated band gaps are 1.7 and 1.1 eV for $\alpha$-V$_2$O$_5$, and $\zeta$-V$_2$O$_5$, respectively, in agreement with published reports [111, 121]. The conduction band of $\alpha$-V$_2$O$_5$ shows a split-off band derived from the V 3d$_{xy}$ states. The split-off band in $\alpha$-V$_2$O$_5$ originates from the distortion of octahedral symmetry, which splits the low energy t$_{2g}$ orbitals forming a separated conduction band.

Figure 8 includes the corresponding charge density plots of the valence band maximum (VBM) and the conduction band minimum (CBM) states projected on the (010) plane for both structures. For $\alpha$-V$_2$O$_5$, the VBM state originates from the large V–O bond length and the charge density is located mostly on the oxygen ions. Meanwhile, the CBM state arises from the the hybridization of V 3d$_{xy}$, 2p$_x$/2p$_y$ i.e. split off band [121],
with the charge density plot revealing more orbital overlap between V 3d and O 2p states. The split-off band acts to localize charge and was shown to be responsible for the formation of heavy polaron results in inhomogenous alkali intercalation [123]. In contrast, the $\zeta$-V$_2$O$_5$ does not show a split-off CBM band, as shown in figure 8(b) [124]. The loss of the split-off band is considered beneficial for homogeneous alkali intercalation since $\zeta$-V$_2$O$_5$ has smaller electron polaron diffusion barriers and improved mobility of intercalated cations compared to $\alpha$-V$_2$O$_5$ [119]. The corresponding charge density plot of VBM shows the greatest electron density is around O ion, where it is spherically symmetric, indicative of ionic bonding.

For $d^0$ systems, DFT at the GGA level can adequately describe the electronic structure. Further improvement can be obtained by considering on-site Coulombic interactions, where the lattice parameters and electronic structure for different $U_{\text{eff}}$ (0.0, 3.0, and 6.6 eV) values have already been reported for $\alpha$-V$_2$O$_5$ [122]. There is no relationship between the lattice parameter and the value of $U_{\text{eff}}$. However, the value of the band gap increases with increasing the value of $U_{\text{eff}}$, where it is related with the charge distribution in the V–O(1) bond i.e. split-off band. The value of $U_{\text{eff}} = 3.0$ eV is commonly used for V$_2$O$_5$, since it yields a band gap matching well with the experimental results. DFT + $U$ calculations were recently employed for studying polaron formation associated with the intercalation of lithium ions in both $\alpha$ and $\zeta$ polymorphs [123, 125]. However, we note different values of $U_{\text{eff}}$ were required in those studies.

5.3. Electronic structure of Pb$_x$V$_2$O$_5$

Here, we focus on synthetically introducing lone pair-induced states into the band gap of the host V$_2$O$_5$ by inserting $(N - 2)$ ions into the structure of V$_2$O$_5$ to form $\beta$- and $\delta$-Pb$_x$V$_2$O$_5$ polymorphs [37, 82] to reduce the ionization potential and improve valence band alignment with the water oxidation redox. Figure 9(a) shows the monoclinic structure of $\beta$-Pb$_{0.33}$V$_2$O$_5$ (space group $C2/m$), where the inserted Pb ions occupy the sites along two rows in the tunnel framework. The Pb$^{2+}$ ion is displaced from the center of its polyhedron as a result of the formation of lone pair orbitals.

To adequately account for the revised lone pair mechanism, we reproduced GGA calculations with spin orbital coupling in figure 9, as reported by reference [13]. Additional on-site Coulombic interactions were not included in those studies, and are beyond the scope of this paper. To the best of our knowledge, no reports exist for studying M$_x$V$_2$O$_5$ (M = Pb$^{2+}$, Sn$^{2+}$) where both effects of spin orbit coupling and $+U_{\text{eff}}$ are adequately considered. Here, we directly compare the measured HAXPES spectra of $\beta$-Pb$_x$V$_2$O$_5$ with our GGA + SO calculations. The $s^2$ electrons interact with the anion p states in the valence band giving rise to bonding (B) and anti-bonding (A) states due to the crystal distortion (i.e. lone pair mechanism). In the absence a lattice distortion, the interaction is composed of negative and positive wavefunction overlap, which is not allowed by the crystal symmetry. The formation of crystal distortion allows a stabilization of the occupied electronic states by hybridizing the unoccupied cation p states with the anti-bonding states, and the interaction becomes symmetry allowed. The energy of both anion p and cation s states is vital in distorting crystal structure (i.e. formation of stereochemically active lone pair). If the cation s has a significant contribution in the top of the valence band, the stronger stabilization of the anti-bonding state will occur and vice versa [75]. The calculated isodensity plots of the oxygen-mediated bonding and antibonding states are shown in figure 9(b) with the latter revealing the characteristic lone pair orbital lobes.

Experimental confirmation of the Pb$^{2+}$ in $\beta$-Pb$_{0.33}$V$_2$O$_5$ was determined using HAXPES, where the presence of Pb$^{2+}$ was confirmed and quantified from the binding energy of the Pb 4f doublets (figure 10). The insertion of Pb into the structure requires a concomitant reduction of V$^{5+}$ to V$^{4+}$, also evidenced from HAXPES (figure 10). The amount of intercalated Pb$^{2+}$ can be quantified based on the ratio of V$^{4+}$ to V$^{5+}$ contributions using a simple peak fitting method [82].

The measured valence band spectrum of $\beta$-Pb$_{0.33}$V$_2$O$_5$ is shown in figure 9(c) from variable photon energy studies employing both Synchrotron and lab-based HAXPES (i.e., 9 keV), with direct comparison to the pristine $\zeta$-V$_2$O$_5$. The valence band with predominantly O 2p character extends from $-9.9$ eV [82, 121]. Pb$^{-}$insertion gives rise to noticeable changes in the valence band region of $\beta$-Pb$_{0.33}$V$_2$O$_5$. A prominent peak emerging at $\sim$9.7 eV is attributed to the bonding state resulting from the hybridization of Pb 6s–O 2p states with predominantly 6s character. Note that the intensity of this feature increases with increasing photon energies from 4 keV to 9 keV due to increased sensitivity of the metal s orbitals at higher photon energies [82]. Additionally, the valence band develops a shoulder, as a result of antibonding states, which extends from the VBM inward by 0.8 eV. This shoulder extends the edge of the valence band and is clearly separated from the partially V 3d states at the bottom of the conduction band, as shown in the lower energy XPS measurements due to the increased sensitivity to the V 3d orbital relative to the metal s orbitals at those energies [82].

The measured electronic structure from HAXPES can be directly compared to DFT calculations of $\beta$-Pb$_{0.33}$V$_2$O$_5$ to confirm the oxygen-mediated lone pair mechanism. Figure 9(d) confirms that the observed antibonding states originates from the hybridization of lone pair 6s$^2$ states of Pb$^{2+}$ with O 2p states. The lone pair states form from the resultant antibonding state mixing with Pb 6p states to form the lone pair state i.e.,
When the concentration of intercalated Pb$^{2+}$ is increased from 0.33 to 0.55, a new phase, layered δ-Pb$_{0.55}$V$_2$O$_5$, is formed (figure 11(a)). The higher Pb-content polymorph exhibits dramatically altered vanadium–oxygen connectivity (double-layered slabs of V$_2$O$_5$) as compared to the structural motifs observed in both β-Pb$_{0.33}$V$_2$O$_5$ (tunnel structure) and α-V$_2$O$_5$ (single-layered). Direct comparison of the valence band regions is shown in figure 11(b) and shows that the increased Pb$^{2+}$ concentration is reflected in an increased signal associated with the bonding and anti-bonding states of the δ-Pb$_{0.55}$V$_2$O$_5$, compared to the β-Pb$_{0.33}$V$_2$O$_5$. Despite the significant change in V–O bonding, the change of polymorph with increased ion interaction does not appear to significantly affect the energetic location of the lone-pair induced mid-gap state (i.e. A, antibonding state). From inspection of the leading edge, a small improvement in the band edge is observed.
5.4. Electronic structure of Sn$_x$V$_2$O$_5$

More dramatic repositioning of the lone pair energy levels requires changing the inserted metal ion, rather than simply increasing the composition/changing polymorph. The criteria for lone pair mid gap engineering are to reduce the ionization potential to reduce the thermodynamic barrier for hole transfer from the quantum dot, whilst retaining significant metal s orbital character to ensure dispersive bands for hole conduction. From consideration of the oxygen mediated lone pair mechanism, replacing Pb$^{2+}$ with the fifth-period post-transition metal ion, Sn$^{2+}$ is expected to allow furthermore mixing of Sn 5p character, resulting in more diffuse lone pair states shifted up toward the Fermi level as observed in the case of SnWO$_4$ and SnO [37, 75]. The effects of intercalation of the Sn$^{2+}$ lone pair into $\zeta$-V$_2$O$_5$, both measured and calculated, are summarized in figure 12(a) [13]. Like $\beta$-Pb$_{0.33}$V$_2$O$_5$, the valence band of spectra of $\beta$-Sn$_{0.33}$V$_2$O$_5$ exhibits predominantly O 2p character and extends from 2–9 eV. Importantly, the prominent antibonding feature with predominantly Sn 5s character appears at 10.8 eV as a result of hybridization of Sn 5s–O 2p states. Unlike $\beta$-Pb$_{0.33}$V$_2$O$_5$, $\beta$-Sn$_{0.33}$V$_2$O$_5$ exhibits a split-off antibonding feature at the top of the valence band which becomes more prominent at lower photon energies. This is especially notable using complementary laboratory-based HAXPES employing an excitation energy of 9 keV. The observed photon energy dependence suggests that the measured antibonding feature results from the mixing of Sn 5s–O 2p–Sn 5p and V 3d states, in contrast to the $\beta$-Pb$_{0.33}$V$_2$O$_5$ where the lone pair state and reduced V 3d states are separated in the HAXPES spectra [82].

Figure 12(b) plots the GGA + SO calculated total and partial density of states of $\beta$-Sn$_{0.33}$V$_2$O$_5$, which reveals oxygen-mediated bonding and antibonding states analogous to those in $\beta$-Pb$_{0.33}$V$_2$O$_5$ [13]. However, the Sn 5s-derived antibonding state now has significantly mixed s, p, d orbital character as shown by the isodensity plot in figure 12(c). This finding is in remarkable agreement with the aforementioned photon-energy dependence studies in figure 12(a), suggesting that increasing the metal–oxygen hybridization has resulted in increased interaction with the partially occupied V 3d orbital. The significant V 3d orbital contribution to the antibonding state (A) means that further improvement in the calculated electronic structure could be obtained by DFT + U with spin–orbit coupling (but are beyond the scope of this review).

Overall, the DFT results (when spin orbital coupling is included) are in excellent agreement with the measured valence band spectra from HAXPES of $\beta$-Sn$_{0.33}$V$_2$O$_5$. The calculated density of states reproduces the measured spectral features, confirming the same underlying oxygen-mediated lone pair mechanism as for Pb$^{2+}$. The increased width of the antibonding (A) state, reflects further reduction of the ionization potential by replacing Pb$^{2+}$ with Sn$^{2+}$ [13]. Further improvement in energetic alignment could possibly be achieved with the $\delta$ polymorph at higher Sn$^{2+}$ concentrations, but the reduced s orbital character may also negatively impact the conductivity of the holes in the nanowire.

5.5. Chemical trends within synthetic lone pair metal oxides

Referring to the revised lone pair mechanism (summarized in figure 13(a)) the oxygen facilitates the formation of the metal sp-derived lone pair state by hybridizing with the metal s orbitals to increase metal s orbital character near the Fermi level. The metal ion determines the energetic separation ($\Delta E$) and orbital
character of the oxygen-mediated bonding (B) and anti-bonding (A) states, the latter being the lone pair orbital.

The extent of oxygen hybridization is significantly reduced as the group number increases from 12 to 16. Increasing the group number across the periodic table results in less hybridization with O 2p due to stabilization of the 6s electrons at the bottom of the valence band [38]. This should result in more s orbital contribution to the valence band with a decrease in the energy range for lower group elements. The O 2p contribution ratio is calculated from integrating intensity of the partial densities from the calculated DFT and apply the values in the following formula: [38]

\[
f_{O2p} = \frac{I(O 2p)}{I(O 2p) + I(Mn s)}\]

This trend is reflected by the calculated decrease in oxygen character in the bonding state (plotted in figure 13(b)) using equation (6), which reveals a similar trend in the synthetic lone pair systems as reported previously for naturally occurring systems by Payne et al [38, 75]. In the case of Hg₅V₂O₅, the Hg 5d and O 2p orbital overlap is not considered to have the same lone pair distortion mechanism as the other M₅V₂O₅. Meanwhile In⁺ is significantly more unstable and was not considered in this study. In addition to changing group, moving period can improve the oxygen hybridization and compensate for a higher binding energy ion needed to increase the energetic separation of the bonding (B) and anti-bonding (A) states. From these considerations, Tl⁺ and Sn²⁺ were identified as promising candidates for lone pair engineering.

To examine the lone pair engineering as a function of metal ion, we quantified the oxidation state (by measuring V reduction) from core-level analysis of the HAXPES (e.g., figure 10) for all the M₅V₂O₅ materials. For fair comparison, we employed both the β and δ-phases of Pb₅V₂O₅ to account for differences associated between polymorphs (Sn and Tl were β- and δ-phases, respectively). The HAXPES measurements of the valence band region are presented in figures 13(c) and (e) and the corresponding DFT in figures 13(d) and (f) captures the correct evolution of electronic structure upon substitution of the inserted metal ion. The increased hybridization of the Tl⁺ (group 13) compared to Pb²⁺ (group 14) does increase the metal 6s character of the A state, but the lower binding energy of the Tl 6s orbital reduces the energetic splitting of the bonding and antibonding states. Overall, the net effect is a lower IP lone pair state for Tl⁰.⁵V₂O₅ compared to Pb⁰.⁵V₂O₅ for the same polymorph (δ-phase). Substituting the group 13 N−₂ ion from the same series does improve raise the IP by a further ∼0.4 eV and is supported by the calculated cross-sectionally weighted DFT shown in figure 13(d). This suggests that δ-Tl₅V₂O₅ would perform better as a photocatalyst than δ-Pb₅V₂O₅ by facilitating better hole transfer from the quantum dot with energies closer to the water oxidation potential.

Shifting series rather than group (i.e., substituting Pb²⁺ with Sn²⁺) significantly increases both the oxygen character in the bonding state and the energetic separation between bonding and antibonding states. The increased energetic separation ultimately lowers the IP more than observed for Tl⁺. As mentioned previously, the δ-phase polymorph is expected to raise the IP for all ions, and the improved IP in the δ-phase Sn₅V₂O₅ case is expected to be further improved, suggesting that further hole barrier height alignment improvement with CdSe (and CdTe) could be obtained with the δ phase of Sn₅V₂O₅. However, the increased energetic splitting results in lone pair states with more V 3d intermixing. The resultant hybridized state is more complicated than the well-defined lone pair states for the Pb²⁺ and Tl⁺ cases. Further inspection using photon-energy dependent HAXPES confirmed significant d orbital character in the antibonding state, explaining the suppressed intensity of the A state in figure 13(d), in agreement with our recent DFT predictions. These data also indicate that in the
Figure 13. (a) Molecular energy level diagrams showing the interaction of ns and np states of lone pair cation with O 2p. (b) DFT calculated O 2p weighting in the bonding states of the transition metals in the natural systems (Ti2O3, PbO, BiVO4) and synthetic systems (δ-Tl0.5V2O5, β-Pb0.33V2O5, and β-Sn0.33V2O5). The O 2p contribution decreases with increasing group number across the periodic table. The valence band spectra of (c) δ-Tl0.5V2O5 and δ-Pb0.5V2O5, (d) β-Pb0.33V2O5, and (e) β-Sn0.33V2O5, along with the simulated valence band spectra of (f) δ-Tl0.5V2O5 and δ-Pb0.33V2O5, and (f) β-Pb0.33V2O5, and β-Sn0.33V2O5.

SnxV2O5/CdX system hole transfer could be further enhanced by increasing the Sn2+ content and stabilizing the δ phase, which represents a synthetic target of utmost importance based on this analysis.

6. Nanowire quantum dot energetic band alignments

Charge separation of photo-excited excitons at engineered interfaces must carefully consider both the thermodynamics and kinetics. Charge separation of photo-excited excitons in light harvesting quantum dots by interface engineering using MxV2O5 phases nanowires engineered interfaces was first demonstrated in 2015 by
Figure 14. (a) The HAXPES spectra of ζ-V$_2$O$_5$ and M$_x$V$_2$O$_5$ (M = Pb$^{2+}$, and Sn$^{2+}$) with and without CdSe QDs, and (b) the corresponding band edge alignments with respect to the standard hydrogen electrode energy (redox levels are shown for illustration). The valence band edge alignments were determined by HAXPES analysis and the corresponding conduction band alignment were deduced from consideration of their measured band gaps.
Figure 15. (a) A schematic of a photoelectrochemical cell depicting how hydrogen evolution can be promoted at either the NW or QD, depending on the band alignment of the heterostructure. (b) The measured hydrogen production amount for the different heterostructures. Both LAA and SILAR attachments are shown for the MₓV₂O₅/CdSe heterostructures, further enhancement is expected by decorating the quantum dots with Pt nanoparticles. (c) The corresponding band alignments associated with HER on the NW (Type II) and the QD (Type I), depicting the charge transfer of photo-excited carriers in the quantum dots.

observed for the case of pristine ζ-V₂O₅ with both CdS and CdSe QD attachments, such that photo-generated electrons should transfer to the V 3d-derived conduction band of ζ-V₂O₅, while holes will accumulate in the QD. Incorporating Pb²⁺ within the structure results in smaller valence band offsets with CdSe (0.8 eV) [36], and CdS [130]. Indeed, a flat valence band alignment is observed for β-phase Pb₀.₃₃V₂O₅/CdS. Replacing Pb²⁺ with Sn²⁺ reduces the IP significantly, and results in a flat valence band alignment with the CdSe [13]. As a result, hole transfer from the quantum dot is facilitated to the MₓV₂O₅ nanowire due to the reduced hole barrier energies. Meanwhile, the metal ion insertion results in vanadium reduction, ensuring the bottommost conduction band states are filled in order to suppress electron transfer from the quantum dot to the nanowire. The net effect is effective charge separation consistent with the aforementioned TA spectral studies [13, 36, 37].

7. Engineered photoelectrochemical performance

The photoelectrochemical measurements of the NW/QD are summarized here and discussed in terms of the engineered electronic band alignments. Linear sweep voltammograms were performed to quantify photocatalytic response. Figure 15(a) shows the experimental setup of the electrochemical cell, in which the working electrode is a fluorine-doped tin oxide (FTO) electrode modified with α-V₂O₅, ζ-V₂O₅, or MₓV₂O₅/CdSe QDs, a Pt was the counter electrode, and a saturated calomel (SCE) was used as the reference electrode. The cells were illuminated by a visible light (400–720 nm); more details were reported previously [13, 36]. All the bare nanowires are initially photo-catalytically inert, and are only responsive when decorated with the quantum dots (with the addition of lactic acid and Ni(3-MPA) in the electrolyte), highlighting the critical role of the interface in spatially separating the photo-generated holes. Figure 15(b) plots the amount of the H₂ produced for various heterostructures. The deposition method of QDs on β-M₀.₃₃V₂O₅ strongly affects the performance
of the NWs/QDs, which is attributed to the role of kinetics and interfacial quality. We note that $\beta$-Pb$_{0.33}$V$_2$O$_5$ produced more hydrogen when QDs were deposited by LAA but the SILAR method is more effective in case of $\beta$-Sn$_{0.33}$V$_2$O$_5$.

From consideration of the measured band alignments from HAXPES shown in figure 14, the observed photocatalytic activity can be explained in terms of the lone pair doping in the nanowire shifting the HER site from the nanowire to the quantum dot. The $\alpha$-V$_2$O$_5$/CdSe QDs heterostructure displays a type II band alignment, such that the valence and conduction band edges of QDs are higher than the respective band edges of the $\alpha$-V$_2$O$_5$ NWs [131–133]. The photo-generated exciton is split at the interface, such that the electrons are transferred to a Ni(3-MPA)cocatalyst, and reduce protons to hydrogen at the nanowire site. Meanwhile the photo-generated holes in the valence band of the QD oxidize lactic acid i.e., sacrificial agent [126]. The reduction in the hydrogen production between $\alpha$- and $\zeta$-phase V$_2$O$_5$/QD reflects the loss of the split-off V $d_{xy}$-derived conduction band state between the polymorphs (figure 8). The incorporation of lone pair active ions within M$_x$V$_2$O$_5$/CdSe QDs results in the formation of a type I heterostructure, as summarized in figure 15(c). Now, the photo-generated electrons are transferred slowly to the nanowire because of the partial filling of the conduction band due to the vanadium reduction, while the photogenerated holes in the QD are transferred to the $\alpha$- and $\zeta$-phase V$_2$O$_5$ nanowires i.e., switching the catalysis sites. The improvements in the hydrogen generation from Pb$^{2+}$ to Sn$^{2+}$ reflects the reduction of the hole barrier energy [13, 36, 37]. Additional improvement in hydrogen production is expected by further decorating the quantum dots with a co-catalyst e.g. Pt nanoparticles.

8. Conclusion

The rational design of photocatalysts for efficient water splitting must employ hybrid systems, where the different components perform light harvesting, charge separation and catalysis. Synergy between the different components must be considered in the design of such systems and therefore a high degree of tunability in the individual components is required for overall optimization. Combining promising QD light harvester and low-overpotential water-oxidation catalysts requires efficient hole separation and transfer at energies close to the H$_2$O/O$_2$ redox for the dark catalyst. Topochemical synthesis of ternary M$_x$V$_2$O$_5$ nanowires, where M is a lone pair active $(N - 2)s^2$ ion, is a promising new class of solid-state charge-separation compounds that can be integrated within hybrid nano-engineered photocatalysts to promote charge separation and transport between the light harvester and water-oxidation catalyst. The ionization potential of the ternary M$_x$V$_2$O$_5$ nanowires can be dramatically reduced by intercalating post-transition metal ions to induce the formation of oxygen-mediated lone pair states in order to band engineer the interfacial alignment between the nanowire and QD valence bands; thereby promoting hole transfer from the QD to the nanowire for hole conduction to the water oxidation catalyst at energies close to the H$_2$O/O$_2$ redox level.

The recent development of this new class of photocatalyst highlights an approach to accelerated materials discovery that focuses on the electronic structure of the buried interfaces between the light harvester and hole conducting nanowire. The accelerated screening of the topochemically synthesized metastable ternary M$_x$V$_2$O$_5$ polymorphs was afforded by the orbital sensitivity of HAXPES to the lone pair states used to validate DFT computations. Meanwhile, the increased effective probing depth of HAXPES enabled determination of the M$_x$V$_2$O$_5$/CdX heterostructure band alignments alignments to explain the observed photolysis. HAXPES studies in tandem with DFT and topochemical synthesis of M$_x$V$_2$O$_5$ have identified the $\delta$-phase Sn$_x$V$_2$O$_5$/CdSe/Pt as promising photocatalyst targets for for efficacious hydrogen generation. Future studies will focus on Pt-free co-catalyst candidates, which will also require consideration of the buried interfaces.

9. Methodology

9.1. Synthesis of $\alpha$-V$_2$O$_5$ nanowires

The $\alpha$-V$_2$O$_5$ nanowires were synthesized by modification of a previously reported hydrothermal reaction. 1.63 g of as-obtained bulk V$_2$O$_5$ (Sigma Aldrich), 8 ml of 2-propanol, and 78 ml of deionized water (18 MΩ cm$^{-1}$) were added to a 125 ml capacity poly(1,1,2,2-tetrafluoroethylene)-lined stainless steel autoclave (Parr) and allowed to react at 210 °C for 48 h. The resulting V$_3$O$_7$-H$_2$O nanowires were calcined at 400 °C. The V$_3$O$_7$ NWs were oxidized in air at 300 °C yielding $\alpha$-V$_2$O$_5$ [134].
9.1.2. Synthesis of \(\zeta\)-V\(_2\)O\(_5\) nanowires

The empty, metastable polymorph \(\zeta\)-V\(_2\)O\(_5\) has been stabilized by topochemical extraction of Cu ions from \(\beta'\)-Cu\(_2\)V\(_2\)O\(_5\). (some residual copper is observed 0.0004 per V\(_2\)O\(_5\)) [111, 119]. The \(\beta'\)-Cu\(_0.5\)V\(_2\)O\(_5\) nanowires were synthesized hydrothermally by dispersing V\(_2\)O\(_5\), VO\((C\(_2\)H\(_2\)O\(_2\))\(_2\), and Cu(NO\(_3\))\(_2\) hemipentahydrate (total mass loading of 300 mg, in a 1:2:1 stoichiometric ratio) in 16 ml of deionized water. The obtained dispersion was added to a 23 ml capacity poly(1,1,2,2-tetrafluoroethylene)-lined stainless steel autoclave (Parr) and was allow to react for 48 h at 210 °C [135]. The resulting nanowires were washed with water and 2-propanol and dried in air. Thereafter, the nanowires were reacted with a 0.5 M aqueous solution of Na\(_2\)S\(_2\)O\(_8\) (using an 8:1 M ratio of Na\(_2\)S\(_2\)O\(_8\) : \(\beta'\)-Cu\(_0.5\)V\(_2\)O\(_5\)) for 24 h at 80 °C.

9.1.3. Hydrothermal synthesis of \(\beta\)-Pb\(_{0.31}\)V\(_2\)O\(_5\) nanowires

0.01230 g of Pb(COOCH\(_3\))\(_2\), 3H\(_2\)O were dissolved in 16 ml of deionized water. In this solution, a 0.1770 g of V\(_2\)O\(_5\) was suspended (1:3 Pb: V\(_2\)O\(_5\) molar ratio). The resulting suspension was added to a 23 ml capacity poly(1,1,2,2-tetrafluoroethylene)-lined stainless-steel autoclave (Parr). The autoclave was heated for 72 h at 250 °C and allowed to cool to room temperature [136].

9.1.4. Topochemical Synthesis of \(\beta\)-Sn\(_{0.25}\)V\(_2\)O\(_5\) nanowires

\(\zeta\)-V\(_2\)O\(_5\) was intimately mixed with a tin oxalate precursors (SnC\(_2\)O\(_4\)) in a 4:1 stoichiometric ratio. Materials were ground together for 30 min using a mortar and pestle in a slurry of dry hexanes. Then, the dried mixture was placed inside a tube furnace and heated under vacuum at 350 °C for 12 h [13].

9.1.5. Synthesis of CdSe QDs

CdSe quantum dots were synthesized as reported previously [137]. An aqueous solution of Se powder and Na\(_2\)SO\(_3\) was heated under refluxing conditions overnight to prepare the selenium precursor, and the solution of 3CdSO\(_4\)·8H\(_2\)O and cysteine was used for preparing the cadmium precursor. Then, the cadmium precursor was added to the selenium precursor and stirred for 30 min.

9.1.6. Synthesis of \(\beta\)-M\(_x\)V\(_2\)O\(_5\)/CdSe QD heterostructures

CdSe QDs were deposited on NWs by both SILAR and LAA methods. Heterostructures were prepared by SILAR method in a glovebag under an Ar atmosphere [36, 136, 138]. The nanowires were dispersed in an ethanol solution of the cadmium precursor (Cd(NO\(_3\))\(_2\) for 45 s with stirring, washed with ethanol, and recovered by centrifugation at 6000 rpm for 2 min. Then, the material was immersed in an ethanol solution of the sodium chalcogenide precursor (Na\(_2\)Se) for a 45 s with stirring, washed with ethanol, and recovered by centrifugation at 6000 rpm for 2 min. For one SILAR cycle, nanowires immersed in the cadmium precursor solution and an ethanol washing, followed by immediate immersion in the chalcogenide precursor an ethanol washing. Here, three complete SILAR cycles were performed.

For the LAA method, NWs/CdSe QDs were prepared as reported before by Pelcher et al [36]. Aqueous dispersions of CdSe QDs were washed to remove unreacted precursors. Then, NWs were added to an aqueous dispersion of purified QDs with constant stirring. The heterostructures were collected via centrifugation and dispersions of CdSe QDs were washed to remove unreacted precursors. Then, NWs were added to an aqueous solution of CdSe QDs and dried at room temperature.

9.2. Computation

DFT calculations were performed for different structures by using the WIEN2k software package, which solves the Kohn–Sham equations using a full potential and linearized-augmented planewaves with the local orbitals (LAPW + lo) [139, 140]. The correlation and exchange potentials for each structure were calculated using the generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE) [141]. The spin orbital coupling treatment is considered for \(\beta\) and \(\delta\)-M\(_x\)V\(_2\)O\(_5\) due to the importance of including its critical role for calculating the electronic properties of heavy elements [39, 142–145]. The planewave cutoff parameter RKMAX was chosen to be 6.5, and the cutoff between core and valence states was set at −6.0 Ry for all materials. The number of K-points used for each structure varied due to difference structures and symmetries of the structures discussed here: \(\alpha\)-V\(_2\)O\(_5\) (4 × 12 × 15), \(\zeta\)-V\(_2\)O\(_5\) (13 × 5 × 13), SnO (10 × 10 × 8), SnO\(_2\) (13 × 8 × 8), Sn\(_2\)O\(_4\) (7 × 12 × 10), BiVO\(_4\) (9 × 11 × 9), \(\delta\)-Ti\(_{0.5}\)V\(_2\)O\(_5\) (17 × 6 × 17), \(\beta\)-M\(_{0.33}\)V\(_2\)O\(_5\) and \(\delta\)-Pb\(_{0.9}\)V\(_2\)O\(_5\) (13 × 5 × 13).

9.3. X-ray photoelectron spectroscopy

XPS measurements were performed using a Phi VersaProbe 5000 laboratory instrument with a monochromated Al Kα source (1.5 keV). The samples were mounted in a glovebox, then transferred to the UHV chamber under inert atmosphere. For neutralization, a flood gun was used.
HAXPES measurements using a photon energy of 6.0 and 3.0 keV were performed at the surface and interface structural analysis beamline (beamline I09) of the Diamond Light Source, Ltd (DLS), UK. The spectra were aligned to the O 1s and V 2p core-levels of reference $\zeta V_2O_5$ (aligned to the Fermi level of a gold foil reference in electrical contact with samples). The scans of the gold reference were performed before and after obtaining each spectrum in order to reducing shifts from beam drift. The instrumental setup has been described in more details by Lee and Duncan [146].

Additional HAXPES measurements at 9.0 keV were conducted using the Scienta lab-HAXPES prototype system with a Ga K$\alpha$ monochromated source of 9.25 eV [101]. The inelastic mean free path (IMFP) for each core region was calculated using the Tanuma, Powell, and Penn (TPP-2M) method [147] and the National Institute of Standards and Technology (NIST) electron IMFP database [148]. Probing depths are about $3 \times$ the IMFP. For energy calibration, the carbon C 1s peak was aligned to 284.5 eV.

9.4. Photoelectrochemistry

The H$_2$ generation measurements were performed either photoelectrochemically (3-electrode cell with heterostructure-modified working electrode) or photocatalytically (dispersed heterostructures). Heterostructures were dispersed into aqueous solutions of Ni(NO$_3$)$_2$, lactic acid, and Nickel-3-Mercaptopropionic acid (Ni(3-MPA)). Here, lactic acid is used in the electrolyte as both the source of protons and as a sacrificial reductant [13], where it functions as a hole scavenger that consumes the photogenerated holes in the valence band of the CdSe QDs [149, 150]. Ni(3-MPA) is used as reduction co-catalyst for all materials. It is a relatively stable and highly active co-catalyst for photocatalytic hydrogen production [151]. For controlling experiments, dispersions of either nanowires or QDs and co-catalyst were used. Dispersion were transferred at ambient temperature and atmospheric pressure to a sealed 100 ml Pyrex flask, and then deaerated with Ar gas for 30 min. A 100 W Xe arc lamp (oriel 133 Photomax) was used for illuminating all samples through a filter transmitting 400–720 nm light for 1 h. For gas quantification, a 10 ml gastight syringe was used for sampling 3 ml of gas from the headspace above the electrolyte in the photocatalytic cell and was analyzed using a gas chromatograph (Perkin Elmer Clarus 580) with a thermal conductivity detector and Ar carrier gas.

Acknowledgments

We thank Peihong Zhang for discussions. This research supported by the National Science Foundation (NSF) Designing Materials to Revolutionize and Engineer our Future (DMREF) program. SAR, LW, JR and LFJP acknowledge support under NSF grant 1627583. NS, and DFW acknowledge partial support from the National Science Foundation under NSF grant 1626967 JLA and SB acknowledge partial support from the National Science Foundation under NSF grant 1627197. The research was funded in part by award #A-1978-20190330 from the Welch Foundation. We note undergraduate contributions in reproducing DFT calculations by Joseph Harvey, supported by the NSF-REU program (Grant No. NSF DMR-1658990). Finally, we thank Susanna K Eriksson, Paul Palmgren, Manfred Mascheck, Tomas Well at Scienta Omicron for access to the Ga K$\alpha$ HAXPES instrument. Research conducted using the Lab-based Ga K$\alpha$ HAXPES system is partially supported by the National Science Foundation, Major Research Instrumentation Program (Grant number NSF DMR-1919704). We thank Diamond Light Source for access to beamline I09 (SI22148) that contributed to the results presented here.

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Reference

[1] Rose R 2019 Energy and climate change: nonpartisan policies for the next US President Task Force Reports (University of Washington)
[2] Miketa A and Saygin D 2015 Africa 2030: Roadmap for a Renewable Energy Future (Abu Dhabi: IRENA)
[64] Kohtani S, Makino S, Kudo A, Tokumura K, Ishigaki Y, Matsunaga T, Nikaido O, Hayakawa K and Nakagaki R 2002 Chem. Lett. 31 660–1
[65] Kudo A 2003 Catal. Surv. Asia 7 31–8
[66] Stoltzfus M W, Woodward P M, Seshadri R, Klepeis I H and Bursten B 2007 Inorg. Chem. 46 3839–50
[67] Noureldeen D and Takahashi K 2016 Catal. Sci. Technol. 6 7656–70
[68] Hosogi Y, Shimolaira Y, Kato H, Kobayashi H and Kudo A 2008 Chem. Mater. 20 1299–307
[69] Yoshimura J, Ebina Y, Kondo J, Domon K and Tanaka A 1993 J. Phys. Chem. 97 1970–3
[70] Kim H G, Hwang D W and Lee J S 2004 J. Am. Chem. Soc. 126 8912–3
[71] Liang Y, Tsubota T, Mootij L P and van de Krol R 2011 J. Phys. Chem. C 115 17594–8
[72] Stoughton S et al 2013 APL Mater. 1 042112
[73] Watson G and Parker S 1999 J. Phys. Chem. B 103 1258–62
[74] Walsh A and Watson G W 2004 Phys. Rev. B 70 235114
[75] Walsh A, Payne D J, Egdell R G and Watson G W 2011 Chem. Soc. Rev. 40 4455–63
[76] Van de Walle C G and Neugebauer J 2003 Nature 423 626
[77] Wang J, Umezawa N and Hosono H 2016 Adv. Energy Mater. 6 1501190
[78] Walsh A and Watson G W 2005 J. Phys. Chem. B 109 18868–75
[79] Peng H, Bikowski A, Zakutayev A and Lany S 2016 APL Mater. 4 106103
[80] Quackenbush N et al 2013 Chem. Mater. 25 3114–23
[81] Wahila M J et al 2016 Chem. Mater. 28 4706–13
[82] Wangoh L, Marley P, Quackenbush N, Sallis S, Fischer D, Woicik J, Banerjee S and Piper I 2014 Appl. Phys. Lett. 104 182108
[83] Wahila M J et al 2015 Appl. Phys. Rev. B 91 205307
[84] Einstein A 1905 Ann. Phys. Lpz. 17 549–60
[85] Hagström S B 2007 Phys. Today 60 74
[86] Koopmans T 1934 Physica 1 104–13
[87] Ohta T, Bostwick A, Seyller T, Horn K and Rotenberg E 2006 Science 313 951–4
[88] Sutter P, Hybertsen M, Sadowisky I and Sutter E 2009 Nano Lett. 9 2654–60
[89] Woicik J C and Woicik J 2016 Hard X-Ray Photoelectron Spectroscopy (HAXPES) (Switzerland: Springer) vol 59
[90] Lindau I, Pianetta P, Doniach S and Spicer W 1974 Nature 250 214
[91] Gallera C, Braicovich L, Duro L, Palenzona A, Panaccione G, Paolicelli G, Ciove C and Zegenhagen J 2005 Nucl. Instrum. Methods Phys. Res., Sect. A 547 113–23
[92] Kobayashi K et al 2003 Appl. Phys. Lett. 83 1005–7
[93] Fadley C S 2016 Hard x-ray photoemission: an overview and future perspective Hard X-Ray Photoelectron Spectroscopy (HAXPES) (Berlin: Springer) pp 1–34
[94] Gorgoi M et al 2009 Nucl. Instrum. Methods Phys. Res., Sect. A 601 48–53
[95] Ueda S 2013 J. Electron Spectrosc. Relat. Phenom. 190 235–41
[96] Masuda T, Ishigaki Y, Makino S, Kudo A, Tokumura K, Ishigaki Y, Matsunaga T, Nikaido O, Hayakawa K and Nakagaki R 2002 Chem. Lett. 31 660–1
[97] Greene J et al 2009 Phys. Rev. Lett. 102 196405
[98] Marley P M, Abtew T A, Farley K E, Horrocks G A, Dennis R V, Zhang P and Banerjee S 2015 Chem. Sci. 6 1712–8
[99] Bystrom A, Wilhelm K A and Brozena O 1993 Acta Chem. Scand. A 41 1119
[100] Bachmann H, Ahmed F R and Barnes W 1961 Z. für Kristallogr.-Cryst. Mater. 115 110–31
[101] Enjalbert R and Galy J 1986 Acta Crystallogr., Sect. C 42 1467–9
[102] Galy J 1992 J. Solid State Chem. 100 229–45
[103] Whittingham M S 2004 Chem. Rev. 104 4271–302
[104] Namedro E and Corberán V 1995 Appl. Catal., A 127 1–40
[105] Cocciandelli J, Graverseau P, Doumerc J, Pouchard M and Hagenmuller P 1991 J. Solid State Chem. 93 497–502
[106] Andrews J L et al 2018 Chem. Rev. 118 4564–85
[107] Galy J, Darriell J, Canatol A and Goodenough J 1970 J. Solid State Chem. 1 339–48
[108] Eyert V and Hick H K 1998 Phys. Rev. B 57 12727
[109] Rapea V and Quina P L D 2016 Mater. Res. Express 3 085005
[110] De Jesus L R et al 2016 Nat. commun. 7 1–9
[111] Tolhurst T M, Leedahl B, Andrews J L, Marley P M, Banerjee S and Moewes A 2016 Phys. Chem. Chem. Phys. 18 15798–806
[112] Horrocks G A et al 2017 Chem. Mater. 29 10386–97
[113] Chauhan S, Sheng A, Cho J, Razek S A, Suwandarate N, Sfeir M Y, Piper I F, Banerjee S and Watson D F 2019 J. Chem. Phys. 151 224702
[114] Jun H, Careem M and Arof A 2013 Renewable Sustainable Energy Rev. 17 148–67
[115] Xu Y, Huang Y and Zhang B 2016 Inorg. Chem. Front. 3 591–615
[116] Watson D F 2010 J. Phys. Chem. Lett. 1 2299–309
[117] Pelcher K E, Milleville C G, Wangoh L, Cho J, Sheng A, Chauhan S, Sfeir M Y, Piper I F, Watson D F and Banerjee S 2016 J. Phys. Chem. C 120 28992–9001
[131] Wang Y, Wang Q, Zhan X, Wang F, Safdar M and He J 2013 Nanoscale 5 8326–39
[132] Ishchenko O, Rogé V, Lamblin G and Lenoble D 2016 Semiconductor Photocatalysis: Materials, Mechanisms and Applications (Rijeka: InTech)
[133] Moniz S J, Shevlin S A, Martin D J, Guo Z X and Tang J 2015 Energy Environ. Sci. 8 731–59
[134] Horrocks G A, Likely M F, Velazquez J M and Banerjee S 2013 J. Mater. Chem. A 1 15263–77
[135] Hu W, Du X, Wu Y and Wang L 2013 J. Power Sources 237 112–8
[136] Marley P M, Stabile A A, Kwan C P, Singh S, Zhang P, Sambandamurthy G and Banerjee S 2013 Adv. Funct. Mater. 23 153–60
[137] Nevins J S, Coughlin K M and Watson D F 2011 ACS Appl. Mater. Interfaces 3 4242–53
[138] Milleville C C, Pelcher K E, Sfeir M Y, Banerjee S and Watson D F 2016 J. Phys. Chem. C 120 5221–32
[139] Schwarz K and Blaha P 2003 Comput. Mater. Sci. 28 259–73
[140] Blacha P, Schwarz K and Madsen G et al 2001 WIEN2k, an Augmented Plane Wave Plus Local Orbitals Program for Calculations Crystal Properties (Vienna: Vienna University of Technology)
[141] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1992 Phys. Rev. B 46 6671
[142] Philipsen P and Barrena B 2000 Phys. Rev. B 61 1773
[143] Nordström L, Wills J, Andersson P H, Söderlind P and Eriksson O 2000 Phys. Rev. B 63 035103
[144] Kotmool K, Chakraborty S, Bovornratana H and Ahuja R 2017 Sci. Rep. 7 42983
[145] Hermann A, Furthmüller J, Gäggeler H W and Schwedtfeger P 2010 Phys. Rev. B 82 155116
[146] Lee T L and Duncan D A 2018 Synchrotron Radiat. News 31 16–22
[147] Tanuma S, Powell C J and Penn D R 1994 Surf. Interface Anal. 21 165–76
[148] Powell C J and Jablonski A 2010 J. Electron Spectrosc. Relat. Phenom. 178 331–46
[149] Gopannagari M, Kumar D P, Reddy D A, Hong S, Song M I and Kim T K 2017 J. Catal. 351 153–60
[150] Schneider J and Bahnemann D W 2013 J. Phys. Chem. Lett. 4 3479–83
[151] Wang F, Wang W G, Wang X J, Wang H Y, Tung C H and Wu L Z 2011 Angew. Chem., Int. Ed. 50 3193–7