

**Imperial College
London**

**CHARGE CARRIER DYNAMICS AND WATER OXIDATION
PHOTOELECTROCHEMICAL PERFORMANCE OF
BISMUTH VANADATE**

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Declaration of Authorship |

I hereby declare that the material presented in this thesis is the result of my own work, except when specific references are made to contributions by others.

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February 2020

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Abstract |

In this thesis, the charge carrier dynamics that govern the photoelectrochemical water oxidation performance of BiVO_4 are investigated using an array of time-resolved transient and steady-state absorption spectroscopic techniques. *Chapter 1* outlines the motivation for this work and gives a brief introduction to the field, highlighting key research on BiVO_4 photoanodes relevant to this work. The experimental methods used herein are detailed in *chapter 2*.

Chapter 3, the first results chapter of this thesis, explores the role of structural defects such as oxygen vacancies, on the photoelectrochemical performance. The electronic occupancy of the defect states are modulated *in situ* electrochemically, thermally and optically, which allows the determination of their energetics and monitor the resulting impact on charge carrier kinetics. The results from this chapter provide insight into how the occupancy of the sub-bandgap electronic states affects charge carrier recombination, trapping, and transport. Occupied sub-bandgap states are observed to trap photogenerated holes in the bulk of the material, whereas the unoccupied counterparts (predominantly within the space-charge layer) function as electron traps which facilitate a thermally activated electron transport through a trapping / de-trapping mechanism, with an activation energy of ~ 0.2 eV.

Chapter 4 investigates the charge transfer and charge extraction processes in the $\text{WO}_3/\text{BiVO}_4$ heterojunction photoanodes, at timescales relevant to water oxidation ($\mu\text{s} - \text{s}$). The enhanced performance of the heterojunction, in relation to the individual counterparts, is attributed to sub – microsecond electron transfer across the materials, leading to spatial separation of charge which minimises recombination losses. The role of applied bias on the charge carrier kinetics of heterojunction is also investigated.

Chapter 5 focuses on the electrochemical water oxidation performance of FeOOH , Ni(Fe)OOH and FeOOHNiOOH electrocatalysts, and investigates the kinetics of water oxidation catalysis under neutral conditions. These electrocatalysts, when functionalised on BiVO_4 photoanodes exhibit significant improvements in the photoelectrochemical water oxidation performance of mesoporous BiVO_4 . The origin of this enhancement is explored, and is observed to be related to fast hole transfer from BiVO_4 to the catalyst layer, minimising recombination losses.

List of Publications |

- (1) **Unraveling Charge Transfer in CoFe Prussian Blue Modified BiVO₄ Photoanodes.**
Moss, B.; Hegner, F. S.; Corby, S.; **Selim, S.**; Francàs, L.; López, N.; Giménez, S.; Galán-Mascarós, J.-R.; Durrant, J. R. *ACS Energy Lett.* **2018**, 337–342. <https://doi.org/10.1021/acsenergylett.8b02225>.
- (2) **Water Oxidation and Electron Extraction Kinetics in Nanostructured Tungsten Trioxide Photoanodes.**
Corby, S.; Francàs, L.; **Selim, S.**; Sachs, M.; Blackman, C.; Kafizas, A.; Durrant, J. R. *J. Am. Chem. Soc.* **2018**, 140 (47), 16168–16177. <https://doi.org/10.1021/jacs.8b08852>.
- (3) **Ultra-Thin Al₂O₃ Coatings on BiVO₄ Photoanodes: Impact on Performance and Charge Carrier Dynamics.**
Kafizas, A.; Xing, X.; **Selim, S.**; Mesa, C. A.; Ma, Y.; Burgess, C.; McLachlan, M. A.; Durrant, J. R. *Catal. Today* **2019**, 321–322 (July), 59–66. <https://doi.org/10.1016/j.cattod.2017.11.014>.
- (4) **Charge Separation, Band-Bending, and Recombination in WO₃ Photoanodes.**
Corby, S.; Pastor, E.; Dong, Y.; Zheng, X.; Francàs, L.; Sachs, M.; **Selim, S.**; Kafizas, A.; Bakulin, A. A.; Durrant, J. R. *J. Phys. Chem. Lett.* **2019**, 10 (18), 5395–5401. <https://doi.org/10.1021/acs.jpclett.9b01935>.
- (5) **WO₃/BiVO₄ : Impact of Charge Separation at the Timescale of Water Oxidation.**
Selim, S.; Francàs, L.; García-Tecedor, M.; Corby, S.; Blackman, C.; Gimenez, S.; Durrant, J. R.; Kafizas, A. *Chem. Sci.* **2019**, 10 (9), 2643–2652. <https://doi.org/10.1039/C8SC04679D>.
- (6) **Beyond Band Bending in the WO₃/BiVO₄ Heterojunction: Insight from DFT and Experiment.**
Ràfols i Bellés, C.; **Selim, S.**; Harrison, N. M.; Ahmad, E. A.; Kafizas, A. *Sustain. Energy Fuels* **2019**, 3 (1), 264–271. <https://doi.org/10.1039/C8SE00420J>.
- (7) **Spectroelectrochemical Study of Water Oxidation on Nickel and Iron Oxyhydroxide Electrocatalysts.**
Francàs, L.; Corby, S.; **Selim, S.**; Lee, D.; Mesa, C. A.; Godin, R.; Pastor, E.; Stephens, I. E. L.; Choi, K. S.; Durrant, J. R. *Nat. Commun.* **2019**, 10 (1), 1–10. <https://doi.org/10.1038/s41467-019-13061-0>.
- (8) **Impact of Oxygen Vacancy Occupancy on Charge Carrier Dynamics in BiVO₄ Photoanodes.**
Selim, S.; Pastor, E.; García-Tecedor, M.; Morris, M. R.; Francàs, L.; Sachs, M.; Moss, B.; Corby, S.; Mesa, C. A.; Gimenez, S.; et al. *J. Am. Chem. Soc.* **2019**. <https://doi.org/10.1021/jacs.9b09056>.

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Chapter 1 | Introduction

In this chapter, we consider the current world energy consumption and the need to utilise renewable energy sources to sustain growing energy demands whilst mitigating climate change. Key theoretical concepts related to photoelectrochemical water oxidation are also introduced, supplemented by a background literature survey on bismuth vanadate photoanodes for this purpose. Based on this, the research objectives that form the basis of this thesis are also outlined.

1.1 Energy challenge and the climate crisis

The emergence of industrialisation over the last 300 years has led to increased and unsustainable reliance on fossil fuels to meet growing global energy demands. Energy demands increased by 1.9% globally, from 2016 to 2017 and by a staggering 2.3% in 2018, as measured by the total primary energy supply (TPES) worldwide. This correlated with a global economy that expanded by 3.7% in the same year.^{1,2} Global developments lead to better living standards and quality of life, and is facilitated by economic growth. It is perhaps not surprising then, that economic growth as measured by the gross domestic product (GDP) is strongly linked to increase in energy consumption *Figure 1.1a*. A breakdown of the TPES shown in *Figure 1.1b* demonstrates that non-renewable fuels featuring coal, oil and natural gas, carry a combined burden of meeting ~80% of the world energy demands. As a result of higher energy consumption, an unprecedented level of CO₂ is continually released into the atmosphere. To put this into perspective, *Figure 1.2a* shows the annual concentration of atmospheric CO₂ averaged at a record-breaking 407.4 ppm in 2018, whereas the pre-industrial CO₂ levels ranged between 180-280 ppm over an 800,000 year period.^{2,3} Furthermore, the global energy-related CO₂ emissions is on an upward trajectory as shown by the annual growth rate of atmospheric CO₂, illustrated in *Figure 1.2b*, and increased by 1.7% in 2018 alone.² Additionally, the dependence on fossil based resources within the next decades is set to expand with the expected economic growth across Africa and Asia. For instance, the urban population of Africa is set to grow by half a billion by the year 2040, leading to a rise in the projected continental oil consumption which will undoubtedly have a profound impact on atmospheric CO₂ levels.⁴ As discussed in a Special Report by the Intergovernmental Panel on Climate Change (IPCC), rising CO₂ levels is already having an observable impact upon global temperatures,^{5,6} which is accelerating climate change and giving rise to unpredictability in extreme weather patterns,⁵ endangering and even threatening extinction across many species, thus posing a huge threat to ecosystems worldwide.⁵

A recent report by the International Energy Agency (IEA) has found coal to be the largest source of CO₂ emission, contributing over 0.3 °C to the 1 °C increase in global average surface temperatures since pre-industrialisation,² for which, human activities has been attributed as the major contributor.⁵ At the current rate of warming, this temperature increase has been projected to exceed 1.5 °C between the years 2030 and 2052.⁵ According to the report, global warming comes at a heavy environmental cost, and is likely to bring forth long-lasting or irreversible damage to the planet, which is projected to affect all biological systems and may lead to a substantial loss of some ecosystems. Effects from rising temperatures have already been documented, such as changes in the climate system, with increase in both land and ocean temperatures,^{5,6} more frequent marine and land heatwaves, as well as changes in global precipitation.⁵ The report also highlights the human cost of

global warming, which can affect the health and livelihoods of people across the world, inflict strains on food and fresh water supplies and economic growth, and specifically threaten the disadvantaged, vulnerable and indigenous communities disproportionately.⁵

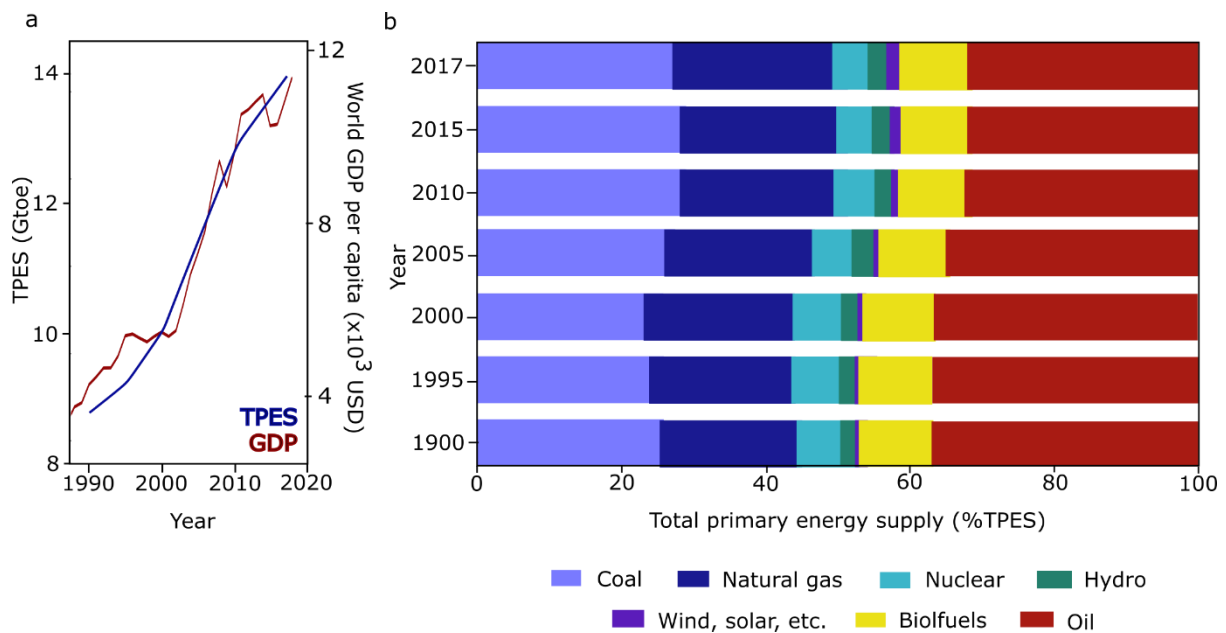


Figure 1.1| Link between total world primary energy supply (TPES) and economic growth between the years 1900 - 2017. (a) The correlation between TPES and the world gross domestic product (GDP) per capita. (b) Breakdown of the sources contributing to the total world primary energy supply (%TPES). The TPES is measured in units of gigatonne of oil equivalent (Gtoe), which is the amount of energy released by burning one tonne of crude oil (1 toe $\sim$ 42 GJ). TPES data obtained from *World Energy Balances 2019* report by the International Energy Agency.¹ GDP data obtained from World Bank national accounts data.⁷

In order to limit the effects of climate change, the IPCC has recommended an absolute limit of 1.5 °C to minimise the impacts of global warming, which can only be achieved if CO₂ emissions are substantially reduced.⁵ To this end, several agreements have been signed internationally in an effort to reduce CO₂ and other greenhouse gas (GHG) emissions.^{8,9} In 2016, the Paris Agreement, the first legally binding global agreement on climate change, was signed and ratified. The main objective of the Paris Agreement is to “limit global temperature increase from preindustrial level to well below 2 °C this century, and pursue efforts to limit this to 1.5 °C”.⁹ However, achieving these goals are not trivial. Since energy generation and use is the prime source of GHG emissions,¹⁰ radical changes in the energy sector is imperative for achieving the set objectives. Limiting global temperature increase to 2 °C alone would require significant efforts to reduce global net anthropogenic related CO₂ emissions by 25% from 2010 levels by 2030, and reach net zero by around 2070.⁵ For an even more ambitious target of 1.5 °C, this decline requires a staggering $\sim$ 45% reduction in CO₂ emissions by 2030, reaching net-zero

by 2050.⁵ Therefore a greater integrated shift towards cleaner energy sources and technological advances are essential to meeting the targets set by the Paris Agreement.

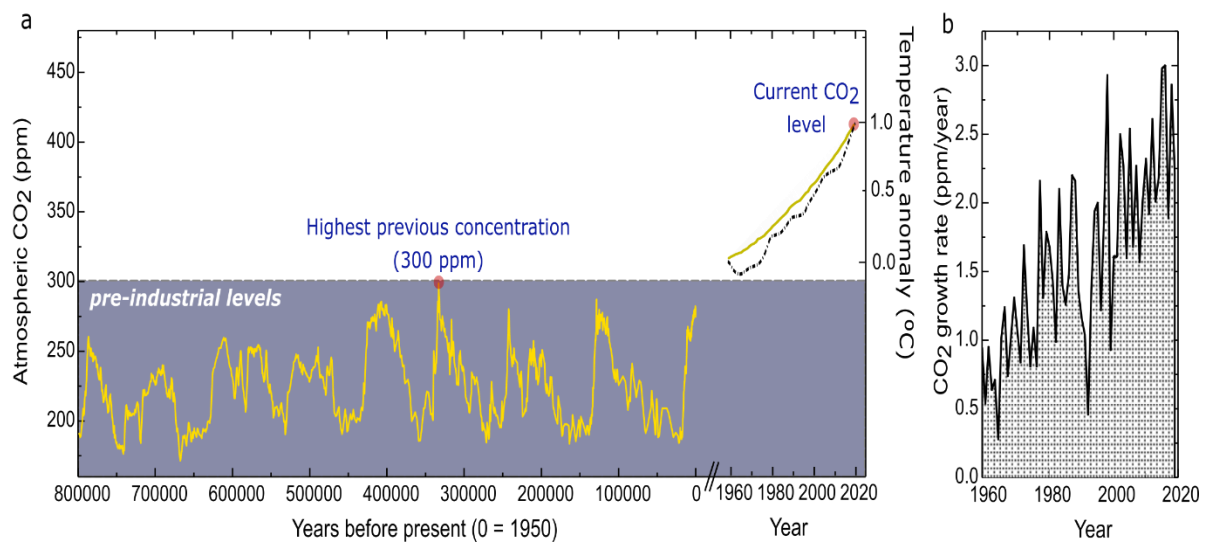


Figure 1.2 | Atmospheric CO₂ levels in parts per million (ppm) over the last 800,000 years and annual growth rate of atmospheric CO₂. (a) The atmospheric CO₂ concentration in the last 800 years (yellow trace) and the correlation between the recent increasing CO₂ concentrations and global anomalous temperatures (black dotted). (b) The annual growth rate of atmospheric CO₂ within the years 1959 and 2020. The atmospheric CO₂ concentration data and the growth rate data were obtained from the referenced publication³ and the Earth System Research Lab (NOAA/ESRL).¹¹ Global anomalous land-ocean temperature data were obtained from the Goddard Institute for Space Studies, NASA (NASA/GISS).⁶

1.2 Renewable sources

The theoretical potential of renewable energy far exceeds both current and projected future global energy demands,¹² which allows opportunities not just to mitigate climate change, but provide a platform for sustainable economic growth. Considerable efforts have been directed towards renewable energy generation that minimise emissions from GHGs. In 2018, electricity generation from renewable sources were higher by 7%, with increased contribution from nuclear energy. As a result, renewables accounted for ~25% of the global power output.² However, the growth in energy generation through renewable sources is still not in-line with the growth in energy demand.² In order to meet the global targets set by the IEA as part of the sustainable development scenario (SDS) which is in-line with the Paris Agreement, renewables need to account for two-thirds of the energy generation by 2040.^{2,10} This should include use of renewable energy across all sectors including transportation, electricity generation and heating.^{2,10}

1.3 A hydrogen economy

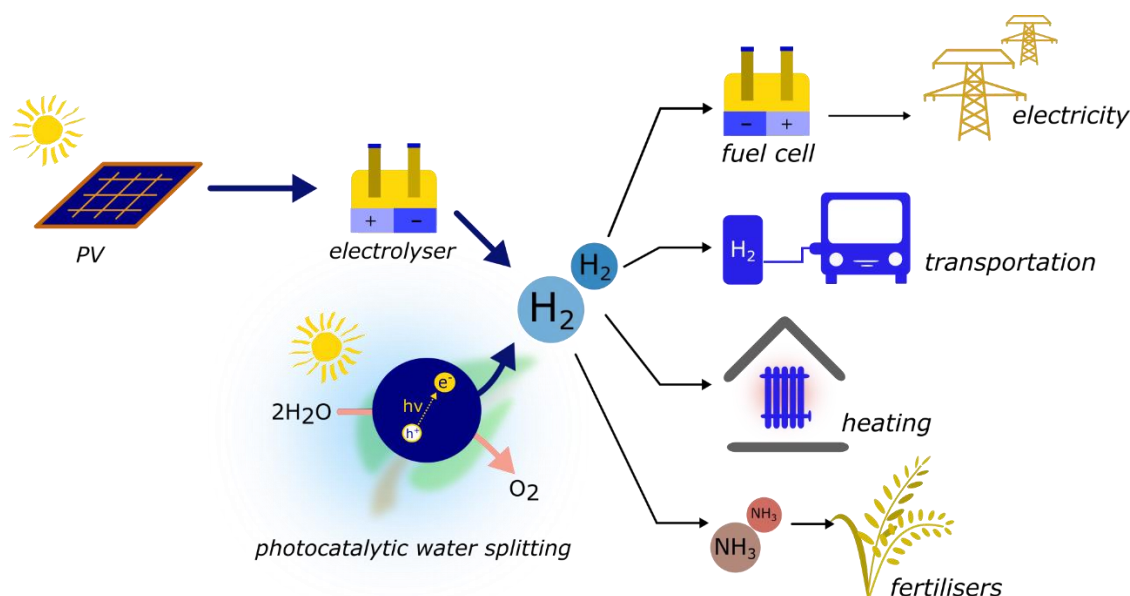


Figure 1.3 | Solar-driven hydrogen production for a hydrogen economy. Hydrogen generated either by photovoltaics coupled to electrolyzers for water electrolysis or by photocatalytic water splitting. The hydrogen produced can then be used to generate electricity using fuel cells, as a chemical fuel for transportation for electric vehicles equipped with fuel cells, and also for household and industrial heating purposes by feeding hydrogen into the gas network grid. Hydrogen is also essential for the synthesis of ammonia for fertiliser production.

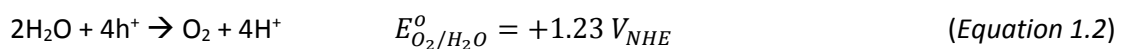
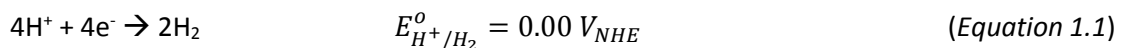
A potential alternative to a carbon-based fuel system is a hydrogen economy. Hydrogen has the potential to be a “clean” chemical fuel because when the energy is released through combustion, or in fuel cells to produce electricity, the only by-product is water. However, the current methods of hydrogen generation *e.g.* steam reformation of methane, which accounts >90% of hydrogen output,¹³ is CO_2 intensive (accounts for ~3% of annual global CO_2 emissions)¹⁴, therefore it is not an ideal decarbonisation pathway for a low-GHG emission energy carrier system at present. Nevertheless, hydrogen can also be produced renewably using solar energy, such as coupling photovoltaics to electrolyzers for water electrolysis, or using photocatalytic solar water-splitting, as shown in *Figure 1.3*. The hydrogen generated can then be used as the energy carrying medium for sectors such as electricity generation using fuel cells, transportation sector for electric vehicles equipped with fuel cells and also for heating homes using hydrogen powered boilers. Currently, a large proportion of the hydrogen produced is used for the synthesis of ammonia, which is a major ingredient for the production of fertilisers.¹⁵ As this relies heavily on steam reformation, a large carbon-footprint is associated with fertiliser production, which can also be circumvented through clean hydrogen generation. This is also illustrated in *Figure 1.3*. Hence, hydrogen can be a key-player in the United Kingdom’s commitment to net-zero emissions by 2050 under the Climate Change Act.¹⁶ It should be noted however that if a hydrogen economy is ever going to be implemented, it would require

significant research into low-cost clean-hydrogen generation processes and substantial investment in infrastructure to support a hydrogen fuelled economy, which is not trivial. According to a recent report by the Committee on Climate Change (CCC), for hydrogen to play a substantial role in the long-term in United Kingdom, the progress in low-carbon hydrogen deployment at scale needs to start imminently, with a roll-out ‘trial and error’ deployment strategy over the next decade.¹⁷

In the foreseeable future however, hydrogen can be incorporated into supply networks without requiring substantial initial infrastructural changes. In the UK, at present the natural gas network can tolerate injection of hydrogen at 20% by volume (which amounts to 7% by energy) without incurring damage to gas pipes and household appliances.^{17,18} A 20% blend of hydrogen into the natural gas network can reduce CO₂ emissions by around 6 million tonnes every year.¹³ Although the carbon footprint reduction associated with 20% hydrogen is not as substantial as it would be for switching to 100% hydrogen, it avoids major infrastructural costs at a national level, reducing switchover costs, and can be a stepping stone in preparation for the adoption of hydrogen across a wider energy system.¹⁷ Currently, the HyDeploy project, the UK’s first grid-injected hydrogen pilot, is running a 10 month live trial testing blends of hydrogen and natural gas for around 130 buildings and homes as part of the Keele University gas network.¹³ However, as mentioned previously, for a hydrogen economy to be truly sustainable and effective in reducing CO₂ emissions in the long-run, hydrogen has to be sourced in a low-carbon manner, implementing routes that employ renewable sources *e.g.* solar water splitting. In this thesis, the fundamental processes underpinning solar water splitting using semiconducting materials are explored, the concept of which is discussed in the next section.

1.4 Photoelectrochemical water splitting

Solar energy can be used to drive the synthesis of chemicals, where energy is stored in the form of chemical bonds. These photocatalytic reactions can be driven on semiconductor surfaces. When a semiconductor absorbs a photon of energy that is greater than its bandgap, an electron (e⁻) is promoted from the valence band to the conduction band, leaving a hole (h⁺) in the valence band. If these electrons and holes possess sufficient potential energy, they can drive surface redox reactions. One prime example of such a reaction is solar-driven water splitting, which generates hydrogen as a chemical fuel. The reduction and oxidation reactions can be written as:



Under standard conditions, the electrochemical cell potential for the water splitting reaction is -1.23 V, which corresponds to a Gibbs free energy (ΔG) of +237 kJ/mol of H_2 . This indicates that water splitting is an endothermic process. In addition, from *Equation 1.2*, it can be seen that four equivalents of holes (h^+) are required per mole of O_2 evolved, which renders this half reaction kinetically challenging.¹⁹ Therefore, oxygen evolution is often considered the kinetic bottleneck for the overall water splitting process, and making this reaction more kinetically facile is a key challenge. Hence water oxidation is the key focus of this thesis. Both half reactions can be theoretically achieved by a single semiconductor material as shown in *Figure 1.4a* in nanoparticulate suspensions, where photogenerated charges diffuse towards the surface to drive surface redox catalysis (*i.e.* proton reduction and water oxidation). In order to account for the thermodynamic redox potentials, the valence and conduction band positions must straddle the electrochemical potentials such that the valence band must be more oxidative than the water oxidation potential and the conduction band must be more reductive than the proton reduction potential.

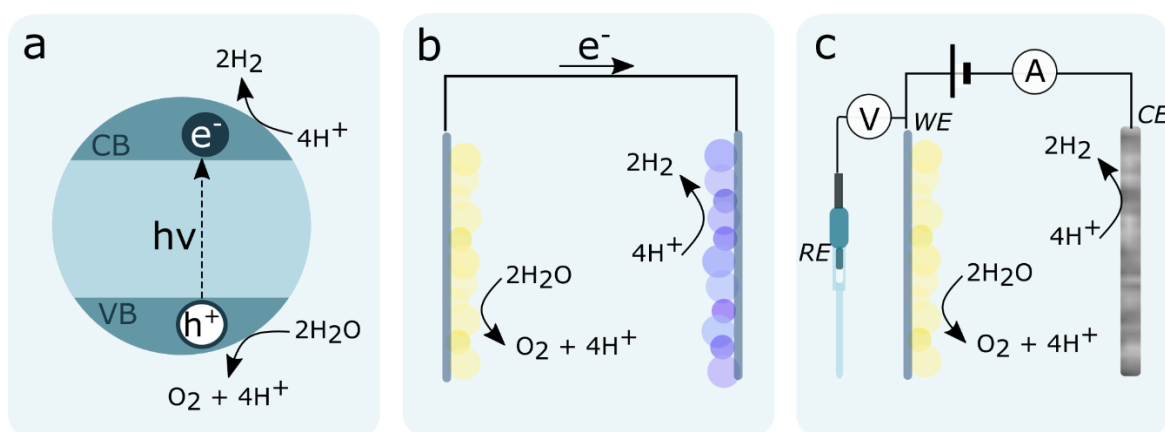


Figure 1.4 | Simplified illustrations of photocatalytic and photoelectrochemical systems employed for solar water splitting. (a) Photocatalytic water splitting system based on semiconductor nanoparticulate suspension where photogenerated electrons and holes diffuse to the surface to drive photocatalytic reactions. (b) A tandem configuration of PEC cell consisting of a photoanode and a photocathode where water oxidation and proton reduction reactions occur, respectively. (c) A three-electrode PEC cell in which an external bias is applied to the photoanode for water oxidation with reference to the reference electrode (RE). Photogenerated electrons then flow to the counter electrode (CE) to reduce protons. Additional electrical bias is applied for the counter reaction to occur.

Given the thermodynamic constraints for a single material, meeting all of these criteria is not trivial. Alternatively, in a photoelectrochemical cell, these half reactions can be decoupled across a photoanode and a photocathode for the water oxidation and proton reduction reactions respectively, as shown in *Figure 1.4b*. This alleviates the need for a single material to have both the valence and conduction band positions straddle the water oxidation and proton reduction potentials, respectively.

To study the characteristics of individual photoelectrodes for one of the half reactions (*i.e.* water oxidation), a three-electrode set up is often employed. An example of a simplified three-electrode set up including a photoanode (as the working electrode, WE), counter electrode (CE) and reference electrode (RE), is shown in *Figure 1.4c*. This allows an electrical bias to be applied between the photoelectrode and the reference electrode (the effect of applied bias is discussed later), while the current flows between the working electrode and the counter electrode where the other half-reaction occurs.

1.4.1 Semiconductors as photoelectrodes

For semiconducting materials to function as photoelectrodes for solar driven photoelectrochemical processes, a set of criteria need to be met. For instance, for a single material based system, to harvest solar energy efficiently and perform solar water splitting, the desirable bandgap of the material should be around $\sim 1.6 - 1.8$ eV to account for redox potentials, and to overcome kinetic overpotentials,²⁰ giving a maximum attainable solar to hydrogen efficiency (%STH) of 31%.^{20,21} Additional factors such as charge self-localisation and thermalisation effects can also further limit the chemical potential of photogenerated charges for charge transfer reactions, introducing additional constraints when selecting optimum semiconductor bandgap.²² Efficiencies are dictated by electron-hole recombination losses (for a given material bandgap) following charge generation, leading to poor charge collection. The common pathways for electron-hole recombination are illustrated in *Figure 1.5*. Upon photoexcitation, the charges need to undergo charge separation, these charges then need to be transported to their respective contacts, *i.e.* in the case of a photoanode, electrons in the conduction band need to reach the back contact to be extracted into the external circuit, while the holes in the valence band need to reach the surface with the electrolyte to drive redox reactions. This is dependent upon how well charges are able to move through the material. Poor charge transport can lead to higher recombination losses and low efficiencies. Furthermore charge carriers are often subject to trapping which can render them inactive. In addition, slow interfacial reaction kinetics can lead to charge accumulation which can also facilitate surface recombination losses, as is often the case for the kinetically slow water oxidation which typically occurs on the 10 ms – s timescale.²³ Surface recombination losses can often be overcome by applying external potentials (discussed in *section 1.4.3*).

To improve the conductivity of semiconductors for practical applications, they are often doped. Doping a semiconductor with donor or acceptor impurities can introduce energy levels associated with the impurities within the bandgap of the semiconductor. For example, introducing dopant ions that introduce electron filled dopant energy levels that are in close proximity to the conduction band, can

give rise to excess electrons (majority carriers) in the system, which can be thermally excited into the conduction band, increasing the conductivity. This is a description of an n-type system which are often employed as photoanodes, and therefore is the focus of this study for water oxidation. Conversely, introducing un-filled energy levels by dopants in close proximity to the valence band, can promote electrons from the valence band into the unoccupied dopant energy levels. This is a p-type system where the majority carriers are holes, and are typically employed as photocathodes. The Fermi level (E_F) is the electrochemical potential of the semiconductor. For an n-doped semiconductor, as the presence of dopant ions introduces charge carrier concentration (electrons) close to the conduction band edge, E_F lies close to the conduction band. The converse is true for a p-type system with the E_F being close to the valence band edge. The degree of ionisation of the dopant levels is dependent upon the energetic position of the dopant energy levels, thus the proximity to the conduction or valence bands, respectively. Typically, they are thermally accessible at room temperature when they are within $\sim 2kT$ of the conduction or valence band energies.²⁴

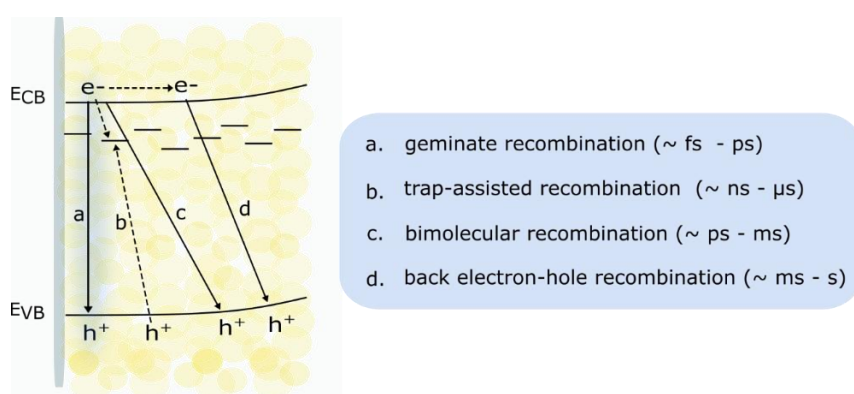


Figure 1.5 | Schematic representation of common electron-hole recombination pathways in metal oxide based photoanodes. (a) The recombination of electron-hole pairs prior to charge separation. This is known as geminate recombination. (b) Once the charges are separated, they may get trapped at defect states, following which they may undergo trap-assisted recombination. (c) Separated charges can also undergo bimolecular recombination. (d) Photogenerated electrons that have been extracted from the materials into the external circuit can come back and recombine with holes that are at the surface. This is often called back electron-hole recombination (BER). The timescales noted for each process is guideline only, and varies from material to material.²⁵

1.4.2 Semiconductor/electrolyte interface

When a semiconductor is brought into contact with an electrolyte, the Fermi level of the semiconductor equilibrates with the redox potential of the electrolyte. For the case of an n-type material (which will be the focus from hereon in), the majority carriers in the semiconductor (electrons) diffuse from the bulk to the interface and are transferred to the electrolyte until an equilibrium is established, this is illustrated in *Figure 1.6b*. The transfer of electrons from the

semiconductor to the electrolyte leaves the region close to the surface of the semiconductor depleted of electrons. This depleted region is known as the space-charge layer (SCL), of width W_{SCL} . Across the SCL, there is a build-up of electric field, giving rise to band-bending, which plays a crucial role in the separation of photogenerated charge. The space-charge field is countered by the adsorption of negative ions in the electrolyte to the semiconductor surface field that resides predominantly within the Helmholtz layer of the electrolyte.

Under illumination, when the energy of the incident photons are higher than the bandgap, photoexcitation of the semiconductor results in the promotion of an electron from the valence band to the conduction band, leaving behind a concomitant hole. The increase in the concentration of electrons in the conduction band induced by photoexcitation, leads to a negative shift of the E_F position and reduces the band bending at the SCL and the W_{SCL} . Within the persisting SCL at the surface, the electric field drives charge separation which forms a gradient in the concentration of holes from the bulk of the semiconductor towards the electrolyte interface. This results in a splitting of the E_F in the SCL into quasi Fermi levels $E_{F,n}$ for electrons and $E_{F,p}$ for holes. This is illustrated in *Figure 1.6c*.

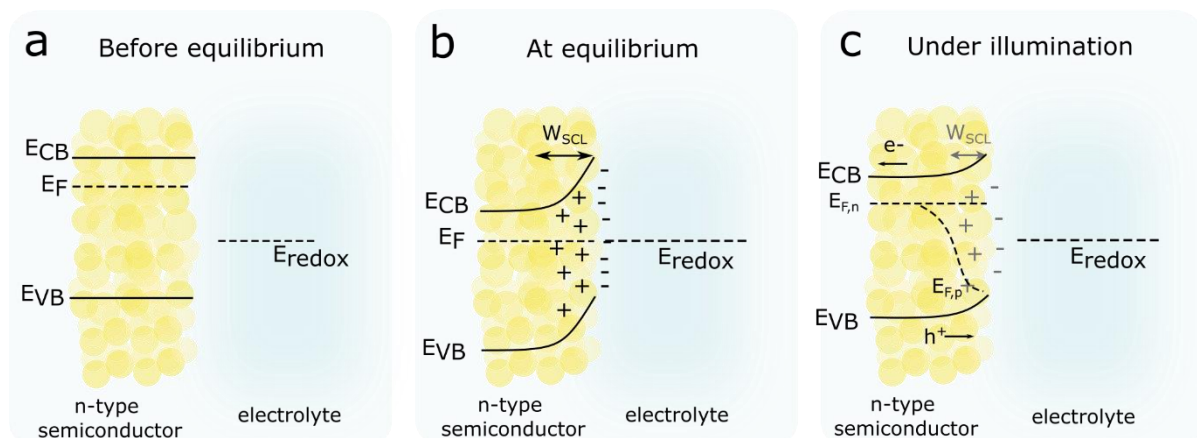


Figure 1.6 | Band diagrams for a photoanode/electrolyte interface. (a) Before equilibrium in the dark, (b) after equilibrium is reached under dark conditions and (c) under illumination. E_{CB} and E_{VB} correspond to the conduction and valence band edges, E_F is the Fermi level of the photoanode and E_{redox} is the redox potential of the electrolyte. W_{SCL} is the space charge layer width, $E_{F,n}$ and $E_{F,p}$ are the electron and hole quasi-Fermi levels, respectively.

1.4.3 Effect of applied potential

The performance of photoanodes is typically evaluated by measuring the photocurrent as a function of applied potential ($J - V$ curves), illustrated in *Figure 1.7*. The dark current is associated with electrochemically catalytic processes by the semiconductor (*i.e.* electrochemical water oxidation). This

occurs at high applied bias when the Fermi level of the semiconductor approaches the valence band of the photoanode, such that holes are generated by electrochemically oxidising the valence band. When illuminated, holes are photogenerated in the valence band, which are able to oxidise water (if the valence band has sufficient potential energy to drive this reaction). The photocurrent onset is thermodynamically limited by the flat band potential (V_{FB}) of the photoanode, which is the potential at which there is no band bending or charge depletion. As depicted in *Figure 1.7*, ideally, the photocurrent onset should be close to the V_{FB} , and should plateau giving a photocurrent response with a high fill-factor (FF). However, experimentally, kinetic overpotentials associated with water oxidation, bulk recombination losses as well as surface recombination processes such as back electron-hole recombination results in deviations from ideal behaviour. In addition, presence of surface defect states can induce Fermi level pinning at the interface (not illustrated in *Figure 1.7*), which can affect band-bending at small applied potentials.²⁶ All of the reasons listed above leads to a delayed photocurrent onset, which is often positively shifted from the V_{FB} , and lower the overall photocurrents obtained than the theoretical maximum given by the optical bandgap.

Typically, positive applied potentials are often required to obtain high photocurrents in photoelectrodes. When a positive potential is applied to a photoanode, this potential drop occurs across the space charge layer at the semiconductor/electrolyte interface, where a higher potential leads to an increase in the space charge layer field and the W_{SCL} . The band-bending within the SCL suppresses loss processes such as back-electron hole recombination which is often found to dominate at potentials close to the photocurrent onset.^{27,28} Moreover, as the W_{SCL} increases with increasing positive bias, the charge separation yields also improve, resulting in a greater number of holes migrating to the semiconductor – electrolyte interface. At applied potentials just positive of the V_{FB} , the band bending within the SCL is often insufficient to drive charge separation, therefore recombination processes dominate and no photocurrent is observed (as shown in *Figure 1.7a*). Under moderate positive applied potentials (*Figure 1.7 b*), the space charge layer width increases, where the increased band bending improves charge separation, and drives holes to the surface. These holes accumulate at the surface and are able to drive water oxidation. However, the accumulated holes at the surface are coulombically attracted to the electrons in the bulk, which can lead to back electron-hole recombination (BER) processes, which are in direct kinetic competition with water oxidation. This results in a back flow of electrons from the external circuit and can often manifest as negative spikes on transient photocurrent measurements.²⁸ When high positive potentials are applied to the photoanode, the greater extent of band bending across the space charge layer can suppress the back electron-hole recombination, allowing the holes accumulated at the surface to drive water oxidation (*Figure 1.7c*). The amount of bias required to turn-off back electron-hole recombination losses can

vary from material to material, for instance, potentials of ~ 0.8 V more positive than the V_{FB} may be required to turn off BER for hematite ($\alpha\text{-Fe}_2\text{O}_3$),²⁸ whereas for bismuth vanadate (BiVO_4), this value has been reported to be ~ 1.2 V.²⁷

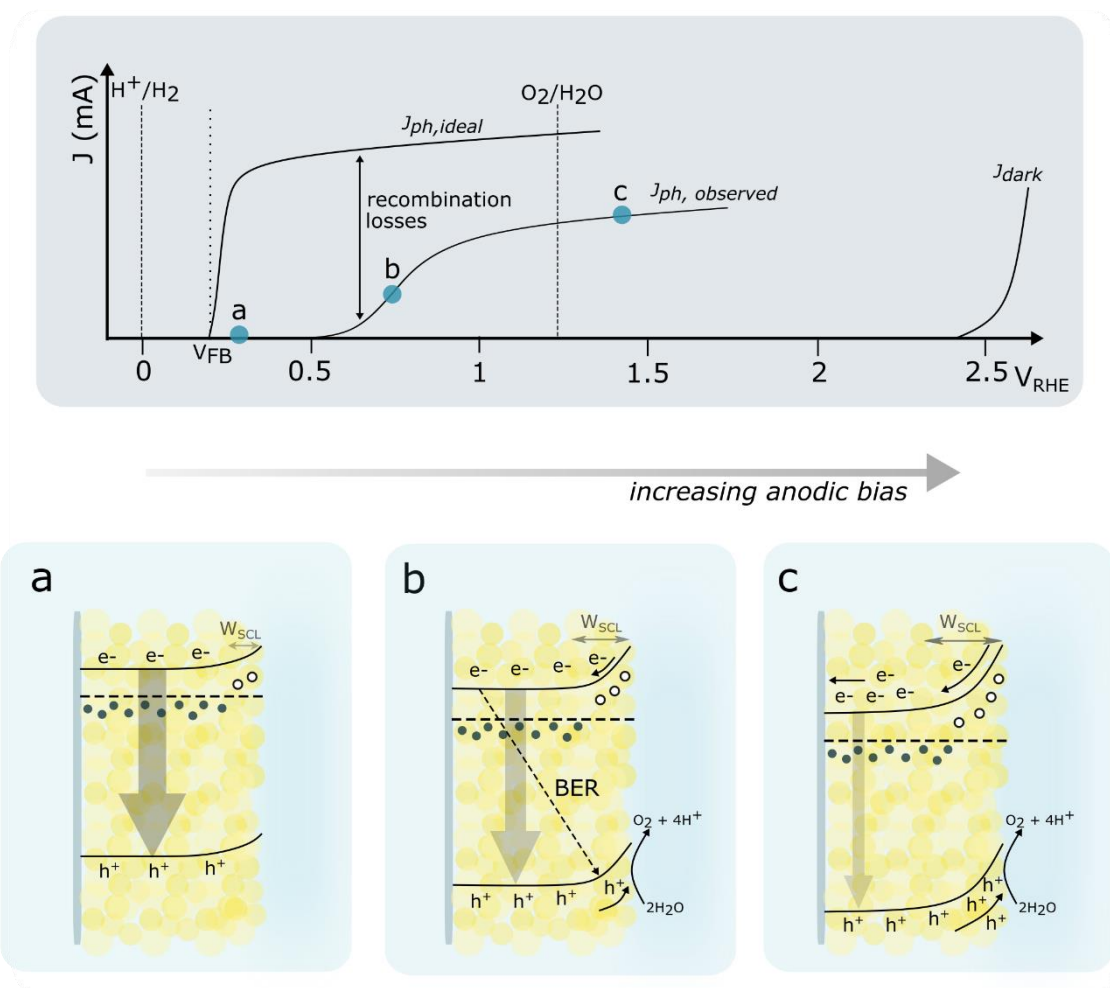


Figure 1.7| Schematic illustration of a current/potential response ($J - V$ curve) for an n-type photoanode. The redox potentials for proton reduction and water oxidation are indicated by the dashed lines. The dark and ideal photocurrent responses (J_{dark} and $J_{ph, ideal}$) are representative of a BiVO_4 photoanode with a flat band potential ~ 0.2 V_{RHE} . The actual observed photocurrent ($J_{ph, observed}$) for a typical BiVO_4 photoanode is also shown. Schematic illustrations of recombination and photoelectrochemical processes with increasing applied potential at points (a), (b) and (c) along the $J_{ph, observed}$ curve are shown underneath.

1.4.4 Metal oxides as photoanodes for water oxidation

To increase the efficiency of photoanodes for water oxidation, several criteria should be met, which have already been discussed above. To summarise, the main desirable properties include: (i) good visible light absorption (to better utilise the solar spectrum), (ii) valence band position must be more

positive than water oxidation potential, (iii) efficient charge separation and transport properties, (iv) low overpotentials for catalysis and (v) high chemical stability. To this end, metal oxide based photoanodes have garnered a lot of interest, owing to their deep valence bands to drive water oxidation, chemical stability in aqueous media, and in some cases, visible light absorption. They also exhibit low toxicity and can be fabricated using low cost methods that are generally up-scalable. *Figure 1.8* shows the band positions and the bandgaps of the most popularly studied materials, which include TiO_2 , WO_3 , $\alpha\text{-Fe}_2\text{O}_3$ and BiVO_4 and their maximum theoretical photocurrents under AM 1.5G illumination.

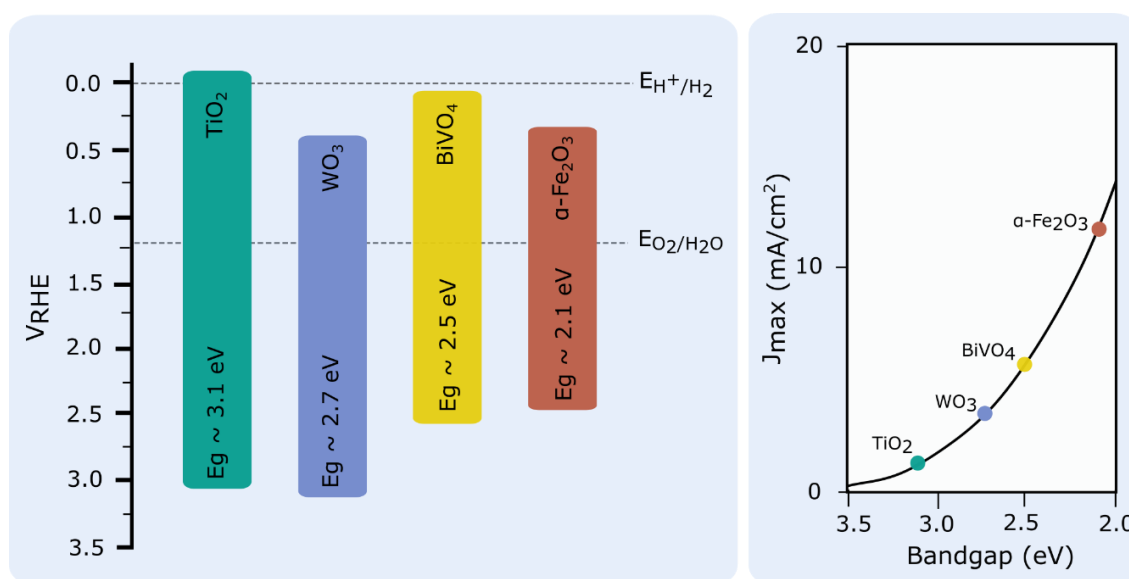


Figure 1.8 | Commonly employed metal oxide semiconductors for water oxidation. Bandgap energies and positions are shown on the left and the theoretical maximum attainable photocurrents (J_{max}) as a function of bandgap is shown on the right. The redox positions for proton reduction and water oxidation are indicated as dotted lines. The J_{max} is calculated under AM 1.5G solar spectrum,²⁹ assuming quantum efficiencies of 100%.

Whilst TiO_2 is one of the most extensively studied photoanode materials, it is the only candidate out of the four that can perform both hydrogen and oxygen evolution half reactions. However, TiO_2 is significantly limited by the large bandgap ($E_g \sim 3.1$ eV) and therefore can only absorb a small fraction of the solar spectrum. The three other materials require external bias or need to be coupled to a photocathode for the proton reduction reaction. WO_3 , also with a relatively wide bandgap, possesses the most oxidising valence band and can show variable selectivity for water oxidation, exhibiting lower Faradaic efficiencies in comparison to the others listed.^{23,30} Fe_2O_3 and BiVO_4 , with bandgaps well within the visible range, ~ 2.1 eV and ~ 2.5 eV respectively, are popular choices. In particular, BiVO_4 has shown a lot of promise in recent literature, therefore it is emerging as a popular candidate for photoanode

applications and is the primary material studied in this thesis. The most notable performances of BiVO₄ photoanodes for water oxidation in recent literature are shown in in *Figure 1.10*.

1.5 Bismuth vanadate photoanodes

1.5.1 Electronic structure

Bismuth vanadate is an n-type ternary metal oxide semiconductor containing ions of formal oxidation state: Bi³⁺ (6s²), V⁵⁺ (3d⁰) and O²⁻ (2p⁶). The main crystalline structures of BiVO₄ include monoclinic scheelite, tetragonal scheelite and tetragonal zircon, of which the monoclinic scheelite structure of BiVO₄ shows the highest photocatalytic activity for water oxidation.³¹ This is often attributed to better photon absorption and a more distorted structure of the monoclinic scheelite phase which aids charge separation.³² In metal oxides, the valence band is typically of O 2p character, which are low-lying, resulting in deep valence band positions and relatively large bandgaps. However, in the case of monoclinic BiVO₄, the presence of Bi³⁺ with filled 6s states allows hybridisation with O 2p states at the top of the valence band edge, leading to a reduction in the bandgap which has been shown by density functional theory (DFT) calculations^{33,34} and observed experimentally.^{34,35} The conduction band minimum is mainly composed of V 3d states. There is however considerable debate regarding the nature of the bandgap. Previously published DFT calculations and experimental data have suggested that the bandgap of BiVO₄ is a direct one.^{33,35} In contrast, other computational studies have reported an indirect bandgap for BiVO₄, however, a direct bandgap also exists at a slightly higher energy.^{36,37} This has also been confirmed experimentally through resonant inelastic X-ray scattering (RIXS) spectroscopy, where the direct band gap is observed ~200 meV above the indirect one.³⁸

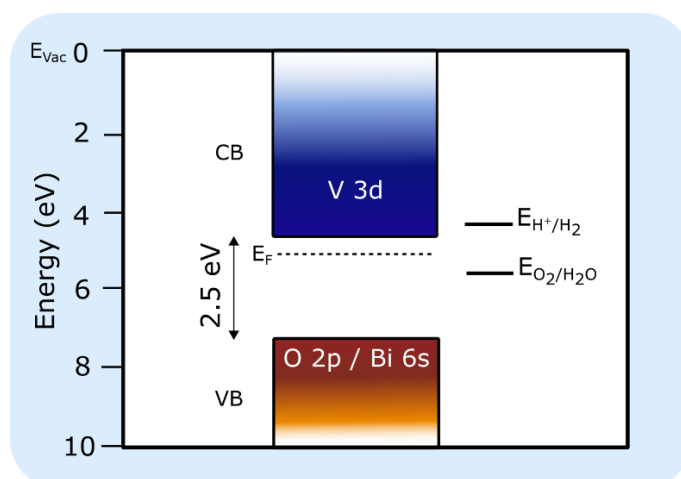


Figure 1.9| Schematic illustration of the electronic structure of monoclinic scheelite BiVO₄. The energetic positions for proton reduction and water oxidation are also indicated, 4.44 and 5.67 eV below the vacuum level, respectively. E_F denotes the Fermi level, which is dependent upon the doping density.

1.5.2 Charge carrier dynamics

Effective hole diffusion lengths of 57 - 100 nm have been reported for BiVO_4 ^{39,40} which is higher than those reported for other metal oxides such as TiO_2 (~10 nm, rutile)⁴¹ and $\alpha\text{-Fe}_2\text{O}_3$ (~2 - 4 nm)⁴². A higher carrier diffusion length implies that a greater amount of holes should be able to diffuse to the space charge layer to drive surface catalysis. Illuminating the sample from the back (through the FTO side) generally results in higher photocurrents in BiVO_4 in comparison to illuminating the sample from the front (through the electrolyte interface side). This has often been attributed to poorer electron transport in comparison to hole transport.⁴³ In addition, low carrier mobilities are typically reported for un-doped BiVO_4 ($0.02 - 0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^{44,45} This may result from the nature of electron transport, where polaronic transport has often been suggested as the culprit behind the low carrier mobilities observed in metal oxides.^{46,47} Polaron formation is a process in which a charge localisation takes place leading to a deformation in the surrounding lattice which stabilises the charge; this is also often known as carrier self-trapping. The extent of interaction between the charge and lattice can dictate the nature of the polaron. For instance, a small polaron is highly localised leading to hopping-like mechanism of transport, whereas a large polaron is more delocalised in comparison and affords a more band-like transport.⁴⁸ Reports of thermally activated hopping of self-trapped carriers^{49,50} and DFT calculations have indicated the formation of small electron polarons in BiVO_4 .⁵¹

Transient absorption spectroscopy (technique described in *section 2.3, chapter 2*) based studies have often been employed to shed light on the charge carrier dynamics, specifically at timescales relevant to water oxidation. Upon bandgap excitation, a broad transient absorption signal is observed when probed at wavelengths in the range 500 – 800 nm in BiVO_4 , which has a peak at 550 nm attributed to photogenerated holes, observed on the microsecond – second ($\mu\text{s} - \text{s}$) timescale.²⁷ By monitoring the transient signal of holes, it is observed that 3 main processes dominate within the $\mu\text{s} - \text{s}$ timescale: bimolecular recombination, back electron-hole recombination (as shown in *Figure 1.5*), and water oxidation. Applied bias plays a huge role in determining which processes dominate, where it can facilitate both initial charge separation, and help switch off back electron-hole recombination (illustrated in *Figure 1.7*). As discussed in *section 1.3.3*, under modest applied potentials, both water oxidation and BER compete, however BER is observed to switch off under high applied potentials ($>1.3 \text{ V}_{\text{RHE}}$).²⁷

1.5.3 Strategies for enhancing photoelectrochemical performance

The flat band potential of BiVO_4 has been reported to be as negative as $\sim 0.1 \text{ V}_{\text{RHE}}$, however the photocurrent onset potential of un-modified is often found to be $0.6 - 0.8 \text{ V}_{\text{RHE}}$ for water oxidation, therefore un-modified BiVO_4 often requires a significant positive applied bias to function. On the other

hand, for oxidation of more facile substrates such as scavengers (*e.g.* sulfite), onset potentials very close to the E_{FB} are observed, indicating a significant presence of surface recombination limiting the water oxidation performance.⁵² To date, several strategies have been employed to result in high performing, stable BiVO_4 photoanodes shown in *Figure 1.10*, achieved by tuning electrolyte composition, adding co-catalysts *etc.* For practical applications, consideration of the long-term stability of photoelectrodes is a critical factor. Leaching of V^{5+} ions into the electrolyte has been found to be key factor in the low stability of BiVO_4 photoanodes, resulting from photocorrosion as holes accumulate at the surface.⁵³ Saturating the electrolyte with V^{5+} ions has been reported to be an effective way to suppress V^{5+} leaching, leading to highly stable BiVO_4 photoanodes (<450 hours) in borate buffer.⁵⁴ Crystallinity of films have also been shown to affect the extent to which BiVO_4 is affected by photocorrosion.^{53,55} Films of low-crystallinity are more susceptible to dissolution of vanadium, whereas when annealed at high temperatures ($\sim 800^\circ\text{C}$), the resulting highly crystalline BiVO_4 exhibits excellent stability under water oxidation conditions (>1100 h).⁵⁵ The choice of electrolyte can also affect the performance, for instance $\text{BiVO}_4/\text{FeOOH}/\text{NiOOH}$ electrodes have been recently reported to be more stable in pH 9 borate buffer⁵⁶ as oppose to pH 7 phosphate buffer.⁵² The long-term instability in phosphate buffer could potentially arise from the formation of bismuth phosphate at the semiconductor/electrolyte interface which modifies the surface of the photoanode.⁵⁷

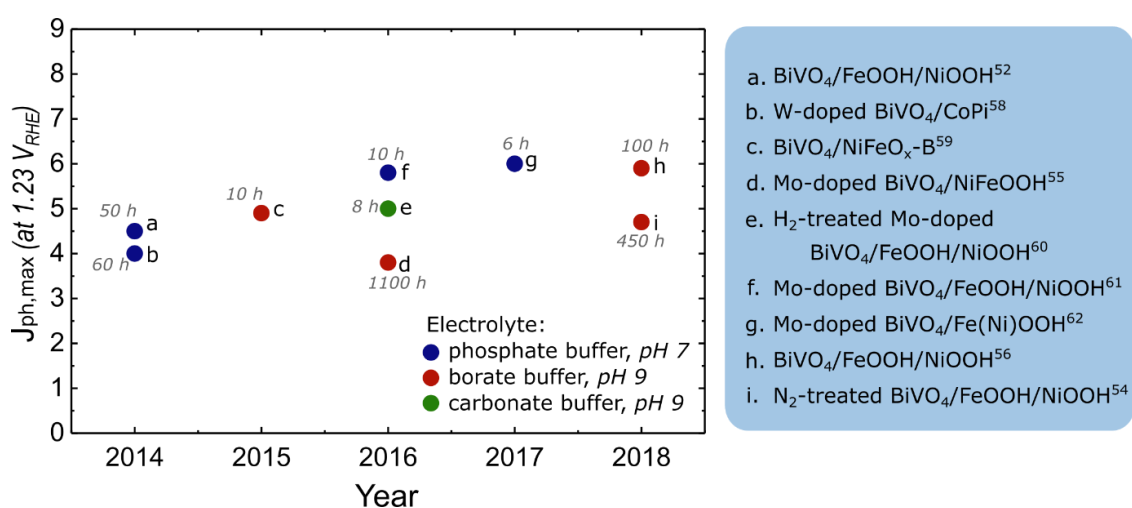


Figure 1.10| Progress of BiVO_4 photoanodes, where BiVO_4 is the single light absorber. The figure compares the photocurrent of BiVO_4 based photoanodes at 1.23 V_{RHE} when coupled with co-catalysts. The stability of the photoanodes under photoelectrochemical water oxidation conditions are noted alongside in grey.

To improve the electrical conductivity of the photoanode, several doping strategies have been employed. Doping is the introduction of impurities into a material to increase the majority carrier

density. The most commonly used dopants for BiVO₄ include tungsten (W) and molybdenum (Mo), where W⁶⁺ and Mo⁶⁺ ions substitute into V⁵⁺ sites.^{63–66} However, presence of dopants can have detrimental effects on the materials, *e.g.* it can introduce additional sub-bandgap electronic states that can function as trap states. Increased majority carrier densities can also reduce the space charge layer widths, which can increase bulk charge carrier recombination. Therefore, optimising the type of dopants used and their concentrations are essential to observe beneficial effects. An effective study of W-doping reported how gradient doping across the film depth can allow band bending to extend across the bulk of the film, leading to an increase in carrier separation efficiencies, where the authors noted an increase in separation efficiency of 60% at 1.23V_{RHE}.⁶⁷ Another avenue of doping often explored is post-synthesis gas treatments, which increases the carrier density without introducing additional metal ions. One popular treatment in recent literature has been H₂-treatment, achieved by annealing the BiVO₄ photoanodes in a H₂ atmosphere.^{39,68} No consensus has been reached on the exact mechanism by which this treatment enhances carrier densities, with reports suggesting the enhancement originates from an increase in oxygen vacancy formation⁶⁹ as well as hydrogen incorporation into BiVO₄.^{39,68} From these doping and annealing studies, it is clear that carrier densities significantly impact upon the photoelectrochemical performance. Oxygen vacancies in metal oxides, including BiVO₄, give rise to the n-type characteristic of the semiconductor and therefore contribute towards the carrier densities of un-doped BiVO₄. As a result, similar to intentional doping (*i.e.* with metal cations), optimising the vacancy concentration can significantly impact upon photoelectrochemical performance.^{70,71} In addition, potential drop across the space charge layer can also ionise n-type dopants (as shown in *Figure 1.6*) induced by the presence of oxygen vacancies, which can interact with photogenerated species.^{72,73} However, the exact effect oxygen vacancies have on the charge carrier dynamics in BiVO₄ is poorly understood and is investigated in this thesis in *chapter 3*.

Spatial separation of charges is paramount to obtaining long-lived charges that are able to perform kinetically challenging reactions such as water oxidation, which occurs on the millisecond – second timescale.^{19,23} In photosynthesis, series of redox co-factors lead to a formation of an electron transport chain (shown in *Figure 1.11a*) that transforms short-lived molecular excited states into long-lived charges, resulting directly from spatial separation of charge carriers. This extends the lifetime of photogenerated species from sub-nanoseconds to greater than milliseconds,²¹ which allows photogenerated species to drive slow redox reactions. In inorganic systems, band offsets of semiconductors can be utilised to mimic energy cascades found in natural photosynthesis, as shown in *Figure 1.11b*, and has been most successfully observed for the WO₃/BiVO₄ heterojunction. WO₃/BiVO₄ heterojunction photoanodes have shown good promise and have garnered great

interest,^{74–76} achieving photocurrents in excess of 6.7 mA cm^{-2} (at $1.23 \text{ V}_{\text{RHE}}$).⁷⁷ Although the charge separation across the junction is deemed responsible for higher photoelectrochemical performance, spectroscopic evidence for the impact on charge carrier dynamics under operational conditions is scarce in literature, and is investigated in this thesis, in *chapter 4*.

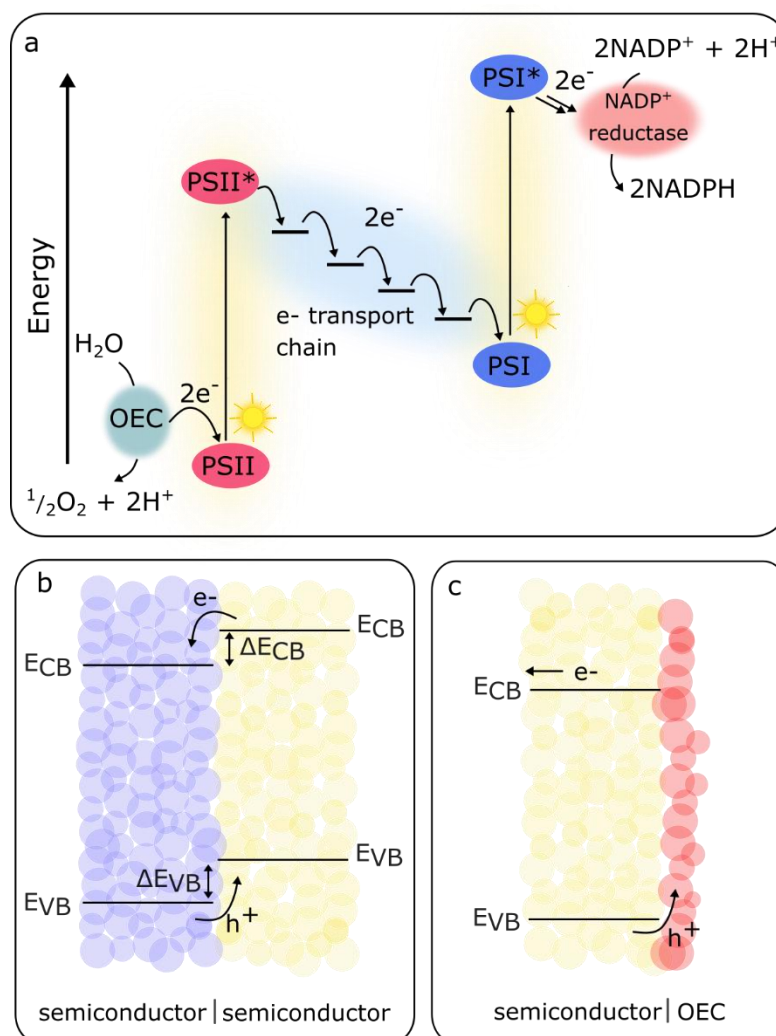


Figure 1.11 | Schematic illustrations of strategies to spatially separate photogenerated charge. (a) Schematic illustration of the z-scheme in natural photosynthesis where electrons liberated from water oxidation at the oxygen evolution centre (OEC) are transferred to PSII. The photoexcited electron at PSII* is transferred through an electron transport chain to reduce PSI where the photoexcited electron at PSI* is ultimately transferred to produce NADPH. The electron chain spatially separates the photogenerated charge across PSII and PSI. (b) A staggered heterojunction between two metal oxide semiconductors, where band offsets between the conduction bands (ΔE_{CB}) and the valence bands (ΔE_{VB}) drives charge separation across the materials. (c) A semiconductor coupled with an electrocatalyst where photogenerated holes are transferred from the valence band of the photoanode to the catalyst layer which subsequently drives the catalysis.

To improve the rate of catalysis, oxygen evolution catalysts are often employed, such that photogenerated holes transfer from the semiconductor to the catalyst layer which then drives water

oxidation. Commonly employed catalysts include CoPi,^{78,79} CoFe – Prussian blue (PB) catalysts⁸⁰ as well as Ni/FeOOH metal oxyhydroxide based catalysts,^{52,56} which have all improved the performance of BiVO₄ photoanodes. However, considerable debate exists in literature regarding the role of catalyst overlayers. For instance, in the case of CoPi, on one hand there are reports of water oxidation driven by CoPi,⁸¹ on the other hand conflicting results have shown CoPi functions as a surface passivation layer,⁷⁸ and increases band bending through the formation of a Schottky junction to improve charge carrier separation.⁷⁹ In addition, it has also been reported that water oxidation on CoPi is several orders of magnitude slower than it is on BiVO₄, indicating that water oxidation on BiVO₄ may be more favourable kinetically.⁷⁹ Ni/FeOOH catalysts when deposited on nanoporous BiVO₄ photoanodes have exhibited remarkable improvement in the water oxidation photoelectrochemical performance, and ranks amongst the highest performing BiVO₄ photoanodes reported.^{52,56} Whilst spectroscopic observations of charge transfer in BiVO₄/PB photoanodes have shown that water oxidation takes place through PB oxidised states, these studies have not been extended to Ni/FeOOH based photoanodes. The electrochemical behaviour of Ni/FeOOH as electrocatalysts and as co-catalysts when functionalised on BiVO₄ are spectroscopically investigated in this thesis, in *chapter 5*.^{52,53,56}

1.6 Thesis outline

As mentioned in the sections above, research on bismuth vanadate based photoanodes have gathered a lot of research interest and has shown the highest photoelectrochemical performance for water oxidation compared to other metal oxide based photoanodes, to date. Although considerable efforts have been invested in optimising the performance, the effect of optimisation strategies on charge carrier dynamics is often poorly understood. In this work a range of steady-state and time-resolved spectroscopic techniques are used in conjunction to probe photoexcited species in BiVO₄ photoanodes. The various materials and techniques used throughout this work are explained in *chapter 2*. Using the spectroscopic tools available, the role of sub-bandgap states induced by chemical defects such as oxygen vacancies are investigated in *chapter 3*. Transient absorption and transient photocurrent measurements are then used in *chapter 4* to investigate charge transfer timescales and charge carrier lifetimes in WO₃/BiVO₄ heterojunction. Finally, BiVO₄ photoanodes functionalised with Ni/FeOOH surface co-catalysts are studied, with comparisons being drawn between the electrochemical and photoelectrochemical performance (functionalised on BiVO₄) of these catalysts when operating at neutral pH.

Chapter 2 | Materials and methods

This chapter outlines the materials and experimental methods employed throughout this thesis, including:

- (a) The details of the synthetic procedures employed to prepare metal oxide photoanodes used throughout the thesis
- (b) The main techniques employed to characterise the materials
- (c) The main experimental techniques used to understand photoanode behaviour and charge carrier dynamics

2.1 Materials synthesis for metal oxides (MO_x)

All materials studied herein were prepared on FTO or quartz substrates, the synthetic procedures for which are detailed below. All aqueous solutions used in the studies herein were prepared using de-ionised (DI) water, where the resistivity of the output water was $\geq 18 \text{ M}\Omega \text{ cm}$.

2.1.1 WO₃

Tungsten oxide (WO₃) photoanodes were prepared using aerosol assisted chemical vapour deposition (AA-CVD) method, previously reported elsewhere.⁸² In brief, the fluorine-doped tin oxide (FTO) substrate was heated to 325 °C. A stock solution of W(CO)₆ (0.6 g, 11.4 mM) was prepared in 1:2 mixture of methanol and acetone, 50 and 100 mL respectively. Depositions of 1 mL of the stock solution results in a film thickness of ~200 nm, as verified previously.⁸² The solution was aerosolised with an ultrasonic humidifier (2 MHz, Liquifog, Johnson Matthey), before being carried into the reaction chamber with N₂ as the carrier gas (0.5 mL/min). Following complete transfer of precursor solution, the FTO substrate was cooled to room temperature over N₂ flow, forming oxygen deficient WO_{3-x} which requires further annealing at 500 °C in air for 1 hour to yield WO₃. The scanning electron microscopy (SEM) image and X-ray diffraction patterns are shown in *Figure 2.1*.

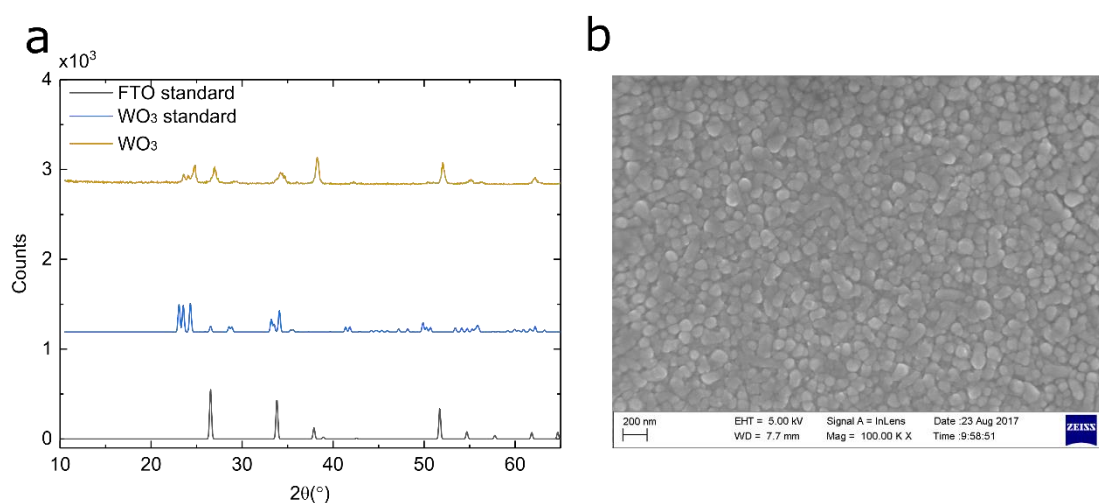


Figure 2.1| Characterisation of WO₃ photoanodes. (a) Typical XRD patterns of WO₃ photoanode alongside reference standards for monoclinic WO₃ and tetragonal cassiterite F:SnO₂ (FTO). (b) SEM images of WO₃ photoanode. Scale bar represents 200 nm.

2.1.2 BiVO_4

Planar bismuth vanadate (BiVO_4) films were prepared using an adapted metal-organic decomposition method described elsewhere.⁸³ Bismuth nitrate pentahydrate (0.1455 g, 200 mM) was dissolved in acetic acid (1.5 mL) and vanadyl acetyl acetone (0.0768 g, 30 mL) was dissolved in acetyl acetone (10 mL). The sol-gel mixture was then prepared by mixing the two solutions followed by stirring at room temperature for 30 minutes. The sol-gel mixture was then deposited on FTO substrate by spin-coating, where 50 μL of the solution was used per layer of deposition. Following the deposition of each layer, the substrates were calcined at 450 $^\circ\text{C}$ for 10 minutes. This process was repeated accordingly for the desired film thicknesses, where each layer corresponded to a film thickness of ~ 25 nm. After the deposition of the final layer, the substrates were calcined at 450 $^\circ\text{C}$ for 5 hours. The scanning electron microscopy (SEM) image and X-ray diffraction patterns are shown in *Figure 2.2*.

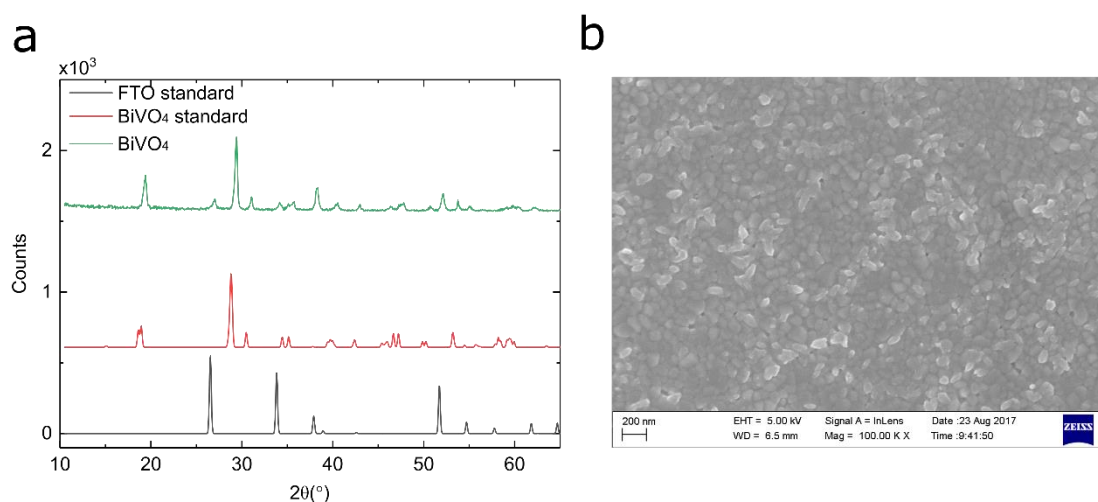


Figure 2.2 | Characterisation of BiVO_4 photoanodes. (a) Typical XRD patterns of BiVO_4 photoanode alongside reference standards for monoclinic BiVO_4 and tetragonal cassiterite F:SnO_2 (FTO). (b) SEM images of BiVO_4 photoanode. Scale bar represents 200 nm.

2.1.3 $\text{WO}_3/\text{BiVO}_4$

For the heterojunction films of $\text{WO}_3/\text{BiVO}_4$ presented in *chapter 4*, the same synthetic procedure outlined in *section 2.1.2* was used to deposit BiVO_4 on the as prepared WO_3 films described in *section 2.1.1*. The scanning electron microscopy (SEM) image and X-ray diffraction patterns are shown in *Figure 2.3*. The absorption spectra of the prepared BiVO_4 and the $\text{WO}_3/\text{BiVO}_4$ photoanodes of varying film thicknesses are presented in *Figure 2.4*.

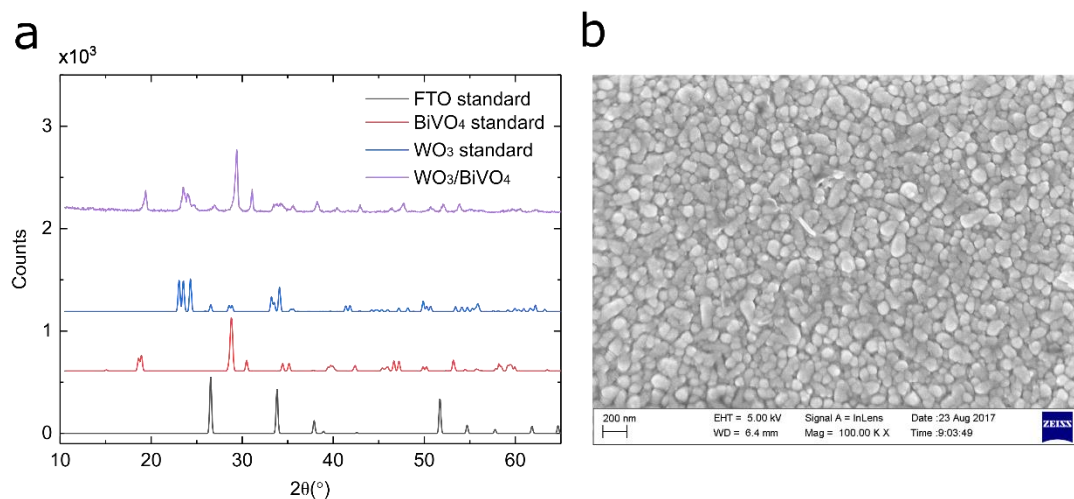


Figure 2.3 | Characterisation of WO₃/BiVO₄ photoanodes. (a) Typical XRD patterns of WO₃/BiVO₄ photoanode alongside reference standards for monoclinic BiVO₄, monoclinic WO₃ and tetragonal cassiterite F:SnO₂ (FTO). (b) SEM images of WO₃/BiVO₄ photoanode. Scale bar represents 200 nm.

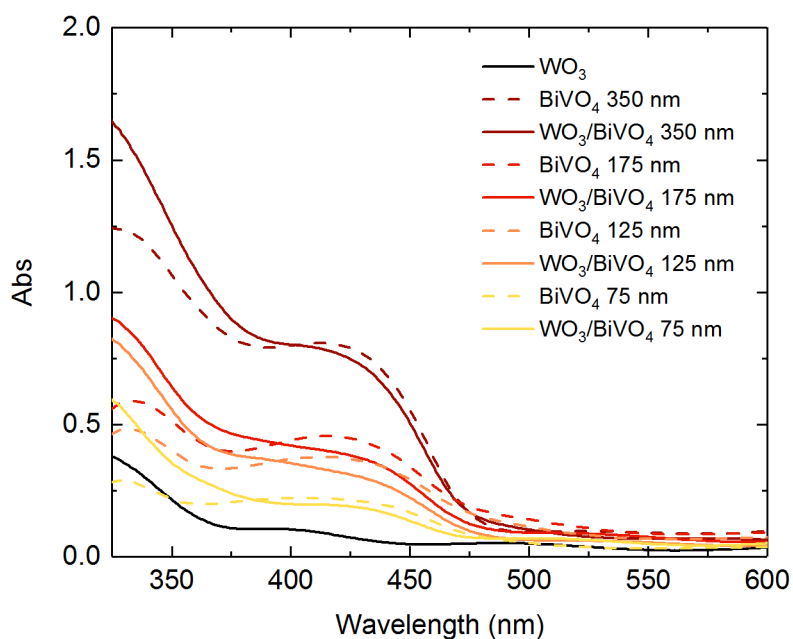


Figure 2.4 | UV-Vis spectra of WO₃ and WO₃/BiVO₄ photoanodes. Absorption spectra of films with varying thickness of BiVO₄ layer. The thickness of WO₃ layer was 200 nm.

2.1.4 MOOH electrocatalysts and nanoporous BiVO₄/MOOH photoanodes

Nanoporous bismuth vanadate (BiVO₄) films coated with and without oxygen evolution co-catalyst, and the catalysts deposited on FTO, studied in *chapter 5*, were kindly provided by the group of Prof. Kyoung-Shin Choi, University of Wisconsin-Madison. The synthetic procedures and characterisation have been published elsewhere and are referenced accordingly, however brief experimental and characterisation details are outlined here.

The three electrocatalysts: FeOOH, Ni(Fe)OOH and FeOOHNiOOH were anodically electrodeposited on FTO substrates in a three-electrode cell consisting of the FTO working electrode (WE), an Ag/AgCl reference electrode (RE) and a platinum counter electrode (CE). The synthetic procedure of the electrocatalyst electrodes have been published previously.⁸⁴

- 1. FeOOH electrodes.** Anodic deposition of FeOOH was conducted in a FeSO₄.H₂O solution (10 mM, 40 mL, pH ~ 4.8) at 70°C. The solution was degassed in N₂ for 30 minutes prior to deposition. The deposition was performed at 1.2 V_{Ag/AgCl}, during which a total charge of 23 mC/cm² was passed. This resulted in a FeOOH film thickness of ~80 nm, which was rinsed with DI water and dried with a gentle stream of air.

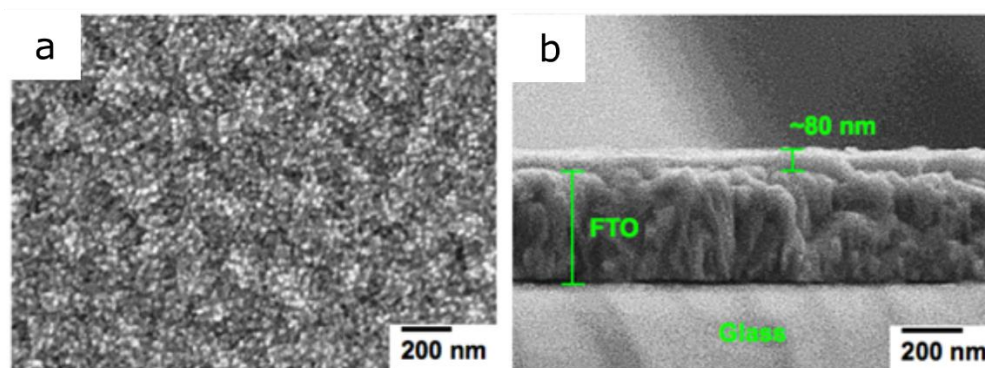


Figure 2.5 | SEM image of FeOOH electrocatalyst electrode. (a) Top view and (b) side view. The scale bar represents 200 nm. Image taken from the referenced publication.⁸⁴

- 2. Ni(Fe)OOH electrodes.** NiOOH was anodically deposited from a NiSO₄.6H₂O aqueous solution (100 mM, 40 mL, pH ~ 6.8 – 7), at 70°C. The deposition was performed at 1.2 V_{Ag/AgCl}, during which a total charge of 150 mC/cm² was passed. The film was then rinsed with DI water and subsequently dried over a gentle stream of air. This resulted in a NiOOH film of thickness ~80 nm. The as-deposited NiOOH was black/grey in colour which gradually turns colourless due to the conversion of NiOOH to Ni(OH)₂. As the plating solution used for NiOOH deposition contained Fe impurities from the Ni source, the as-prepared NiOOH films had a Fe content of

1% as determined by inductively coupled plasma optical spectrometry (ICP-OES). As the electrolytes used to evaluate the oxygen evolution characteristics also contained Fe impurities, additional Fe may have also incorporated into NiOOH lattice during investigation. For this reason, NiOOH used in this study is denoted as Ni(Fe)OOH.

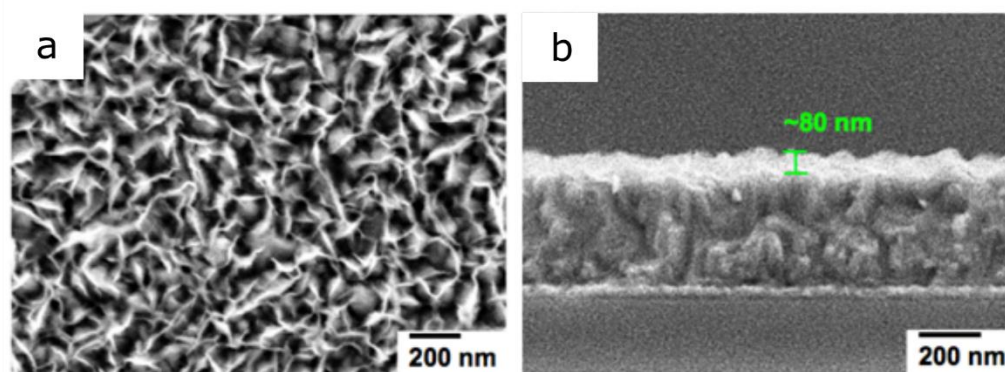


Figure 2.6 | SEM image of Ni(Fe)OOH electrocatalyst electrode. (a) Top view and (b) side view. The scale bar represents 200 nm. Image taken from the referenced publication.⁸⁴

3. **FeOOHNiOOH electrodes.** The FeOOHNiOOH films were prepared by sequential deposition of FeOOH and NiOOH layers using the methods described above. Although the same amount of charge used to prepare the individual electrodes (23 mC/cm² and 150 mC/cm² for FeOOH and NiOOH, respectively) were also used herein, the overall thickness of the FeOOHNiOOH electrode was determined to be ~120 nm. This indicated significant mixing Ni and Fe layers, and a proportion of the NiOOH being deposited within the voids of the FeOOH layer. The resulting electrode was rinsed with DI water and dried with a gentle stream of air. The atomic ratio of Fe:Ni in the as-prepared FeOOHNiOOH films was 79:21, as determined by ICP-OES.

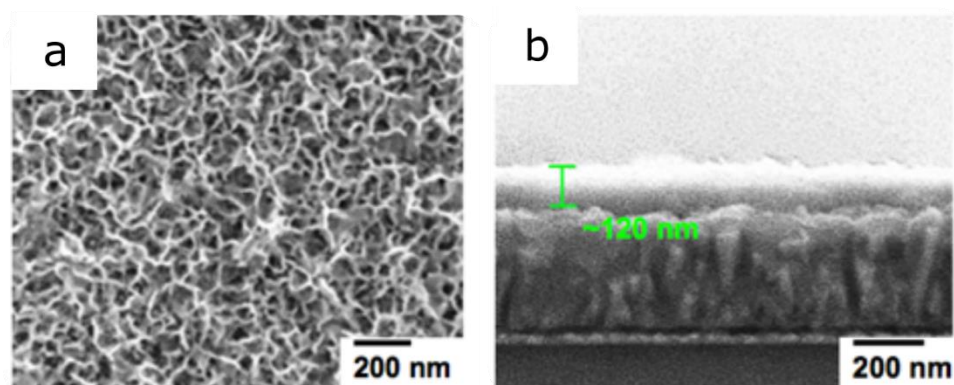


Figure 2. 7 | SEM image of FeOOHNiOOH electrocatalyst electrode. (a) Top view and (b) side view. The scale bar represents 200 nm. Image taken from the referenced publication.⁸⁴

Nanoporous BiVO_4 photoanodes were prepared using electrodeposition method reported previously.⁵² Firstly, BiOI electrodes were prepared by electrodeposition. A $\text{Bi}(\text{NO}_3)_3$ solution (0.04 M) was prepared by dissolving $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in KI solution (0.4 M, 50 mL) and the pH was adjusted to 1.7 by adding HNO_3 . Absolute ethanol (20 mL) containing p-benzoquinone (0.23 M) was then added to the solution and stirred vigorously. A three-electrode cell was used for the electrodeposition, with an FTO working electrode, a Ag/AgCl reference electrode and a platinum counter electrode. BiOI was deposited cathodically by applying a potential of $-0.1 \text{ V}_{\text{Ag/AgCl}}$ at room temperature for 3-5 minutes, passing a total charge of 0.13 C/cm^2 . The BiOI electrode was then placed in a solution of dimethyl sulfoxide (0.15 – 0.2 mL) containing vanadyl acetylacetonate (0.2 M), and heated in a muffle furnace to anneal at 450°C for 2 hours, which converted the BiOI to BiVO_4 . Excess V_2O_5 on the electrodes was removed by soaking the electrodes in NaOH (1 M) for 30 minutes. The resulting BiVO_4 electrodes were then rinsed with DI water and dried in room temperature. The nanoporous BiVO_4 photoanodes were 450-500 nm in thickness. This is shown in SEM image shown in Figure 2.8, provided by the group of Prof. Choi.

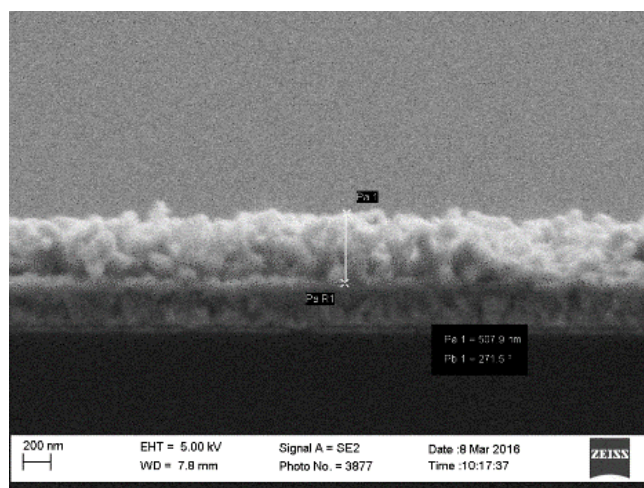


Figure 2.8 | SEM image of nanoporous BiVO_4 photoanode. The scale bar represents 200 nm.

- 1. $\text{BiVO}_4/\text{FeOOH}$ films.** FeOOH was photo-electrodeposited onto nanoporous BiVO_4 photoanodes, in a FeSO_4 solution (0.1 M). The FeSO_4 solution was degassed with nitrogen for 1 hour before photodeposition. Photodeposition was conducted in a standard three-electrode cell described above, and irradiated with a Xe arc lamp (300 W) equipped with an AM1.5G filter, neutral density and IR filters. The light intensity was adjusted to 1 mW/cm^2 . During illumination, photogenerated holes in BiVO_4 oxidise Fe^{2+} in solution to Fe^{3+} , which precipitate as FeOOH on the BiVO_4 surface. An external bias of $0.25 \text{ V}_{\text{Ag/AgCl}}$ was also applied to facilitate the deposition process, which lasted for 20 min during which a total charge of $\sim 45 \text{ mC/cm}^2$

was passed. Following this step, a further electrodeposition of FeOOH was also performed in the same solution by applying a potential of 1.2 V_{Ag/AgCl} for 1 minute. This step ensured maximal coverage of BiVO₄ surface and any exposed FTO surface to the electrolyte.

2. **BiVO₄/Ni(Fe)OOH films.** A similar procedure used to deposit FeOOH on BiVO₄ was used to also deposit Ni(Fe)OOH, except for the plating solution which was NiSO₄ (0.1 M) and the pH was adjusted to 6.5 – 7.2 by addition of NaOH. During illumination, the photogenerated holes in BiVO₄ oxidise the Ni²⁺ in solution to Ni³⁺ which precipitates out as NiOOH on BiVO₄ surface. Iron impurities in electrolyte can spontaneously incorporate into the NiOOH lattice, which has been shown previously, forming Ni(Fe)OOH.⁸⁴ An external bias of 0.11 V_{Ag/AgCl} was also applied, passing a total charge of ~22 mC/cm². After photodeposition, an electrodeposition step of NiOOH was also conducted in the same solution, by applying a potential of +1.2 V_{Ag/AgCl} for 1 minute.
3. **BiVO₄/FeOOHNiOOH films.** To prepare the mixed double layer catalysts on BiVO₄, FeOOH and NiOOH were deposited consecutively using the conditions described above.

2.2 Materials and characterisation

2.2.1 SEM, XPS, XRD

Morphologies of films were determined using scanning electron microscopy (SEM) images which were obtained with a LEO 1525 scanning electron microscope (FESEM, 5kV). XRD measurements to determine the phase composition of metal oxide films were kindly provided by Dr. Andreas Kafizas, Imperial College London. The measurements were obtained using a Bruker-Axs diffractometer equipped with a PSD LinxEye detector. The instrument uses a Cu source for X-ray generation (V = 40 kV, I = 30 mA) with Cu K α 1 (λ = 1.54056 Å) and Cu K α 2 radiation (λ = 1.54439 Å) emitted with an intensity ratio of 2:1. The incident beam was kept at 1° and the angular range of the patterns collected between $10 \leq 2\theta^\circ \leq 66$ with a step size of 0.05°. X-ray photoemission spectroscopy analysis was kindly provided by Mr. Benjamin Moss. The data were obtained from a Thermo Scientific K-Alpha spectrometer equipped with an Al K α X-ray source (1486.6 eV) coupled with an 180° double focussing hemispherical analyser with a 2S detector at an operating pressure of 1×10^{-8} mbar and a flood gun to minimise charging effects from photoemission. Films were mounted on to the sample holder adhered with carbon tape. All core lines were referenced against the C 1s (C-C), which is at 248.8 eV. Data were subsequently processed and analysed on the CASAXPS software package.

2.2.2 Photoelectrochemical characterisation

Photoelectrochemical (PEC) measurements were conducted in a home-built three electrode cell. The PEC cell consisted of quartz windows (area 0.5 cm²), where the photoanode material was placed as the working electrode, a Pt mesh was utilised as the counter electrode and a saturated KCl Ag/AgCl was employed as the reference electrode (Metrohm). Applied potentials were measured vs Ag/AgCl ($V_{Ag/AgCl}$) and were converted to applied potentials vs the reversible hydrogen electrode (RHE) using the Nernst equation:

$$V_{RHE} = V_{Ag/AgCl} + 0.0591 \times pH + V_{Ag/AgCl}^0 \quad (\text{Equation 2.1})$$

Where $V_{Ag/AgCl}^0$ is the standard potential of the Ag/AgCl reference electrode in saturated potassium chloride solution (197 mV). Unless stated otherwise, the measurements were conducted in a 0.1 M potassium phosphate buffer to maintain a constant pH of 7. An Autolab potentiostat (PGSTAT 101, Metrohm) was used to apply the potential to the cell and the data were recorded with Nova software (Metrohm).

2.2.2.1 Linear sweep voltammetry (LSV)

Linear-sweep voltammetry (LSV) measurements were performed in a home-built photoelectrochemical set-up, illustrated in *Figure 2.9*. The set-up consisted of a Xe-lamp light source, filters and lenses, a home-built three-electrode PEC cell coupled to a potentiostat.

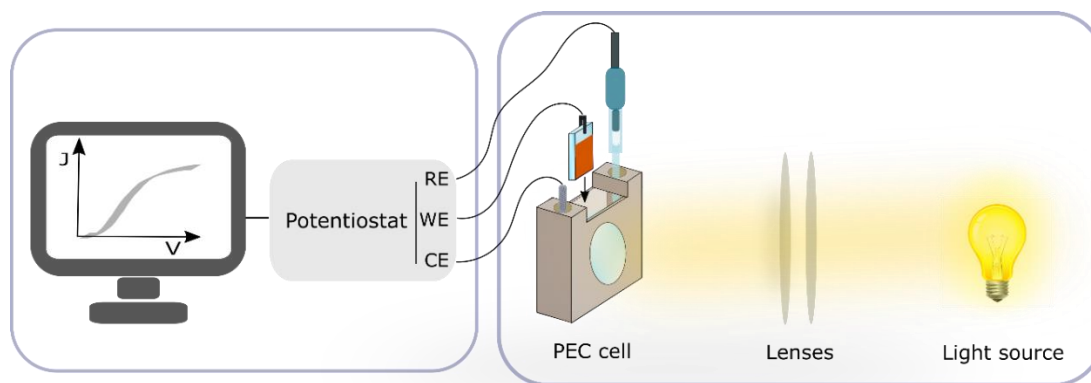


Figure 2.9 | Schematic illustration of the photoelectrochemical set-up.

To obtain the same photon flux as AM 1.5G at wavelengths lower than 650 nm, the power output of the Xe-light source (75 W, Hammamatsu) was calibrated using a KG3 filter and a Si-photodiode. Integrating the solar AM 1.5G spectrum up to 650 nm, the Si-photodiode should produce a current of 7.2 mA cm⁻², which was then used to adjust the position of the sample to correspond to 1 sun

irradiation conditions (see *Figure A5* for spectral output). Unless specified otherwise, the scan rate used for linear sweep voltammetry was 10 mV/s.

2.2.2.2 Absorbed photon-to-current conversion efficiency measurements (APCE)

To determine the APCE of the photoanodes under simulated 1 sun equivalent illumination, the photon flux of the simulated 1 sun illumination source (Xe lamp) (*Figure A5* in *appendix*) was first determined below 500 nm which is typically the absorption onset of the films, the following equation was used:

$$\#photons = \int_{350\text{ nm}}^{500\text{ nm}} Flux(\lambda).d(\lambda) \quad (\text{Equation 2.2})$$

The absorbance of the films were also determined from the UV-Vis data in the region 350 – 500 nm using the equation:

$$Absorptance = 1 - 10^{-A} \quad (\text{Equation 2.3})$$

Where A is the absorbance of the film. The number of photons absorbed was then calculated using:

$$\#photons\ absorbed = \int_{350\text{ nm}}^{500\text{ nm}} (\#photons \times Absorptance).d(\lambda) \quad (\text{Equation 2.4})$$

From the photocurrents obtained from the films under simulated 1 sun illumination at 1.23 V_{RHE}, the APCE was determined using:

$$APCE = \frac{J\ (A\ cm^{-2}) / 1.602 \times 10^{-19} (C)}{\#photons\ absorbed\ (cm^{-2}s^{-1})} \quad (\text{Equation 2.5})$$

2.2.2.3 Incident photon-to-current conversion efficiency measurements (IPCE)

Incident photon-to-current conversion efficiency measurements were conducted in a setup illustrated in *Figure 2.10*. The light from the Xe lamp was fitted with a monochromator (OBB-2001, Photon Technology International). The intensity of the monochromated light was measured using an optical power meter (PM 100, Thorlabs) equipped with a silicon photodiode (S120UV, Thorlabs). The IPCE was determined using the following equation:

$$IPCE = \frac{J_{ph} \times h \times c}{P_{\lambda} \times \lambda \times e} \quad (\text{Equation 2.6})$$

Where J_{ph} (mA cm⁻²) is the photocurrent density, h is the Planck's constant, c is the speed of light, P_λ (mW cm⁻²) is the power intensity of the monochromatic light at a given wavelength λ(nm) and e is the charge of an electron.

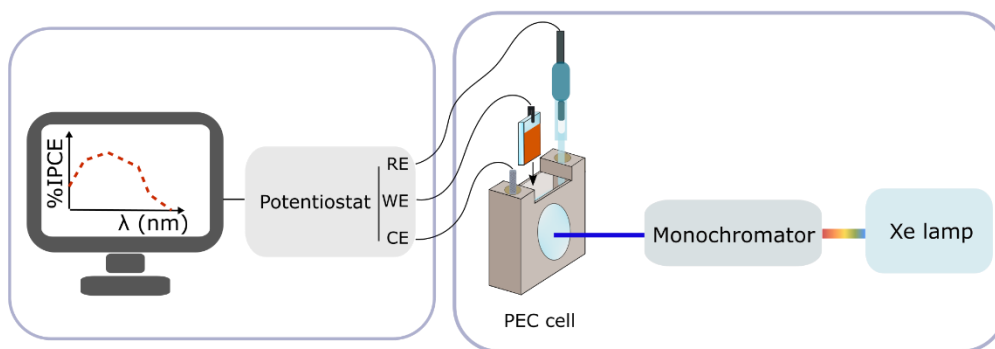


Figure 2.10| Schematic illustration of the IPCE set-up.

2.3 Transient absorption spectroscopy (TAS)

Transient absorption spectroscopy is a powerful tool which can be employed to observe the charge-carrier dynamics of photogenerated species, and is therefore highly applicable to the study of photoelectrodes for solar water splitting. Essentially, it is a time-resolved pump-probe technique, illustrated in *Figure 2.11*. The first part of this section outlines the main principles of TAS. Subsequent parts of the section describe the set up for the TAS systems employed in this thesis for the study of processes at fast and slow timescales.

2.3.1 Principles of TAS

TAS is a time-resolved pump-probe technique which was originally developed by Lord Porter to study the behaviour of short-lived radical species.⁸⁵ Typically, a short light pulse (pump) is used to excite the material in question, and the resulting change in the optical density of the material due to the photogenerated species (*i.e.* photogenerated holes and electrons) are monitored using a second light beam (probe) which is time-delayed with respect to the pump. This relies on the premise that photogenerated species have their own signature optical absorption profile. Therefore the change in the optical density of the sample with respect to the ground state can be used to detect photogenerated species, and follow processes such as charge carrier generation, trapping, recombination and catalysis. The time-resolution of the measurements is limited by the pulse-width of the pump and probe beams.

2.3.2 Calculating the change in the optical density (ΔOD)

According to the Beer-Lambert law, the optical density (OD) of a sample is defined as:

$$OD(\lambda, t) = -\log(T(\lambda, t)) = -\log\left(\frac{I(\lambda, t)}{I(\lambda_i)}\right) = \epsilon(\lambda) \cdot c(t) \cdot l \quad (\text{Equation 2.7})$$

Where $T(\lambda, t)$ represents the transmittance as a function of time at a given wavelength, $I(\lambda_i)$ and $I(\lambda, t)$ are the intensities of incident and transmitted light, $\epsilon(\lambda)$ is the molar extinction coefficient of the material, $c(t)$ is the concentration of species as a function of time, and l is the path-length.

Following photoexcitation, the change in the optical density of the sample $\Delta OD(\lambda, t)$ is given by:

$$\Delta OD(\lambda, t) = OD(t, \lambda) - OD_0(\lambda) \quad (\text{Equation 2.8})$$

This can also be expressed as:

$$\Delta OD(\lambda, t) = -\log\left(\frac{I(\lambda, t)}{I(\lambda_i)}\right) + \log\left(\frac{I(\lambda, t_0)}{I(\lambda_i)}\right) = -\log\left(\frac{I(\lambda, t)}{I(\lambda, t_0)}\right) \quad (\text{Equation 2.9})$$

Since the intensity of the transmitted light ($I(\lambda, t)$) is a summation of the intensity before excitation pulse ($I(\lambda, t_0)$) and change in the intensity of the transmitted light ($\Delta I(\lambda, t)$), the $\Delta OD(\lambda, t)$ can then be expressed as:

$$\Delta OD(\lambda, t) = -\log\left(\frac{I(\lambda, t_0) + \Delta I(\lambda, t)}{I(\lambda, t_0)}\right) = -\log\left(1 + \frac{\Delta I(\lambda, t)}{I(\lambda, t_0)}\right) \quad (\text{Equation 2.10})$$

The $\Delta OD(\lambda, t)$ signal is calculated from the change in the light intensity detected by the change in potential ($\Delta V(\lambda, t)$) detected by the photodiode, where $\Delta OD(\lambda, t)$ is proportional to $\Delta V(\lambda, t)$. Therefore, *equation 2.10* can be rewritten as:

$$\Delta OD(\lambda, t) = -\log\left(1 + \frac{\Delta V(\lambda, t)}{V(\lambda, t_0)}\right) \approx -\frac{1}{2.303} \ln\left(1 + \frac{\Delta V(\lambda, t)}{V(\lambda, t_0)}\right) \quad (\text{Equation 2.11})$$

where $V(\lambda, t_0)$ is the potential measured by the photodiode prior to excitation.

For small values of x , $\ln(1 + x) \approx x$, therefore, the $\Delta OD(\lambda, t)$ can be given by:

$$\Delta OD(\lambda, t) \approx -\frac{1}{2.303} \times \frac{\Delta V(\lambda, t)}{V(\lambda, t_0)} \quad (\text{Equation 2.12})$$

2.3.3 Contributions to the optical signal

Photoexcitation of samples from the ground state to the excited state will result in a change in the optical signal observed, with contributions from:

- (1) A positive signal ($\Delta OD > 0$) resulting from the appearance of new absorption bands associated with photogenerated species
- (2) A negative signal ($\Delta OD < 0$) originating from the decrease in the ground state absorption, due to depopulation of ground state following photoexcitation (ground state bleach). Processes such as stimulated emission can also increase the light intensity received by the detector therefore will also manifest as a negative signal.

2.3.4 Ultrafast pump – probe (fs-TAS) measurements

Transient absorption measurements were conducted on the femtosecond – nanosecond timescale using a regeneratively amplified Ti:sapphire laser system (Solstice, Spectra-Physics) and Helios spectrometers (Ultrafast Systems), which generates 800 nm laser pulses (pulse width: 92 fs, repetition rate: 1 kHz). To generate the pump, a fraction of the 800 nm beam was directed through a sequence of optical parametric amplifier (TOPAS Prime, Spectra-Physics) and a frequency mixer (NirUVVis, Light Conversion) to tune the excitation wavelength. The intensity of the pump was modulated using neutral density filters, and measured using an energy meter (VEGA, P/N 7Z01560, OPHIR Photonics), fitted with a 0.5 mm diameter aperture. The pump beam at the sample was slightly larger than 0.5 mm. A visible white light continuum (WLC) was used as the probe, generated from a fraction of the 800 nm pulse, focused onto a Ti:sapphire crystal. The probe beam is delayed with respect to the pump beam by a motorised delay stage, by changing the path length of the probe beam, before the generation of the WLC. To reduce the noise, the WLC was split into two beams, where one is passed through the sample, and the other is used as reference. Both beams are subsequently focused onto separate fibre-optic coupled multichannel spectrometers (CMOS sensors). Alternate pump pulses were blocked using a synchronised chopper (500 Hz). As such, absorption spectra of the excited and unexcited sample were obtained to determine the time-resolved absorption difference spectrum. Time zero were then adjusted such that it occurs at the half-amplitude of the initial rise. The presented decay kinetics were averaged over a spectral range of ca. 5 nm. The setup is illustrated in *Figure 2.11*.

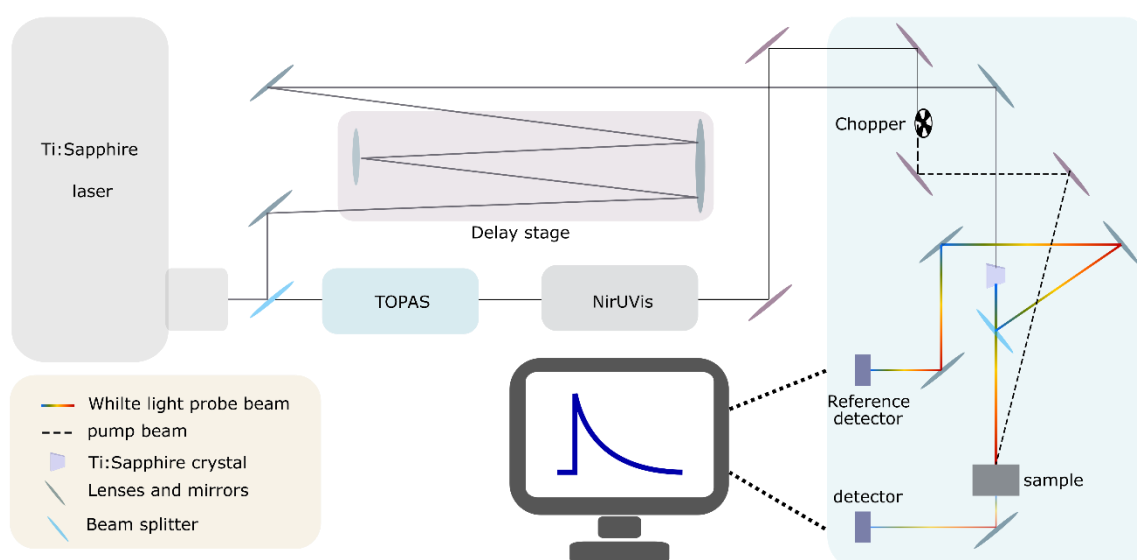


Figure 2.11| Schematic illustration of the TAS set-up for ultra-fast pump-probe measurements.

2.3.5 Ultrafast pump – push – probe measurements

Three-pulse ultra-fast UV *pump*- IR *push* – Vis *probe* technique is similar to the pump-probe technique. However, this approach employs a third low energy (2060 nm, 0.6 eV) push pulse to selectively excite trapped electrons from defect states into the conduction band, an approach previously applied to organic semiconductors.⁸⁶ Thus, the population of sub-bandgap states can be selectively modulated, allowing the resulting impact on charge carrier dynamics to be investigated.

These measurements were obtained using a modified transient absorption set up described earlier. A fraction of the 800 nm beam was used to seed a β -barium borate (BBO) doubling crystal. BBO produced 400 nm light by second harmonic generation which was used as the “*pump*”. To generate the *push*, a fraction of the 800 nm beam was directed through a sequence of optical parametric amplifier (TOPAS Prime, Spectra-Physics) and a frequency mixer (NirUVis, Light Conversion) and tuned to 2060 nm. The intensities used were between the range 3 – 10 mJ cm⁻². The time delay between the *pump* and the *push* was adjusted and fixed at ~10 picosecond with a mechanical stage. The *probe* (a visible white light continuum) was generated from a fraction of the 800 nm pulse, focused onto a Ti:Sapphire crystal. The output of the *pump* (modulated at 500 Hz), the broadband visible-near-infrared (~400 - 850 nm) *probe* and the *push* were focused onto a ~ 0.2 mm² spot on the sample. The same detection system used for the pump-probe measurements was employed in these experiments.

2.3.6 Microsecond – second TAS measurements

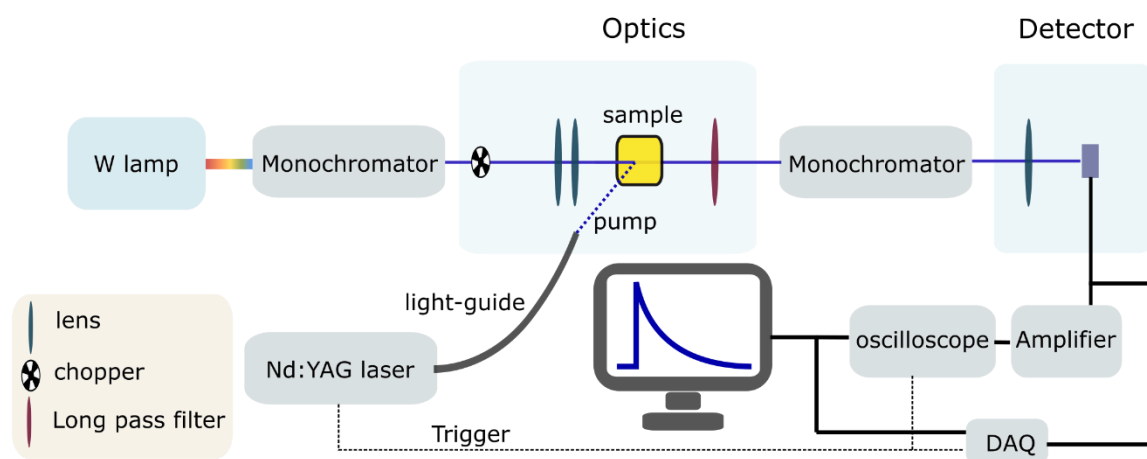


Figure 2.12| Schematic illustration of the TAS set-up for microsecond-second pump-probe measurements.

Transient absorption spectroscopy measurements on the microsecond – second timescale were carried out on a home-built configuration consisting of a Nd:YAG laser (OPOTEK Inc., Opolette 355 laser system, 7 ns pulse width) at 355 nm. The setup employed is illustrated in *Figure 2.12*. The laser

frequency was set to 0.7 Hz, and the laser intensity adjusted to $300 \mu\text{J cm}^{-2}$ (unless stated otherwise). The light source used for the probe beam is a 100 W Bentham IL1 tungsten lamp coupled to a monochromator (OBB-2001, Photon Technology International). To filter scattered laser light, the probe beam passed through longpass filters and another monochromator set to the same wavelength as the probe beam. To detect the transmitted photons, a Si-photodiode was employed (Hamamatsu). The obtained data were processed through an amplifier (Costronics) and subsequently recorded by an oscilloscope (Tektronics TDS 2012B) for the μs -ms timescale, and the ms-s timescale data were recorded with a DAQ card (National Instruments, NI USB-6211). For each transient absorption decay, the data were averaged over 100 laser pulses. The kinetic traces were subsequently smoothed using an in-house MatLab app, designed and kindly provided by Michael Sachs and Benjamin Moss, Imperial College London. The system and data acquisition were controlled by a home-programmed Labview software. The electrical bias was applied using an Autolab potentiostat (PGSTAT 101, Metrohm).

2.4 Transient photocurrent measurements (TPC)

To determine the charge extraction properties of the photoanode materials, transient photocurrent (TPC) data were obtained with a modified TAS setup (μs -s TAS, *section 2.3.6*) and the same excitation source as TA measurements, however the probe beam was blocked. Signals were recorded on an oscilloscope (Tektronics TDS 2012B) which was coupled to a ministat (Sycopel Scientific Ltd.) that was connected to a three-electrode PEC cell (with the sample as the working electrode, including saturated Ag/AgCl electrode and platinum mesh as reference and counter electrodes, respectively). The ministat was fitted with an external resistor (typically 98Ω) which was placed in series with the counter electrode. The laser-induced transient signals were measured as a change in potential across the external resistor, which were subsequently converted from volts to current using Ohm's law to yield time-resolved transient photocurrent signals. Time resolved charge extraction from the photoanodes was subsequently determined by integrating the transient photocurrent trace.

2.5 Steady state absorption spectroscopy (UV-Vis)

Transmission spectra of films were measured using an UV-Vis spectrometer (Cary-60, Agilent Technologies). Diffuse reflectance of nanostructured films were obtained using an UV-Vis spectrometer equipped with an integrated sphere (Shimadzu).

2.6 Spectroelectrochemistry (SEC)

Spectroelectrochemistry (SEC) allows the determination of change in the optical density (ΔOD) of a material resulting from applied potential, and thus oxidation or reduction of sample under steady-state conditions.

In this thesis, the data are measured as the difference in the optical absorption spectra as a function of applied potential, with respect to the open-circuit potential (unless stated otherwise). The technique is detailed in Pastor et al.⁸⁷ Absorption spectra were taken using a Cary 60 UV-Vis spectrometer (Agilent Technologies), fitted with a PEC cell.

2.7 Spectroelectrochemical – photo-induced absorption spectroscopy (SEC-PIAS)

Spectroelectrochemical – photo-induced absorption spectroscopy (SEC-PIAS) is a steady-state pump - probe technique employed in the studies herein to study the photo-induced population of accumulated species under continuous illumination, at a constant applied potential where processes such as back electron-hole recombination is turned off. SEC-PIAS has been reported previously for studies of metal oxide photoelectrodes under operational conditions.^{23,88–91} This technique uses a modified – TAS setup (outlined in *section 2.3.6*), however a continuous LED light source (365 nm) is used instead of a laser pulse, to photogenerate species, which allows the system to reach steady-state. The LED light pulses were generated using a frequency generator to generate 5 V square-wave typically at a frequency of 0.1 Hz, that also triggers the MOSFET (STMicroelectronics), the LED power supply (TTI), the oscilloscope (Tektronics) and the DAQ card (National Instruments). Both the optical changes in the sample (recorded as ΔOD) and the concomitant transient photocurrents (TPC) were recorded simultaneously. The TPC were recorded using the oscilloscope coupled to an Autolab PGSTAT 101 potentiostat (Metrohm). The set-up is illustrated in *Figure 2.13*.

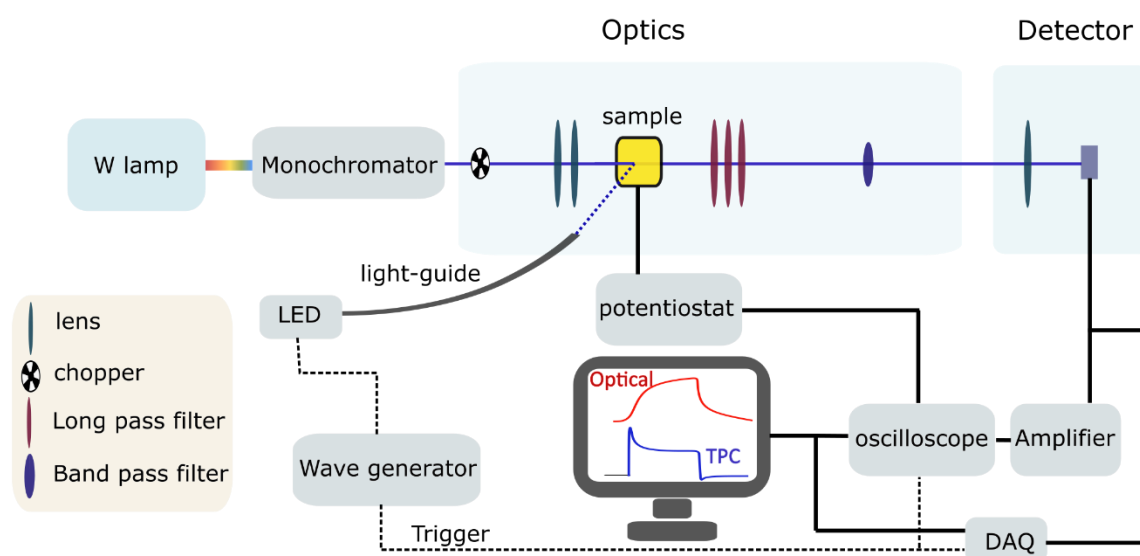


Figure 2.13 | Schematic illustration of the SEC-PIAS set up used to monitor the photo-induced optical and the transient photocurrent signal under continuous illumination.

When the LED is switched on, accumulation of photogenerated species (*i.e.* electrons, holes) results in an increase in the optical signal (ΔOD). Steady state conditions are reached when the flux of photogenerated species towards the photoelectrode surface equal the rate of consumption of the

species. The steady-state spectrum of the photogenerated species can be obtained by recording the optical signal across different wavelengths, at a given light intensity and applied potential. When the LED is switched off, the optical signal decay correspond to the consumption of the accumulated species by recombination, or photoelectrochemical reaction. The concomitant photocurrent signals associated with the LED ON/OFF cycle is also recorded. Immediately following LED switch on, a positive transient spike is often observed. This can be attributed to initial recombination processes that occurs within the material. After this fast decay, a positive steady-state current is observed for the n-type materials studied herein, corresponding to photoelectrochemical oxidation (*i.e.* water oxidation). After the LED is switched off, negative transient spike may be observed which may correspond to back electron-hole recombination processes.²⁸

2.8 Step potential – spectroelectrochemistry (SP-SEC)

Step potential – spectroelectrochemistry is another example of a steady-state pump-probe technique, much like SEC-PIAS, which detects the change in the optical absorption of the sample. However, the LED light source is replaced with a square wave of oxidative and reductive potentials which acts as the pump. A similar setup to that outlined in *section 2.7* was used for these measurements to optically monitor the potential induced accumulated charge under steady-state conditions, with the square-wave of applied potential being generated by the PalmSens3 potentiostat, which also acted as an electrical trigger for the measurement. This is illustrated in *Figure 2.14*. Much like SEC-PIAS, both the optical changes in the sample (recorded as ΔOD) and the concomitant transient photocurrents (TPC) are recorded simultaneously. This technique has been detailed previously by Francas *et al.*⁸⁴

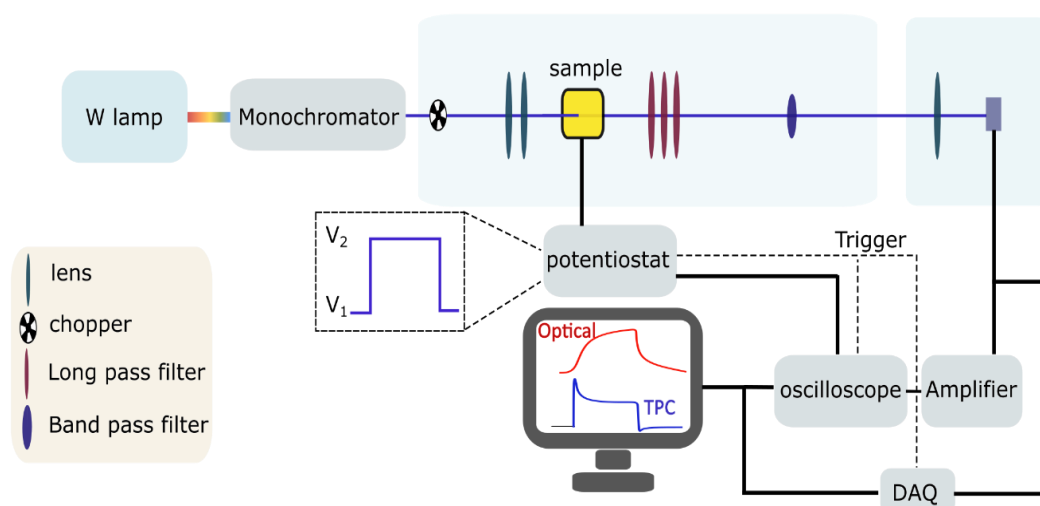


Figure 2.14| Schematic illustration of the SP-SEC set up used to monitor the electrochemically induced optical and the transient photocurrent signal when a square-wave of potential is applied to the system.

2.8.1 Estimation of extinction coefficients

SP-SEC is specifically useful in the estimation of the extinction coefficients, which has been employed in *chapters 3 and 5*, and published elsewhere.⁸⁴ Using spectroelectrochemistry, optical signature of species that accumulate under a given condition, *i.e.* catalysis, can be determined. Then using SP-SEC, a pulse of reductive (V_1) and oxidative potentials (V_2) is applied to the sample, during which the change in the optical response of the sample, monitored at a wavelength at which the accumulated species absorb, is obtained. Concomitantly, the TPC is also recorded, giving rise to transient spikes when the potential is switched between V_2 and V_1 . The species observed optically that accumulate under V_2 are reduced when V_1 is applied. Hence, the optical and electrical signals can be correlated such that, integrating the transient spike can give an estimation of the number of charges required to reduce the accumulated charge that is observed optically. This is illustrated in *Figure 2.15*. A gradient of a plot of the optical signal vs. the number of charge can then be used to estimate the extinction of the optically observed species.

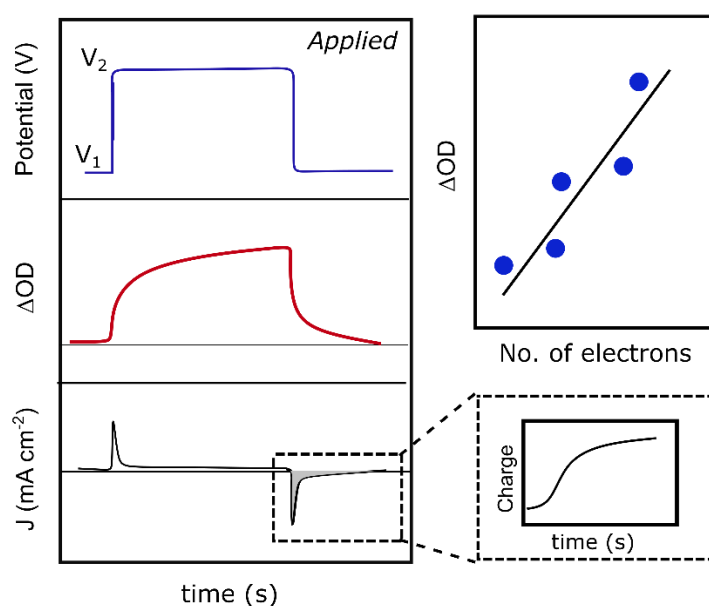


Figure 2.15| Estimation of extinction coefficients of accumulated charge using step potential – spectroelectrochemistry measurements. Typical absorption and transient photocurrent signal obtained when a square-potential wave is applied to the system. Integrating the negative transient spike gives a value for the number of charges required to reduce the oxidised species observed in the optical signal. Correlating this values across a range of applied potentials gives an estimation of the extinction coefficient.

2.9 Kinetic analyses

The steady-state absorption spectroscopic techniques outlined in *sections 2.7* and *2.8* can provide kinetic data for electrochemical and photoelectrochemical processes such as water oxidation. Under steady-state conditions and high applied potentials where back electron-hole recombination is negligible, we can consider a simple kinetic model reported previously.^{84,89–92} This model assumes a Faradaic efficiency of unity (all surface accumulated holes are transferred to the electrolyte for water oxidation). The accumulated holes at the surface can be related to the observed photocurrent according to the following equation:

$$J_{ph} = J_{holes} = k_{WO} \cdot \rho_s^\beta \quad (\text{Equation 2.13})$$

Here, J_{holes} is the flux of photogenerated holes toward the surface, which is equal to the photocurrent density (J_{ph}) observed for water oxidation under steady-state conditions, k_{WO} is the rate constant for water oxidation, ρ_s is the surface hole (oxidising equivalent) density and β is the reaction order. The number of accumulated oxidising equivalent species (*i.e.* holes) can be converted from the optical signal (ΔOD) using the extinction coefficient. The surface hole density and the resulting photocurrent can be modulated with different intensities of light irradiated on the photoelectrode. *Equation 2.13* can be expressed on a log-log scale to give *Equation 2.14* which suggests that J_{ph} should increase linearly with increasing ρ_s , the slope of which should correspond to β , which is also the number of holes (ρ_s) that need to accumulate to overcome the rate-limiting step (RLS) of the reaction.

$$\log(J_{ph}) = \log(k_{WO}) + \beta \log(\rho_s) \quad (\text{Equation 2.14})$$

This type of analysis can provide insight into the mechanistic information related to photoelectrochemical processes such as water oxidation. Analogous analyses can also be employed for electrochemical systems to study electrochemical water oxidation by electrocatalysts (as shown in *chapter 5* and reported previously⁸⁴). Under electrochemical conditions however, the surface active oxidising species and the observed current density can be modulated by applying different catalytic potentials. The turn over frequencies (TOF) for O₂ evolution and the lifetime of oxidised species (reaction time constant, τ) can also be determined from the optically detected holes or MOOH(++) species (oxidising equivalents) and the measured current densities using *equations 2.15* and *2.16*. The flux of electrons (electrons/s) can be determined from the current density.

$$TOF (s^{-1}) = \frac{\text{number of electrons} \times s^{-1}}{4[\text{oxidising equivalent}]} \quad (\text{Equation 2.15})$$

$$\tau (s) = \frac{[\text{oxidising equivalent}]}{\text{number of electrons} \times s^{-1}} \quad (\text{Equation 2.16})$$

Chapter 3 | Charge carrier trapping in oxygen vacancies in BiVO₄

In this chapter, the role of structural defects such as oxygen vacancies on the performance of photoanodes is investigated, using BiVO₄ photoanode as a model system. Whilst electronic states associated with such vacancies have been proposed to mediate hole transfer for surface oxidation reactions, enhance light absorption, mediate charge carrier recombination and / or enable efficient charge separation, a clear consensus of their function is lacking in literature. By directly modulating the electronic occupancy of sub-bandgap states induced by oxygen vacancies *in situ* using an array of electrochemical, thermal, and optical approaches, the energetics and impact on charge carrier kinetics are determined. The results from this study provide insight into how the occupation of sub-bandgap electronic states can affect charge carrier recombination, trapping and transport processes. Bulk, un-ionised states function as deep hole traps, with such trapped holes being energetically unable to drive water oxidation. On the other hand, ionised states within the space-charge layer function as shallow electron traps, localising electrons which are later extracted from the photoanode, with an activation energy of ~ 0.2 eV. As such, impact of oxygen vacancies on charge carrier dynamics and thereby on overall photoelectrochemical performance is considered.

The majority of the results presented in this chapter is included in the following publication:

Impact of oxygen vacancy occupancy on charge carrier dynamics in BiVO₄ photoanodes

S. Selim, E. Pastor, M. García-Tecedor, M. R. Morris, L. Francàs, M. Sachs, B. Moss, S. Corby, C. A. Mesa, S. Gimenez, A. Kafizas, A. A. Bakulin, and J. R. Durrant

J. Am. Chem. Soc. 2019, 141, 47, 18791-18798; DOI: [10.1021/jacs.9b09056](https://doi.org/10.1021/jacs.9b09056)

3.1 Introduction

Metal oxides are central to many electronic, catalytic and photonic devices, ranging from photocatalysis to transparent conductors. This widespread use is driven by their versatile chemical and electronic properties. Considerable effort has been devoted to the synthesis of metal oxides with enhanced photocatalytic and photoelectrochemical (PEC) performance. One aspect, which is critical for performance and the source of much debate and controversy, is the role of structural defects on catalytic activity.⁹³ In particular, these materials typically exhibit significant densities of oxygen vacancies. Such oxygen vacancies have been reported to play a key role in the photoelectrochemical function of these materials, and indeed their function for many other applications.^{70,94–97} However, how these states impact upon the charge carrier dynamics which determine photoelectrochemical function remains poorly understood,^{69,98–101} and is the primary focus of this chapter.

3.1.1 Oxygen vacancies

Oxygen vacancies are a consequence of sub-stoichiometric oxygen densities in the crystal lattice, resulting in two excess electrons in the system per oxygen vacancy site, leading to the reduction of adjacent metal centres (can form V^{4+} species in bismuth vanadate ($BiVO_4$)).^{63,71,95,96,102,103} These defects typically generates shallow sub-bandgap states that result in n-type doping of metal oxides^{69,70,103,104} and substantially impact upon materials and device performance, as has been widely discussed for hematite ($\alpha\text{-Fe}_2\text{O}_3$),^{105,106} tungsten oxide (WO_3)^{70,97}, strontium titanate ($SrTiO_3$)^{107–109} and bismuth vanadate ($BiVO_4$).^{71,96,102} In $BiVO_4$, the conduction band is mainly of V 3d character,^{33,34} with oxygen vacancy formation leading to the localisation of electrons on neighbouring vanadium sites,¹⁰³ reducing them from V^{5+} to V^{4+} . These localised electronic states will be referred to herein as V_{OV}^{5+}/V_{OV}^{4+} oxygen vacancy states to distinguish them from conduction band (CB) states, which for simplicity are labelled: V_{CB}^{4+} (occupied CB state) and V_{CB}^{5+} (unoccupied CB states).

Metal oxide oxygen vacancies have been proposed to impact upon PEC performance through several mechanisms. On the positive side, they have been reported to improve light absorption,¹¹⁰ and increase the concentration of bulk carriers,^{69,102} thus aiding transport.⁶⁹ The intrinsic doping resulting from these states enables space-charge layer generation at the metal oxide/electrolyte junction¹¹¹ which can drive charge separation under operational conditions (as discussed in *chapter 1*).^{27,28,91} On the other hand, such defects can induce detrimental structural and phase changes,⁹⁸ and have been reported to act as recombination centres that reduce quantum yields.¹⁰⁵ Most importantly, surface oxygen vacancies are often proposed to have a direct role in catalytic processes like water oxidation, impacting upon photocurrent onset potentials^{105,106} and enabling surface adsorption processes that accelerate reactivity.^{112,113} Additionally, computational studies have shown that although electronic

states that arise from oxygen vacancies are sub-bandgap, they contribute to the n-type character of BiVO₄ and enhance the polaronic charge carrier transport properties,⁵¹ however experimental studies on the impact on charge carrier dynamics is scarce. Moreover, typically the carrier mobility of BiVO₄ is on the order of 0.02 – 0.04 cm² V⁻¹ s⁻¹,^{44,45,114} which is several orders of magnitude lower than other oxides such as ZnO (100 – 200 cm² V⁻¹ s⁻¹),¹¹⁵ therefore understanding the role oxygen vacancies play in the charge carrier mobility and transport is of significant interest.

To date, most of the studies have focused on measuring the impact of oxygen vacancies on the overall PEC performance, often correlated with computational analyses of the electronic properties of these states. Studies that directly probe the impact of these vacancies upon the charge carrier separation, recombination, trapping, transport and interfacial catalytic processes which underlie PEC function have been relatively limited, and are often contradictory, thereby limiting our understanding of the impact of these states on PEC performance. Such studies have in particular been complicated by a lack of consensus over the spectral signatures of these states, resulting in significant ambiguities in the interpretation of spectroscopic analyses of oxygen vacancy function.

3.1.2 Complications associated with signal assignments and data interpretation

The fast timescale charge carrier dynamics in metal oxides such as BiVO₄ are typically assessed by ultrafast transient optical studies. However such studies have often yielded conflicting assignments of observed spectroscopic features, with different reports assigning similar spectral features not only to photogenerated conduction band electrons and valence band holes, but also to surface trapped holes driving water oxidation catalysis or to band-edge shifts arising from thermal effects.^{72,112,116–120} For example, a band-edge absorption feature (~580 nm) present in the transient absorption spectra on the ultra-fast timescale of α-Fe₂O₃ has been associated with valence band holes that oxidise water,¹²¹ surface states that mediate charge transfer for water oxidation,¹²² thermal effects that lead to lattice expansions,¹²⁰ as well as oxygen vacancies states close to conduction band that function as hole traps,^{72,73} which all lead to contradictory interpretation of spectral signatures. As such, the use of spectroscopic studies to determine kinetic processes related to oxygen vacancies is often controversial, further complicated by the uncertainty over the assignment of the observed spectral features.

3.2 In this chapter

In this chapter, a strong optical feature observed in transient spectroscopic studies of BiVO_4 ($\lambda \sim 470$ nm, see *Figure 3.3* below) around its bandgap^{116,118,119} is investigated. This feature appears spectroscopically analogous to a similar feature observed in $\alpha\text{-Fe}_2\text{O}_3$ at 580 nm as discussed earlier, which has been previously assigned in some studies to originate from unoccupied oxygen vacancy states in $\alpha\text{-Fe}_2\text{O}_3$.^{72,73} Since there is considerable dispute over the assignment of these features in both metal oxides, with other studies relating this spectral feature to photogenerated holes that undergo water oxidation,^{119,121–124} or suggesting that it is directly related to structural changes resulting from thermal effects of pulsed laser excitation,^{118,120} confirmation of the spectral assignment is lacking. Such controversies are symptomatic of the limited understanding of the optical signals observed following optical excitation of these metal oxides. Herein, these ambiguities are addressed by directly modulating the population of $V_{\text{OV}}^{5+}/V_{\text{OV}}^{4+}$ states in BiVO_4 using five complementary electrochemical, thermal and all-optical methods. Remarkable agreement between these techniques allows the identification of the spectroscopic fingerprint of these states, their energetics, their impact upon charge carrier dynamics and ultimately the photoelectrochemical performance. The combined optical and electrochemical data demonstrate that these oxygen vacancies do not have a direct catalytic activity towards water oxidation. Rather, the results suggest that occupied V_{OV}^{4+} states are the primary loss pathway for photogenerated valence band holes, whilst unoccupied V_{OV}^{5+} states function as shallow electron traps and control the extraction of photogenerated conduction band electrons (the majority carriers) to the external circuit.

3.3 Experimental methods

Most of the experimental details are covered in *chapter 2*. Only the additional techniques specific to the studies in this chapter are detailed here. This study employs flat, dense BiVO_4 photoanodes fabricated by metal-organic decomposition (see *chapter 2* for details) with a monoclinic scheelite structure as determined by X-ray diffraction (XRD) (*Figure 2.2, chapter 2*). X-ray photoelectron spectroscopy (XPS), a surface sensitive technique, reveals that $\sim 3\text{-}4\%$ of all surface vanadium centres are in the V^{4+} state, indicating a surface oxygen vacancy density tentatively on the order of $1\text{-}2\%$ per V centre (assuming 2 equivalents of V^{4+} are generated per oxygen vacancy), (see *Figure 3.1* for details). It should be noted however, that the bulk and surface concentrations of oxygen vacancies may differ. Photoelectrochemical (PEC) measurements reported herein were conducted in a three-electrode cell, unless stated otherwise. Photoelectrochemical water oxidation performance of the photoanodes is presented in *Figure 3.2b*, and is typical of such photoanodes reported in the literature.^{27,83}

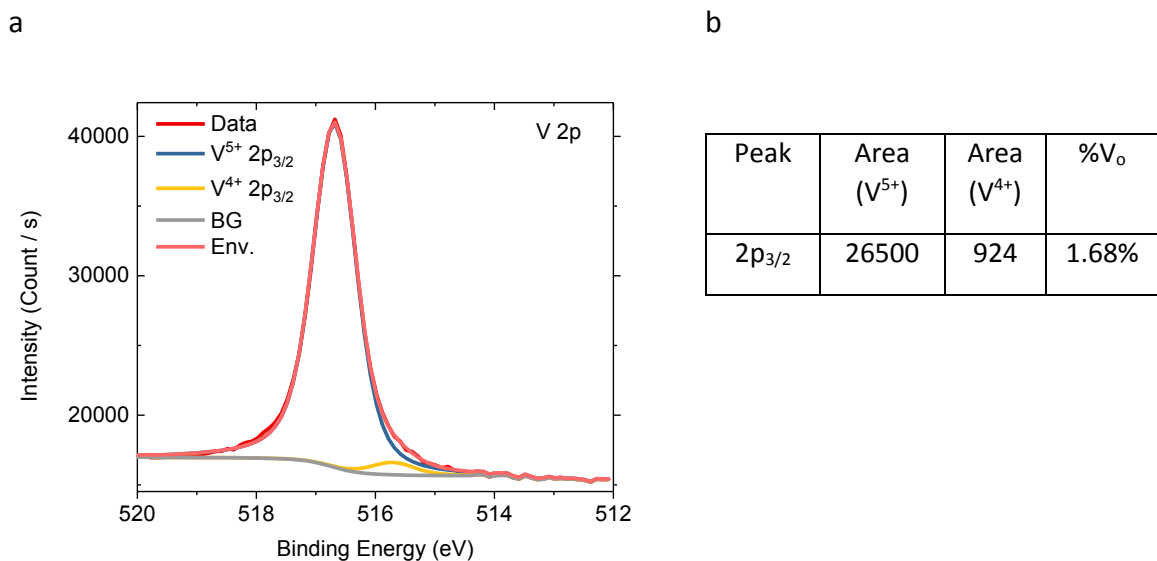


Figure 3.1 | XPS analysis. (a) XPS scan of V(2p_{3/2}) showing small proportion of V⁴⁺. (b) Determination of % oxygen vacancy (V_o) in BiVO₄ from the relative area of V⁴⁺ and V⁵⁺ from V(2p_{3/2}) contributions. Since the excess electrons from each oxygen vacancy site gives rise to two equivalents of V⁴⁺ species, the surface %[V_o] is calculated using:

$$\%[V_o] = \left(\frac{Area_{V^{4+}}}{Area_{V^{4+}} + Area_{V^{5+}}} \right) \times \frac{1}{2} \times 100\%.$$

3.3.1 Temperature dependence studies

Thermal energy (*i.e.*: heating) can be used to thermally excite electrons from dopant states close to the band edge into conduction band states, monitored most typically as a thermally induced increase in electrical conductivity. The effect of temperature on material properties such as charge transport, defect state occupation as well as charge carrier dynamics can be investigated using the techniques outlined in *chapter 2* and below.

3.3.1.1 Thermally induced (transient) absorption spectroscopy

Steady state thermal difference measurements are presented as the difference in the optical absorption spectra as a function of applied temperature, with respect to the lab temperature (295 K). Absorption spectra were taken using a Cary 60 UV-Vis spectrometer (Agilent Technologies), fitted with a temperature cell.

Temperature dependent μ s-TAS data were also collected in a quartz cuvette placed inside the temperature cell. The measurements were taken under an inert atmosphere, where the sample was degassed with Ar.

3.3.1.2 Temperature dependence charge extraction (TPC)

Temperature dependent transient photocurrent measurements were conducted using the same method outlined in *chapter 2*. TPC measurements were conducted under PEC conditions, where the working and counter electrodes were enclosed in quartz cuvette placed inside the temperature cell holder. The reference electrode (sat. KCl Ag/AgCl) was placed in a separate container that was connected to the electrolyte in the quartz cuvette using a salt-bridge. As such, the applied potential was not corrected for temperature.

3.3.1.3 Determination of activation energy

Activation energy of thermal trapping/de-trapping processes from TPC and TA measurements were calculated by determining the $t_{50\%}$ of charge extraction and TA signal decay as a function of temperature, respectively. The $t_{50\%}$ values were then used to calculate the activation energy using Arrhenius analysis, using equation:

$$\ln\left(\frac{1}{t_{50\%}}\right) = \ln(A) - \frac{Ea}{RT}\left(\frac{1}{T}\right) \quad (\text{Equation 3.1})$$

3.3.2 Determination of density of states optically

The change in electronic occupancy of sub-bandgap states, or the density of sub-bandgap states (DOS), was determined from the spectroelectrochemical difference spectra as a function of applied bias (relative to V_{oc}). Since a ΔOD corresponds to the change in the population of a given transition or state, by taking the derivative of ΔOD (465 nm) vs the applied potential, the states could be mapped from the spectral feature as function of bias.

3.3.3 Determination of space-charge layer width (W_{SCL})

The space-charge layer width (W_{SCL}) is calculated using the equation:

$$W_{SCL} = \sqrt{\frac{2\epsilon\epsilon_0(V-V_{FB})}{eN_D}} \quad (\text{Equation 3.2})$$

where ϵ and ϵ_0 are the relative permittivity of BiVO_4 (68),¹²⁵ and vacuum permittivity ($8.854 \times 10^{-12} \text{ F m}^{-1}$), respectively; V is the applied potential; and e is the electronic charge ($1.602 \times 10^{-19} \text{ C}$), with donor density (N_D) and flat-band potential (E_{FB}) values of $9.1 \times 10^{20} \text{ cm}^{-3}$ and 0.35 V_{RHE} , respectively (determined via Mott-Schottky analysis, see *section A.1* in *Appendix*).

It is noted that the following experiments were not performed myself. Impedance measurements to determine the sample capacitance, flat-band potential and donor density were conducted by Dr. Miguel Garcia-Tecedor (Universitat Jaume I, Spain) (details of which are included in *section A.1* in

Appendix). Some of the ultra-fast three-pulse pump-push-probe measurements were conducted by Dr. Ernest Pastor (Imperial College London, UK). X-ray photoelectron spectroscopy measurements were conducted by Mr. Benjamin Moss (Imperial College London, UK) (outlined in *section 2.2.1* in *chapter 2*) and temperature dependence μ s-TAS data were kindly provided by Dr. Madeleine Morris (Imperial College London, UK).

3.4 Results

3.4.1 (Photo)electrochemical characterisation of BiVO_4 samples

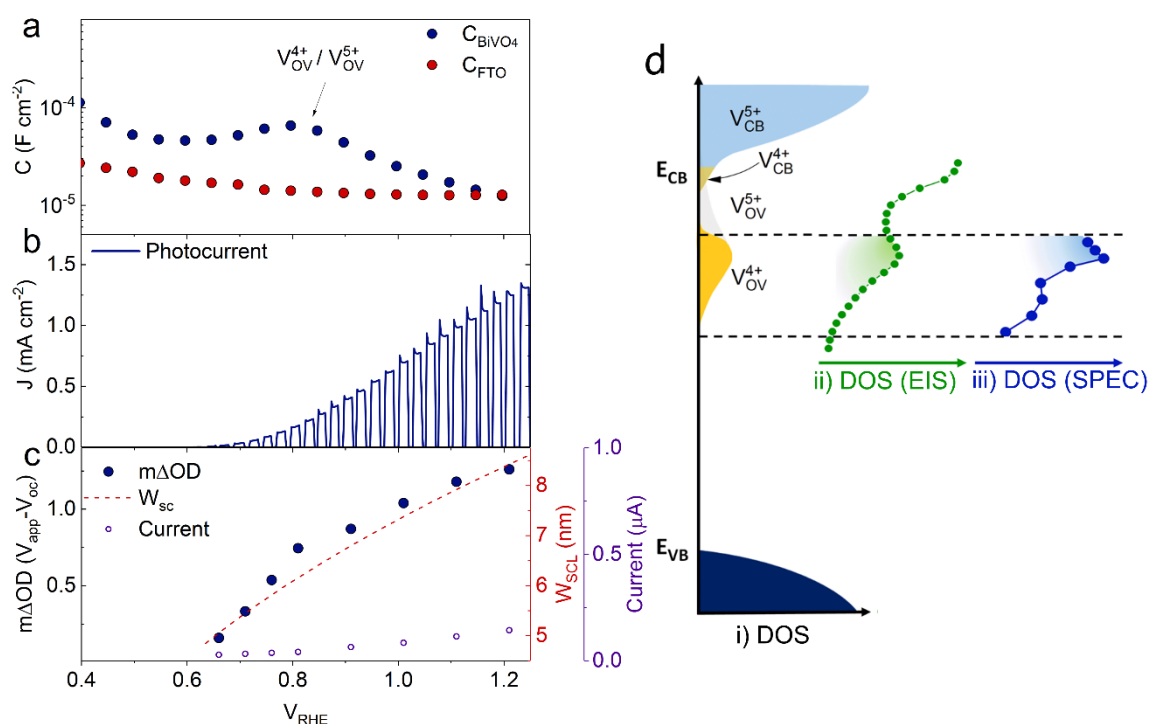


Figure 3.2 | Relationship between the capacitance associated with $V_{\text{OV}}^{4+}/V_{\text{OV}}^{5+}$, the photoelectrochemical response and the space charge layer formation in BiVO_4 photoanodes. (a) The capacitance associated with $V_{\text{OV}}^{5+}/V_{\text{OV}}^{4+}$ in BiVO_4 photoanode and the FTO substrate as a function of applied potential, in dark. (b) The photocurrent obtained under equivalent 1 sun illumination. (c) The optical signal observed in spectroelectrochemical measurements as a function of applied potential at 465 nm, relative to the V_{OC} (0.6 V_{RHE}), plotted against the space-charge layer width of the film. The dark steady state current measured whilst applying the potential is also presented (purple open circles, right axis). All measurements were taken in 0.1 M phosphate buffer. (d) Schematic representation of sub-bandgap states associated with oxygen vacancies (amplified for illustration) in BiVO_4 . i), Sub-bandgap states in relation to band edges. For illustration the yellow shaded regions represent occupied (reduced) states (V_{OV}^{4+}). ii), Density of states (DOS), arising from the $V_{\text{OV}}^{5+}/V_{\text{OV}}^{4+}$ redox couple determined from impedance spectroscopy (green). iii), DOS derived from spectroelectrochemistry measurements, tracking the optical absorbance at 470 nm as a function of applied bias (blue) (relative to the open-circuit potential of 0.6 V_{RHE}).

The photoelectrochemical response of the BiVO₄ photoanodes studied in this chapter, under continuous illumination is shown in *Figure 3.2b*. To extract useful electrochemical parameters of the photoanodes, impedance spectroscopy was employed. Dark impedance analysis of the BiVO₄ photoanodes reveals the presence of a capacitance peak at $\sim 0.8 V_{RHE}$, as illustrated in *Figure 3.2a*. The flat-band potential (E_{FB}), donor density (N_D) of the photoanodes were also determined to be $0.35 V_{RHE}$ and $9.1 \times 10^{20} \text{ cm}^{-3}$ respectively, through Mott-Schottky analysis (*Figure A1 in appendix*). The observed capacitance is positive of the electrode flat band potential and coincides with the onset of photocurrent generation in these photoanodes (*Figures 3.2a and 3.2b*), both indicative of it being associated with space-charge layer formation at the electrode surface. Given that n-type doping of BiVO₄ primarily results from oxygen vacancies, this space charge layer formation, and the associated capacitance can be assigned to the depletion of the V_{OV}^{4+} states, resulting in the formation of unoccupied (ionised) V_{OV}^{5+} states. This assignment is consistent with DFT calculations indicating sub-bandgap donor levels induced by oxygen vacancies in BiVO₄.^{51,69,104} Therefore, the observed capacitance is assigned, as previously,¹²⁶ to the V_{OV}^{5+}/V_{OV}^{4+} couple. This is illustrated in *Figure 3.2d*.

3.4.2 Modulation of sub-bandgap electronic states and spectral assignment

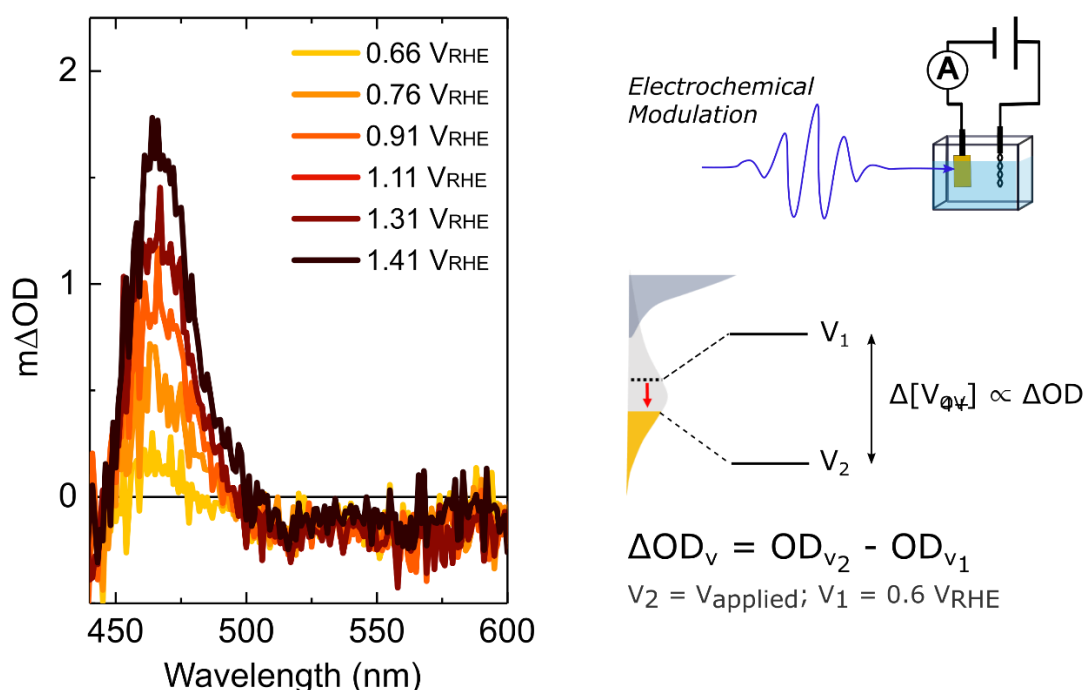


Figure 3.3| Difference spectra showing the optical absorption feature at 470 nm observed following the increase in the V_{OV}^{5+} concentration using electrochemical modulation. Bias induced spectroelectrochemical difference spectrum, measured at oxidising potentials relative to the spectrum at the open circuit potential ($0.6 V_{RHE}$) and assigned to the electrochemical oxidation of V_{OV}^{4+} to V_{OV}^{5+} . Spectra were measured in 0.1 M phosphate buffer.

Since these states associated with the V_{OV}^{5+}/V_{OV}^{4+} redox couple are found to be close to the CB edge, to probe further the oxidation/reduction of V_{OV}^{5+}/V_{OV}^{4+} states and their impact upon charge carrier dynamics, a series of differential absorption spectroscopy measurements were performed. Firstly, the sample was modified electrochemically where the redox state can be altered by applying a potential. Upon electrochemical oxidation of the sample in the dark, a strong absorption peaking at 470 nm is observed as shown in *Figure 3.3*, which grows in amplitude with increasing anodic potential. Since this optical signal tracks the change in the oxidation state of the electronic states, differentiation of this optical signal amplitude as a function of applied potential allows the determination of the associated density of states (*Figure 3.2d(iii)*).

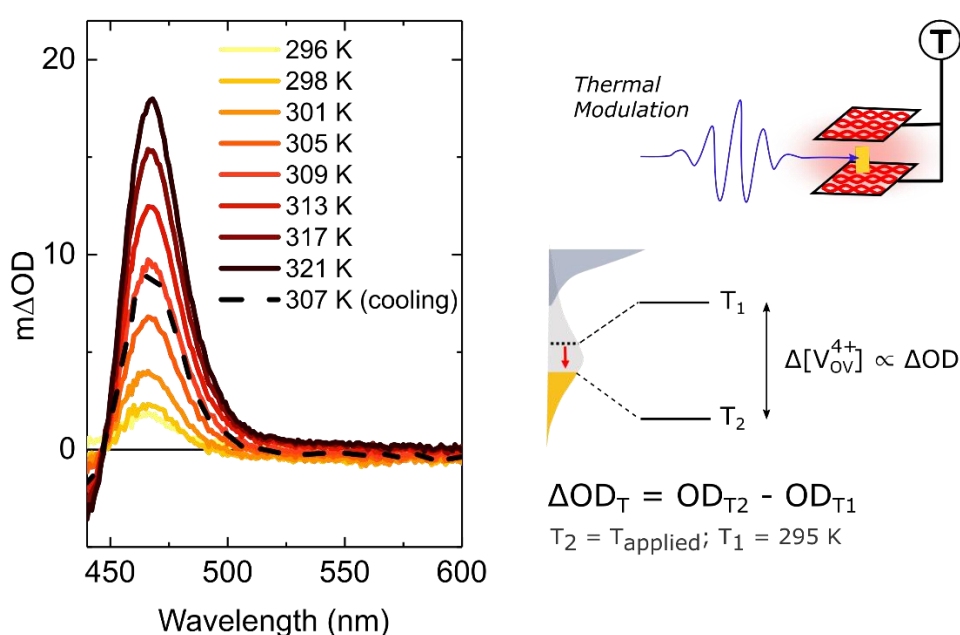


Figure 3.4 | Difference spectra showing the optical absorption feature at 470 nm observed following the increase in the V_{OV}^{5+} concentration using thermal modulation. Thermally induced difference absorption spectrum, measured at temperatures relative to the spectrum at 295 K, assigned to thermal excitation of electrons from V_{OV}^{4+} to the conduction band. Spectra were measured in 0.1 M phosphate buffer, under open circuit conditions.

Strikingly, the population distribution obtained from these spectroelectrochemical measurements correlates closely with the distribution of the V_{OV}^{5+}/V_{OV}^{4+} states obtained through impedance spectroscopy (*Figure 3.2d(ii)*). Based on this, it is concluded that the 470 nm signal tracks the oxidation of the vanadium ions adjacent to oxygen vacancy sites, from V_{OV}^{4+} to V_{OV}^{5+} and therefore is a direct probe of the V_{OV}^{5+} concentration. Consistent with this assignment, the dependence of the magnitude of this feature upon applied bias is in reasonable agreement with the expected potential dependence of the space-charge layer width attributed to oxygen vacancy ionisation (see *Figure 3.2c* and below for further discussion of this assignment). In the literature, charge localisation in BiVO_4 has been

proposed to give rise to the formation of lattice distortions or polarons centred on vanadium ions^{40,49,50} with several studies trying to identify these states.^{51,103} While the experiments reported herein do not provide structural information, the sensitivity of the 470 nm optical signal to the concentration of the V_{OV}^{5+}/V_{OV}^{4+} linked to oxygen vacancies can provide a powerful tool to explore phenomena directly influenced by the presence of such defects as well as their impact on catalysis.

In addition to applied bias, an alternative route widely used to modulate the ionisation of shallow dopant species in semiconductors is thermal heating, monitored most typically as a thermally induced increase in electrical conductivity.^{40,49,50} In Figure 3.4 the dependence of the $BiVO_4$ absorption spectrum as a function of temperature is monitored, under open – circuit conditions in electrolyte. Increasing the temperature from 295 K to 301 K resulted in the appearance of an absorption at 470 nm, indistinguishable in shape from that induced electrochemically under anodic bias. This thermally induced feature is therefore assigned to the thermal release of electrons from V_{OV}^{4+} , forming the V_{OV}^{5+} associated with the 470 nm feature as assigned above. The thermal effect on the oxidation state, and thus the electronic occupancy of the sub-bandgap defect states play a significant role on the photoelectrochemical performance of the $BiVO_4$ photoelectrodes and is discussed further later.

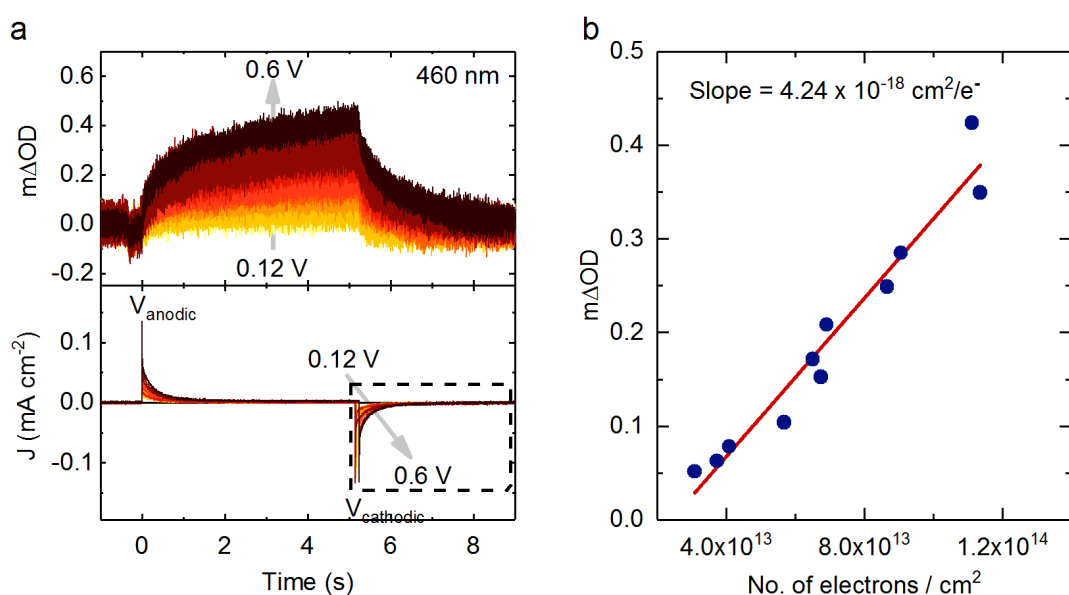


Figure 3.5| Determination of extinction coefficient of the sub-bandgap states associated with oxygen vacancies. A 5 second pulse of anodic potential in the range of 0.12 V - 0.6 V (vs Ag/AgCl) is applied to oxidise $[V_{OV}^{4+}]$ to $[V_{OV}^{5+}]$ which is followed by an 8 second pulse of cathodic potential (0.01 V_{Ag/AgCl} (initial V_{oc})) to reduce the oxidised $[V_{OV}^{5+}]$ back to $[V_{OV}^{4+}]$. (a) The optical signal corresponding to the change in the oxidation state of $[V_{OV}^{4+}]$ to $[V_{OV}^{5+}]$ probed at 460 nm (top panel) and the concomitant transient current signal associated with the oxidation of $[V_{OV}^{4+}]$ (positive spike) and reduction of $[V_{OV}^{5+}]$ (negative spike) (bottom panel). (b) Plot of the optical signal ($[V_{OV}^{5+}]$) vs the number of electrons required to reduce $[V_{OV}^{5+}]$ to $[V_{OV}^{4+}]$, calculated by integrating the negative spike in the transient current. The measurements were conducted in the dark.

To determine the extinction coefficient of the optical feature at ~ 470 nm associated with the V_{OV}^{4+}/V_{OV}^{5+} states, step-potential absorption spectroscopy was employed (see *chapter 2* for details). Upon application of a square pulse of oxidative and reductive potentials allowing time for the system to reach steady-state at each potential, the change in the oxidation state of the V_{OV}^{4+}/V_{OV}^{5+} species can be correlated with the associated optical and electronic current response. Integration of the transient current spikes can yield the number of electrons required to reduce the V_{OV}^{5+} species observed optically. This is shown in *Figure 3.5* below. The determined value of the extinction coefficient of the V_{OV}^{5+} species ($4.24 \times 10^{-18} \Delta OD/electron$) can then be used to calculate the density of $[V_{OV}^{4+}]$ states accessed electrochemically and thermally (from the electrochemical and thermal response to the difference spectra shown in *Figure 3.3* and *Figure 3.4*). In contrast to thermal modulation, electrochemical access to V_{OV}^{4+} states is limited to within the space charge layer (W_{SCL}) (where the potential drop takes place), whereas the bulk of the material is accessible by the former. Crucially, taking into consideration of the accessible density of V_{OV}^{4+} states by thermal and electrochemical perturbations, the similarity in the values obtained, as shown in *Figure 3.6*, is a strong indication of the bulk distribution of V_{OV}^{4+} originating from oxygen vacancies in $BiVO_4$.

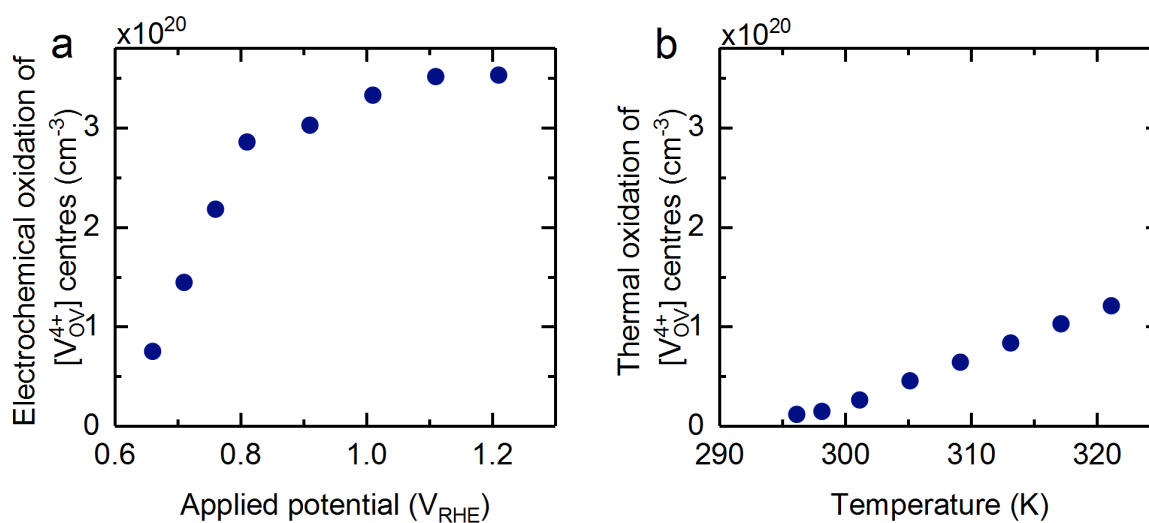


Figure 3.6] Comparison of the number of $[V_{OV}^{4+}]$ centres accessible electrochemically and thermally in $BiVO_4$ photoanodes. (a) States accessible electrochemically within the space-charge layer width (W_{SCL}) as a function of applied potential. The W_{SCL} for a given potential is obtained as shown in *Figure 3.2*. (b) States accessible thermally across the thickness of the film as a function of temperature. The film thickness of the $BiVO_4$ photoanodes was 350 nm. The extinction coefficient value ($4.24 \times 10^{-18} \text{ cm}^2/e^-$) used to convert the optical signal in *Figure 3.3* and *3.4* to the number of $[V_{OV}^{4+}]$ centres was determined in *Figure 3.5*. Whilst the number of $[V_{OV}^{4+}]$ centres accessible by applied potential saturates after 0.8 V_{RHE} , consistent with these states being associated with surface space charge layer formation, no such saturation is observed at elevated temperatures, within the temperature range studied herein signifying that thermal oxidation is a bulk process.

From the electrochemical and thermal perturbation measurements, the sub-bandgap states originating from oxygen vacancies are observed to be energetically in close proximity to the conduction band. Therefore, to investigate whether these states interact with photogenerated carriers, transient absorption (TA) spectroscopy is employed to examine the changes resulting from pulsed laser excitation of a BiVO₄ photoanode under open-circuit conditions. As shown in *Figure 3.7*, the same ~470 nm spectral feature is observed in the TA spectrum at 20 ps following bandgap excitation of BiVO₄. Based on the thermal and electrochemical data reported above, the transient feature indicates that a photoinduced increase in concentration of V_{OV}⁵⁺ states (due to oxidation of V_{OV}⁴⁺ states) takes place shortly after photoexcitation. This is rationalised in terms of ultra-fast hole trapping of some valence band holes into bulk V_{OV}⁴⁺ states, as illustrated in *Figure 3.7* and discussed further below. This deep trapping process could also be described as equivalent to a recombination process between valence band holes and electrons trapped in shallow oxygen vacancy defect sites. This trapping/recombination is likely to be a key determinant for bulk hole diffusion lengths in BiVO₄ (typically measured as ~100 nm).⁴⁰

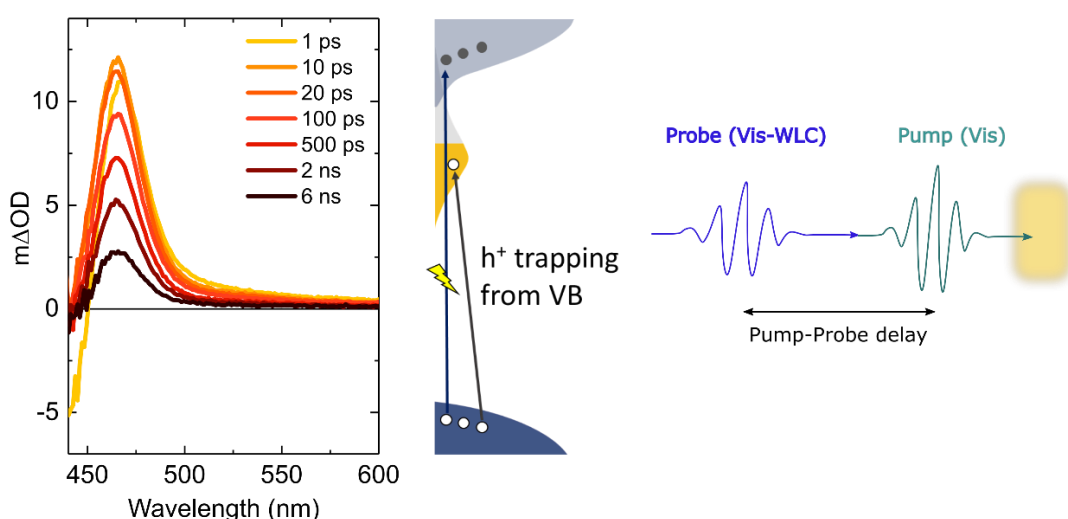


Figure 3.7 | Difference spectra showing the optical absorption feature at 470 nm observed following the increase in the V_{OV}⁵⁺ concentration due to hole trapping following photoexcitation. Transient absorption difference spectra following excitation with $\lambda_{\text{ex}}(\text{pump})$ at 355 nm, measured in 0.1 M phosphate buffer, under open circuit conditions, where trapping of holes leads to oxidation of V_{OV}⁴⁺ to V_{OV}⁵⁺.

The final technique employed as a further confirmation of the assignment of this optical signal by modulating the occupancy of BiVO₄ oxygen vacancy defect states is an optical UV *pump* – IR *push* – visible *probe* technique (illustrated in *Figure 3.8*, and outlined in *section 2.3.5, chapter 2*), a method previously applied to organic semiconductors,^{86,127,128} but not to metal oxide photoelectrodes. *Figure 3.8* shows an enhancement in the optical response at 470 nm in the push on-off TA spectrum in air,

consistent with electron excitation out of V_{OV}^{4+} states (see *Figure A2* in *appendix* for additional data). The ability of a 0.6 eV IR light pulse to excite electrons out of these sub-bandgap oxygen vacancy states into the conduction band further confirms the assignment of the 470 nm optical feature to V_{OV}^{5+} concentration and also confirms that they are energetically close to the conduction band edge as shown in *Figure 3.2*.

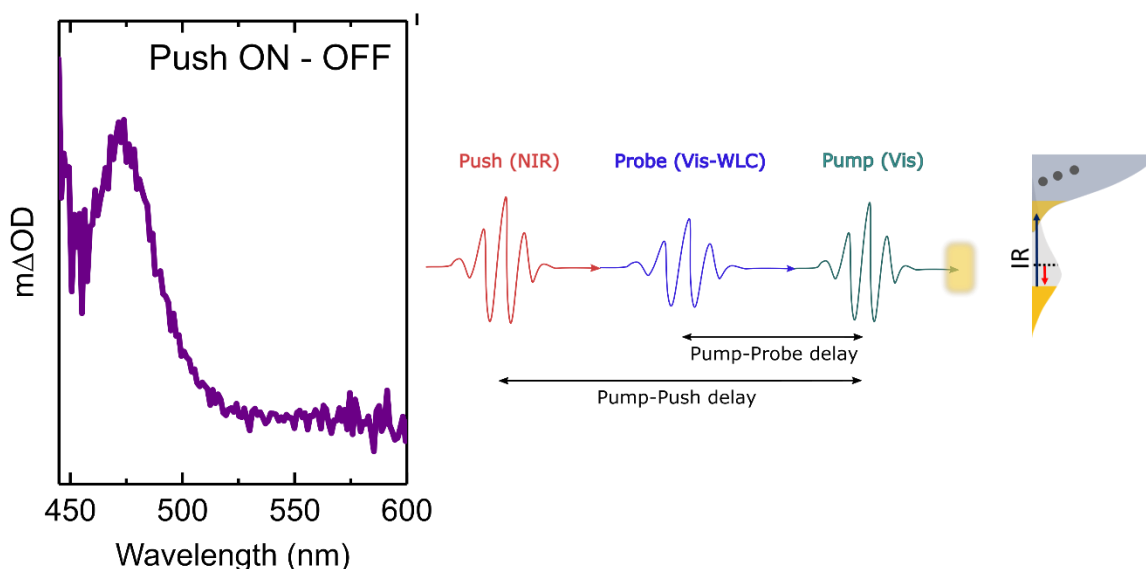


Figure 3.8 | Difference spectra showing the optical absorption feature at 470 nm observed following the increase in the V_{OV}^{5+} concentration due to IR (push) excitation from V_{OV}^{4+} states.

3-pulse UV pump – IR push – visible probe transient optical spectrum showing the push ON minus push OFF spectrum measured at a 4ps push – probe time delay following excitation with IR (2060 nm, 0.6 eV) push pulse, measured in air.

As a further confirmation, temperature dependence of the transient absorption spectra shown in *Figure 3.9 (top panel)* is consistent with the hypothesis that the observed signal at ~470 nm is related to the concentration of V_{OV}^{5+} species. Increasing the temperature leads to a lower concentration of V_{OV}^{4+} states that are available in the bulk to trap holes from the valence band. In line with this, the amplitude of the signal at ~470 nm is observed to decrease with increasing temperature. In addition, this is also reflected in the Push On – Off spectra following IR (push) excitation (*Figure 3.9 (bottom panel)*), where increasing the temperature leads to a lower concentration of V_{OV}^{4+} that are available to be excited into the conduction band using IR excitation. However further experiments are required to consolidate the effect of trapping processes when the change in concentration of V_{OV}^{4+} is induced by multiple factors simultaneously (*i.e.* thermal excitations and IR excitations).

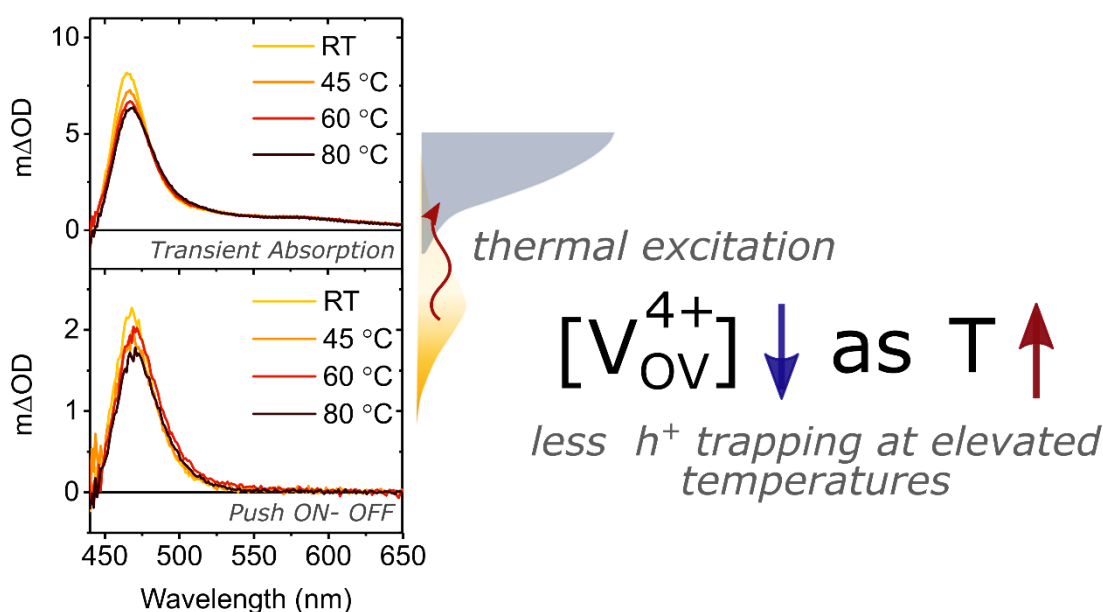


Figure 3.9 | Temperature dependence of pump (top panel) and pump – push (bottom panel) transient absorption spectral response showing decrease in hole trapping resulting from less available V_{OV}^{4+} states. Spectra shown at a pump – probe time delay of 17 ps. Sample was excited with $\lambda(\text{pump})$: 400 nm and $\lambda(\text{push})$: 2060 nm, measured in air.

3.4.3 Charge carrier trapping into oxygen vacancies and implications on electron extraction properties

As the transient absorption data strongly indicate that oxygen vacancies partake in charge carrier trapping processes, the kinetics of charge carrier trapping and de-trapping into and out of BiVO_4 oxygen vacancy states is now considered. Typical pump and pump-push induced transient absorption kinetics monitored at 470 nm are shown in *Figure 3.10*. The kinetics of the 470 nm absorption following bandgap excitation are biphasic (*Figure 3.10a*, blue trace), exhibiting an instrument response limited (~ 200 fs) rise and followed by a smaller ~ 10 ps increase in absorption. These kinetics are assigned to partial, deep hole trapping into bulk V_{OV}^{4+} states. The additional 470 nm absorption induced by the IR push pulse decays on the nanosecond timescale (*Figure 3.10a*, red and purple trace), indicates that the BiVO_4 conduction band electrons generated by the IR pulse tend to relax relatively slowly back into the ionised oxygen vacancy state from which they were excited. The initial positive photoinduced absorption decays on the nanosecond timescale, and evolves on the microsecond timescale into a transient bleach signal assigned to electron trapping into V_{OV}^{5+} states within the space charge layer (*Figure 3.10b* and *Figure 3.11* for further details). From this data, it can be seen that space-charge layer, and consequentially the unoccupied V_{OV}^{5+} states plays a significant role on the fate of photogenerated charge. This is illustrated in *Figure 3.11* and discussed below.

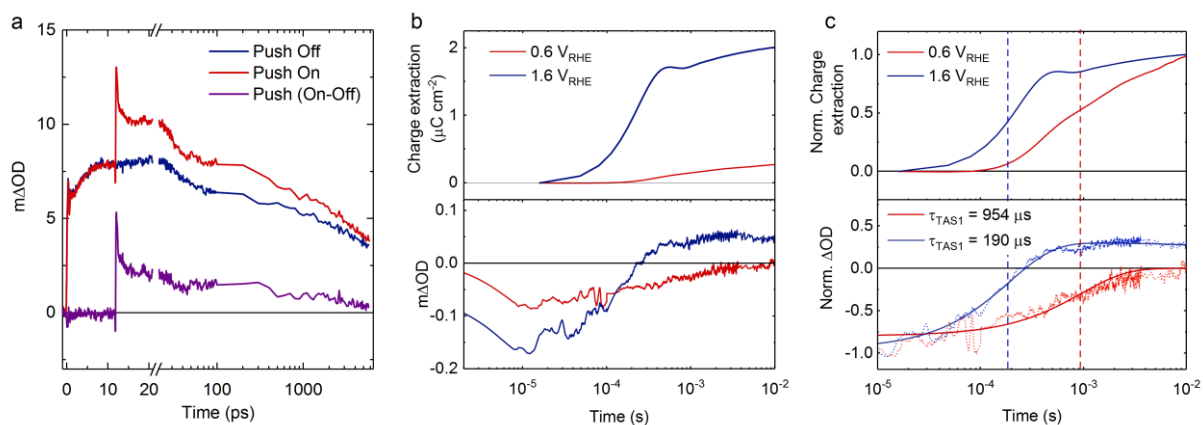


Figure 3. 10 | Kinetics associated with electron trapping and extraction to and from oxygen vacancy states. (a) 3-pulse pump-push-probe measurement in air, showing the enhancement of the signal at 470 nm following push with 2060 nm pulse (3 mJ cm^{-2}) at a pump-probe time delay of 10.4 ps, following the initial pump excitation at 400 nm ($200 \mu\text{J cm}^{-2}$). (b) Transient charge extraction from BiVO_4 photoanode obtained with transient photocurrent measurements (top panel) with the concomitant transient absorption kinetics probed at 460 nm (bottom panel) showing the bleach in the signal due to electron trapping at $0.6 V_{\text{RHE}}$ (red) and $1.6 V_{\text{RHE}}$ (blue). (c) TPC and fitting of TA kinetics at 460 nm at $0.6 V_{\text{RHE}}$ (red) and $1.6 V_{\text{RHE}}$ (blue). TA kinetics were fitted using the exponential functions: $y=Ae^{-t/\tau_{\text{TAS1}}}$ and $y=Ae^{-t/\tau_{\text{TAS1}}}+Be^{-t/\tau_{\text{TAS2}}}$ for $0.6 V_{\text{RHE}}$ and $1.6 V_{\text{RHE}}$ respectively, where τ_{TAS1} represents time scale of charge extraction, and τ_{TAS2} represents decay of long-lived holes at the surface.

Under inert atmosphere when there is negligible band-bending, rapid hole trapping into $\text{V}_{\text{OV}}^{4+}$ states followed by electron trapping into resulting $\text{V}_{\text{OV}}^{5+}$ states leads to a net recombination and no bleach is observed (*Figure 3.11a*, top panel). Under these conditions, the overlay of the TA spectra (*Figure 3.11b*, top panel) at 6 ns and 5 μs shows that the spectrum by 5 μs has contributions from two main features – a peak at 470 nm (due to hole trapping into $\text{V}_{\text{OV}}^{4+}$ states) and a broader feature that extends into longer wavelengths. Photogenerated holes in BiVO_4 give rise to a broad absorption spectrum, absorbing most strongly at $\sim 550 \text{ nm}$, which has been reported to correlate with water oxidation in studies under applied bias, and further confirmed using chemical scavengers.^{27,79,92} Therefore, it is likely that the spectra at 5 μs has features from both trapped holes resulting in $\text{V}_{\text{OV}}^{5+}$, and holes in the valence band. This signal however decays rapidly by 100 ms.

In contrast, under open-circuit conditions, surface band bending is present due to equilibration of the Fermi level of the photoanode and the electrolyte. This equilibration results in the formation of $\text{V}_{\text{OV}}^{5+}$ within the space-charge layer (in the dark). Following photoexcitation, while bulk processes still take place, electron trapping into $\text{V}_{\text{OV}}^{5+}$ states in the space charge layer results in a loss of ground state absorption which manifests as a transient bleach on the microsecond timescale (*Figure 3.11a* bottom panel). This is also observed in the TA spectra (*Figure 3.11b*, bottom panel), where the signal observed at 550 nm also decays more slowly due to the presence of band bending. As expected, the transient bleach recovers back to zero when holes recombine with these trapped electrons under open-circuit

conditions. In agreement with this assignment, the magnitude of this long-lived bleach signal increases with anodic bias as shown in *Figure 3.10b*. To probe the fate of the electrons that are trapped in the V_{OV}^{4+} states within the space charge layer under operational conditions (*i.e.* applied bias), transient photocurrent measurements can be employed to investigate kinetics of charge extraction. The recovery of transient bleach signal exhibits similar kinetics to those measured for charge extraction (*Figure 3.10c*), consistent with the assignment and indicates that electron extraction is associated with electron release from V_{OV}^{4+} states. These assignments are in qualitative agreement and are analogous to those observed also for $\alpha\text{-Fe}_2\text{O}_3$ ⁷³ and WO_3 ⁹⁷ therefore is representative of charge extraction processes across common metal oxide photoelectrodes.

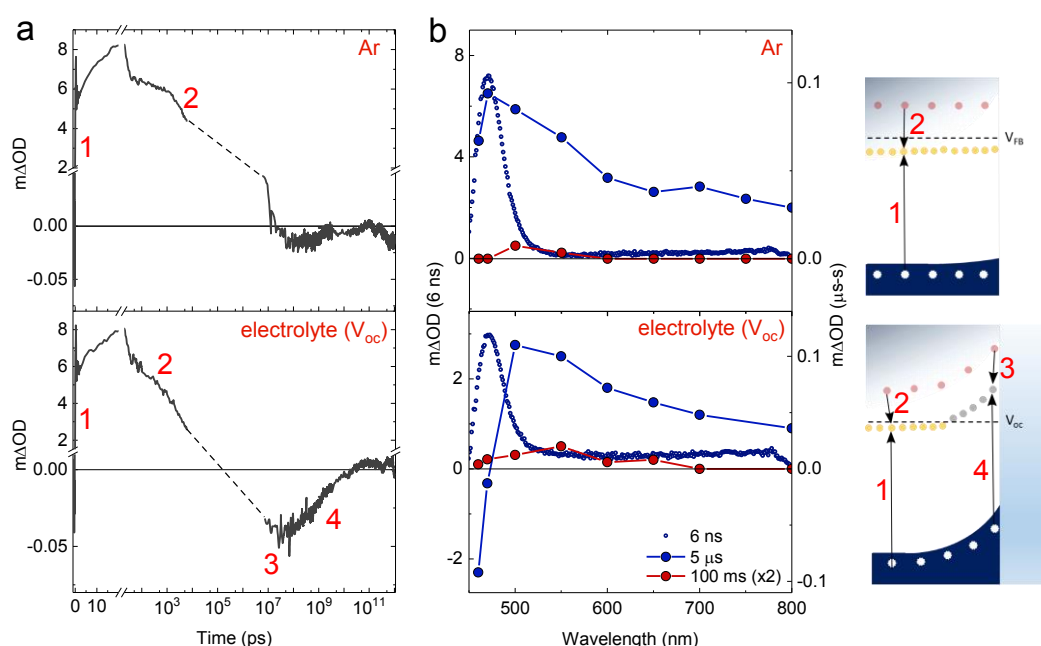


Figure 3.11| Effect of charge carrier trapping on charge carrier dynamics under inert atmosphere and in electrolyte. (a) Transient absorption kinetics spanning from fs-ns timescale probed at 470 nm, to the μs -s timescale probed at 470 nm (dotted line is added to guide the eye) under inert atmosphere (top panel) and under open-circuit conditions (bottom panel). (b) TAS spectra of BiVO_4 under inert atmosphere (Ar) (top panel) and under open circuit conditions (bottom panel) at 6 ns (purple), 5 μs (blue) and 100 ms (x2) (red); (excitation density: $300 \mu\text{J cm}^{-2}$ (μs -s) and $250 \mu\text{J cm}^{-2}$ (fs-ns) at 355 nm). The schematic adjacent to the panels illustrate the processes giving rise to the charge carrier dynamics where processes (1) and (2) outline bulk hole and electron trapping into V_{OV} states. Process (3) shows electron trapping into oxidised V_{OV}^{5+} within the space charge layer, which subsequently recombine with surface holes (4).

3.4.4 Impact of electron trapping on water oxidation performance

The results presented in this chapter indicate that the BiVO_4 oxygen vacancy states are energetically in close proximity to the conduction band edge, such that de-trapping of electrons from these states (*i.e.* ionisation of V_{OV}^{4+} to generate V_{OV}^{5+} is thermally activated, consistent with the thermally induced

absorption changes reported in *Figure 3.4* earlier). In order to investigate the importance of such thermally activated de-trapping on the PEC function of BiVO₄, further temperature dependence studies of charge extraction and recombination were undertaken. *Figure 3.12a* shows the temperature dependence of charge extraction (*i.e.* integrated photocurrent), measured at an applied bias near the photocurrent onset (0.6 V_{RHE}) where charge extraction is critically limited by electron de-trapping, manifesting as slower charge extraction as shown in *Figure 3.10c*. It is apparent that with increasing temperature, the kinetics of charge extraction accelerate and the yield of extracted charge increases (*Figure 3.12a*). From the temperature dependence of the extraction half-time, the activation barrier of $E_{a,\text{extraction}} \sim 0.22$ eV (*Figure 3.12c*) is obtained. As these extraction kinetics also track the recovery of the transient bleach signal discussed above (*Figures 3.10b* and *3.10c*), this activation energy can be assigned to thermally induced release of electrons trapped as V_{OV}^{4+} to generate mobile charge carriers, which is consistent with previous computational studies.⁵¹

Figure 3.12b shows the decay kinetics of photoinduced bulk valence band holes in BiVO₄ measured in an inert atmosphere as a function of temperature, assigned to charge recombination. Again, the kinetics are observed to accelerate with increasing temperature (*Figure 3.12b*) with a very similar activation barrier ($E_{a,\text{recombination}} \sim 0.18$ eV, *Figure 3.12d*). The similarity of these two activation energies suggests the kinetics of both processes are controlled by the thermal excitation of electrons from occupied oxygen vacancy states, enabling transport either to the external back contact (for electron extraction) or recombination with holes. Similar charge transport activation energies have previously been reported for BiVO₄ from thermal conductivity and current-voltage spectroscopy studies, although in these cases, it was assigned to thermally activated small polaron hopping transport.^{50,129} This ~ 0.2 eV activation energy measured herein might explain why oxygen vacancies in BiVO₄ have low doping efficiency with the measured density of mobile electrons typically being several orders of magnitude lower than the measured density of oxygen vacancy sites. From a functional perspective, this ~ 0.2 eV can indicate that the doping efficiency of such photoelectrodes may be affected by the localisation of electrons in dopant (oxygen vacancy) states, thus limiting bulk conductivity,⁴⁵ which can be overcome at elevated temperatures. This is further reflected in the enhanced photoelectrochemical performance of BiVO₄ photoanodes operating at higher temperatures, as shown in *Figure 3.12e*, and reported previously.¹³⁰ Given that accelerated electron extraction is observed at elevated temperatures, the higher performance of BiVO₄ photoanodes can result from enhanced electron transport with increasing temperature.

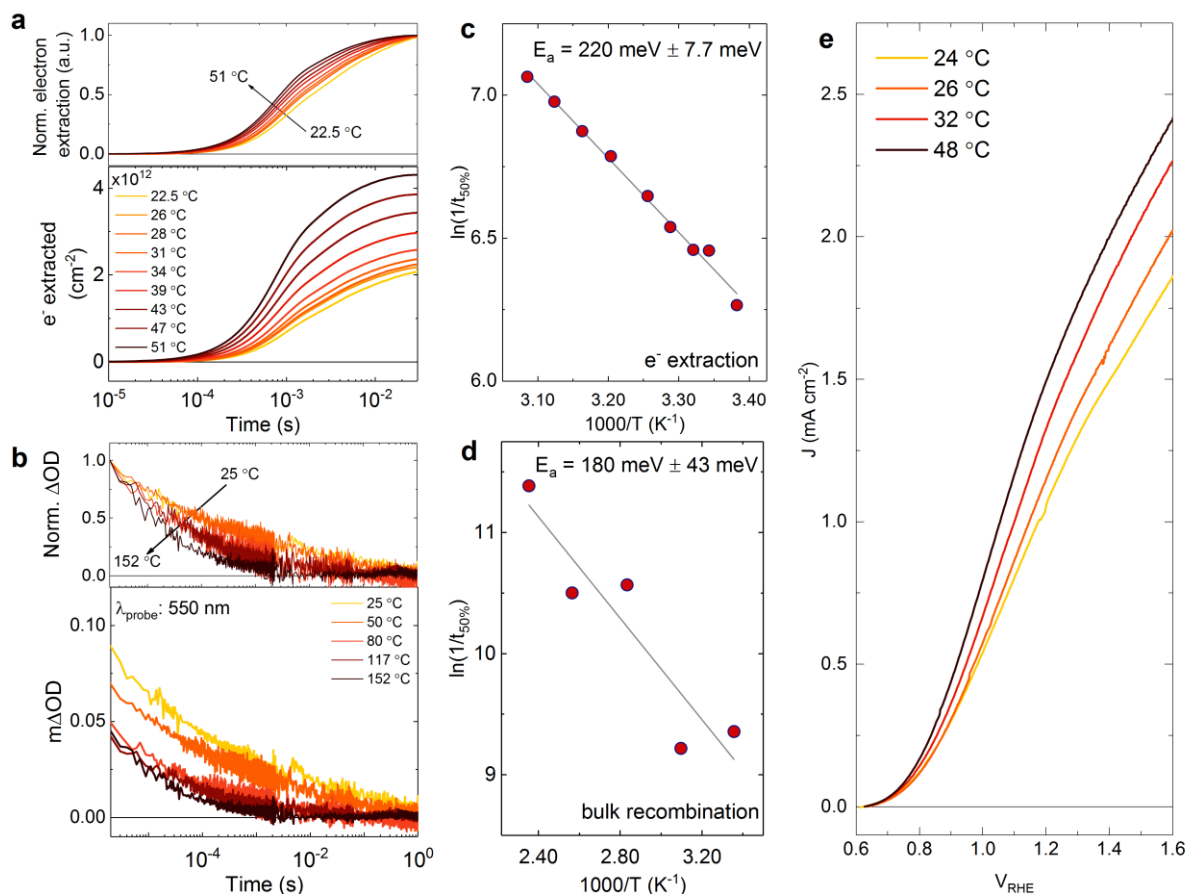


Figure 3.12 | Temperature dependence studies of charge extraction, charge carrier dynamics and photoelectrochemical performance. (a) Transient electron extraction from the BiVO₄ photoanode obtained with transient photocurrent measurements with the normalised data (top panel), measured at 0.6 V_{RHE} in 0.1 M phosphate buffer (pH 7) with λ_{ex}: 355 nm (300 μJ cm⁻²). (b) Transient absorption kinetics of holes in BiVO₄ in inert atmosphere (Ar) with λ_{pump}: 355 nm and λ_{probe}: 550 nm with the normalised data on the top panel. (c) Activation energy for the electron extraction process. (d) Activation energy for the bulk recombination process. (e) Photoelectrochemical performance of BiVO₄ photoanode under equivalent 1 sun illumination showing the increase in photocurrent at higher temperatures. It is noted that the film used for the TPC study does have a more cathodic photocurrent onset compared to the one used for linear sweep voltammetry. This is attributed to variations in BiVO₄ films.

3.5 Discussion

The results above allow the explicit assignment of the 470 nm optical absorption observed in the *in situ* modulation studies of V_{OV}⁴⁺/V_{OV}⁵⁺ states located energetically close to the BiVO₄ conduction band. This near-edge absorption peak is analogous to an absorption feature observed in α-Fe₂O₃ at 580 nm, which has previously been associated with oxygen vacancy induced shallow trap states.^{72,73,131} The spectroelectrochemical data allows us to rule out that this feature results exclusively from thermally induced structural changes, as suggested elsewhere.^{118,120} The similarity in the magnitude of density of V_{OV}⁴⁺ states accessible thermally and electrochemically indicates that these states are not confined to the surface of BiVO₄, rather they are distributed throughout the bulk of the material. Crucially, the

energetic location of these close to the conduction band confirms that this optical signal is not associated with states that are directly involved in water oxidation as suggested in several other studies.^{116,119,121–123} In particular, the 470 nm transient absorption feature has previously been reported for BiVO₄ but assigned to surface trapped holes that participate in water oxidation catalysis.^{116,119} Similar conclusions have also been reported for the analogous feature in α -Fe₂O₃.^{121–123} However, the impedance, spectroelectrochemical, thermal and IR push data all indicate that this feature originates from state lying energetically close to the conduction band edge. The energetic placement of these states precludes the holes trapped in these states from driving water oxidation (more negative than the thermodynamic water oxidation potential of 1.23 V_{RHE}). This conclusion is also consistent with recent studies by our group, where investigation of charge carrier trapping in oxygen vacancies in tungsten oxide, points towards a general behaviour amongst n-type metal oxides.⁷⁰ It is worth noting that the actual spectroscopic origin of the 470 nm signal observed herein, is less clear. Whilst it may derive from optical excitation from valence band to ionised oxygen vacancies, as proposed previously for the analogous feature in α -Fe₂O₃,^{72,73} the second-derivative-like response of the optical spectra,¹¹⁸ could suggest that it alternatively arises from electroabsorbance effects, where photogenerated charge localisation can induce changes in the dipole moment of the material.¹³² This can result in broadening of the ground state absorption features that resemble the second-derivative of the ground state absorption spectrum.^{132,133} Although localisation of holes and electrons into V_{OV}⁴⁺/V_{OV}⁵⁺ states (close to conduction band edge) may yield these broadening effects, further probe of the origin of the transition is beyond the scope of this work. Nonetheless, the results herein clearly indicate this feature can be used as a spectral fingerprint for V_{OV}⁵⁺ states and reveal important functional information.

A similar charge transport activation energy has previously been reported for BiVO₄ from thermal conductivity studies, although in this case it was assigned to thermally activated small polaron hopping transport.⁵⁰ This ~0.2 eV activation energy we measure might explain why oxygen vacancies in BiVO₄ have a low doping efficiency, with the measured density of mobile electrons typically being several orders of magnitude lower than the measured density of oxygen vacancy sites. From a functional perspective, this indicates the doping efficiency of such photoelectrodes will be severely affected by the localisation of electrons in dopant (oxygen vacancy) states, thus limiting bulk conductivity,⁴⁵ which can be overcome at elevated temperatures. This is further reflected in the enhanced photoelectrochemical performance of BiVO₄ photoanodes operating at higher temperatures, as shown in *Figure 3.12e* and reported previously.¹³⁰ Given that the Faradaic efficiency for water oxidation is reported to be high (~90%) and temperature independent,¹³⁰ this, together with our

charge extraction data suggests that the performance enhancement does not result from improved catalysis, but rather is a direct consequence of enhanced electron transport.

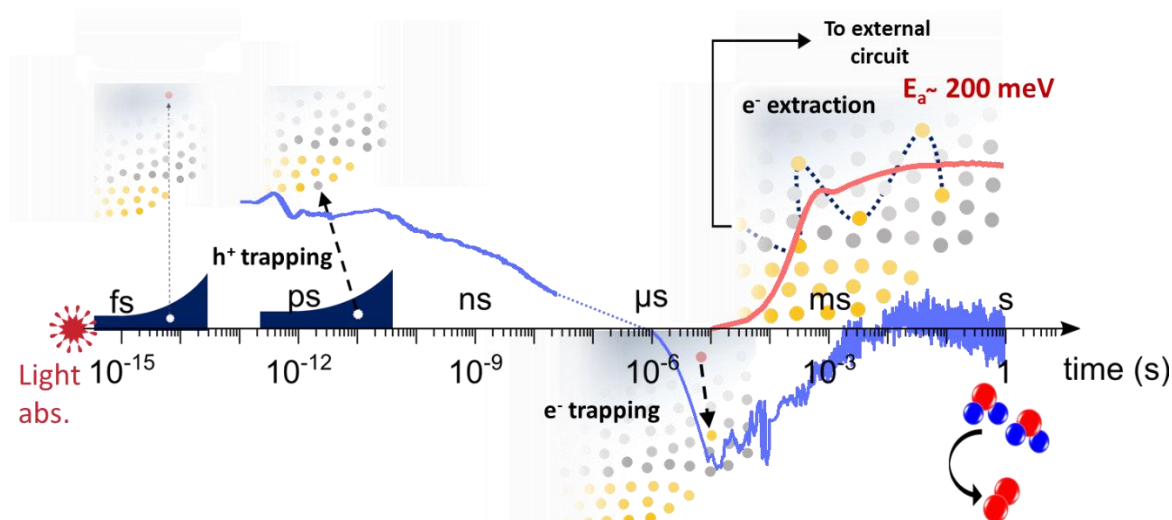


Figure 3.13| Schematic illustration of the role of oxygen vacancies in charge carrier trapping and electron transport in BiVO₄ from the timescale of light absorption to water oxidation. Following charge generation, valence band holes trap into bulk V_{OV}^{4+} states leading to a positive TA signal (ps – ns). Within microseconds, electrons trap into V_{OV}^{5+} states within the space-charge layer causing the TA signal to bleach. On the millisecond timescale electrons are extracted through the electrical circuit causing the bleach to recover and the accumulated holes oxidise water. The charge extraction process takes place via thermal de-trapping from V_{OV}^{4+} with an activation barrier (E_a) of ~0.2 eV. For illustration, yellow states represent occupied V_{OV}^{4+} states, whereas grey states represent un-occupied V_{OV}^{5+} states.

In addition, experimentally, it is difficult to differentiate whether charge transport occurs predominantly via polaron-hopping mechanism where electrons are self-trapped or whether electronic states associated with defects play a role in the charge transport mechanism. Distinguishing between self-trapped carrier (small and large) and a carrier trapped in the ‘vicinity’ of a defect is not trivial (as they both give rise to a vanadium oxidation state of +4), especially as the presence of defects might itself influence the dynamics of polaron formation. Electrochemical oxidation of V_{OV}^{4+} states increases the concentration of V_{OV}^{5+} states which manifests as a positive peak at ~470 nm detected by spectroelectrochemistry measurements (Figure 3.3). This redox process observed optically to correlate with an increase in unoccupied electronic states (V_{OV}^{5+}) below the conduction band (Figure 3.2d(iii)) is unlikely to be observed for the case of an electron polaron although electrons trapped at oxygen vacancies may also induce wider lattice deformations analogous to those associated with such polarons. For the case of a self-trapped electron at a vanadium centre (formation of a polaron), this localisation may induce a stabilised electronic state below the conduction band. However, upon electrochemical oxidation of the electrode (oxidising the V^{4+}), it is unlikely for the stabilised electronic state to be present. On the contrary, when performing electrochemical oxidation (in the dark) using

spectroelectrochemistry (*Figure 3.3*), the oxidised V^{5+} is observed, for which the density of states is mapped below the conduction band (*Figure 3.2*), which correlates with the capacitance associated with the V_{OV}^{4+}/V_{OV}^{5+} redox couple.¹²⁶ Based on this and complementary data, it can be concluded that the 470 nm optical signal is a probe of phenomena directly linked to oxygen vacancies. Although it is acknowledged that electrons trapped at defect sites may also incur lattice stabilisation therefore, the data presented herein does not rule out polaron formation, while further computational studies and experimental measurements such as x-ray and time-resolved Raman might be necessary to unravel the link between defects and polaronic states.

3.6 Conclusion

Figure 3.13 summarises some of the key functional processes underlying water oxidation in BiVO_4 photoanodes, and the role oxygen vacancies play. In addition to their role in space-charge layer formation and n-type doping of bulk BiVO_4 to reduce resistance losses during bulk charge transport, oxygen vacancy states participate in the trapping of photogenerated electrons and holes. In the bulk, hole trapping is a significant loss pathway, as this deep trapping is strongly exothermic, with the resultant oxidised oxygen vacancy states being energetically unable to drive water oxidation. On the other hand, electron trapping is reversible, with a de-trapping activation energy of ~ 0.2 eV. Such electron trapping occurs particularly in the space-charge layer, where most oxygen vacancies are ionised (unoccupied) in the dark, resulting in a thermally activated electron extraction into the external circuit. Thermally activated electron extraction is consistent with enhanced PEC water splitting performance at higher temperatures, important for technological application of such photoanodes under one sun or concentrated sunlight. Given the prevalence of oxygen vacancy formation in metal oxides and their impact on the electronic structure,^{72,73,97} the optimisation of oxygen vacancy ionisation may be used as a tool to increase the performance of metal oxide-based water splitting devices.

Chapter 4 | Charge separation in $\text{WO}_3/\text{BiVO}_4$ photoanodes

The four hole oxidation of water has long been considered the kinetic bottleneck for overall solar-driven water splitting, and thus requires the formation of long-lived photogenerated holes to overcome this kinetic barrier. However, photogenerated charges are prone to recombination unless they can be spatially separated. This can be achieved by coupling materials with staggered conduction and valence band positions, providing a thermodynamic driving force for charge separation. This has most widely been demonstrated in the $\text{WO}_3/\text{BiVO}_4$ junction, in which quantum efficiencies for the water oxidation reaction can approach near unity. However, the charge carrier dynamics in this system remain poorly characterised over timescales relevant to water oxidation (μs - s). In this chapter, the effect of charge separation on carrier lifetime, and the voltage dependence of this process, is probed from the microsecond to second timescale using transient absorption spectroscopy and transient photocurrent measurements, revealing sub- μs electron transfer from BiVO_4 to WO_3 . The interface formed between BiVO_4 and WO_3 is shown to overcome the “dead-layer effect” encountered in BiVO_4 alone, when directly deposited on FTO. Moreover, this study sheds light on the role of the $\text{WO}_3/\text{BiVO}_4$ junction in enhancing the efficiency of the water oxidation reaction, where charge separation across the $\text{WO}_3/\text{BiVO}_4$ junction improves both the yield and lifetime of holes present in the BiVO_4 layer over timescales relevant to water oxidation.

The majority of the results presented in this chapter is included in the following publication:

$\text{WO}_3/\text{BiVO}_4$: Impact of charge separation at the timescale of water oxidation

S. Selim, L. Francàs, M. García-Tecedor, S. Corby, C. Blackman, S. Gimenez, J. R. Durrant and A. Kafizas, *Chem. Sci.*, 2019, **10**, 2643–2652. DOI: [10.1039/C8SC04679D](https://doi.org/10.1039/C8SC04679D)

4.1 Introduction

Time-resolved studies have shown that water oxidation on metal oxides is kinetically slow, which typically takes place over several hundred milliseconds.^{27,134,135} Moreover, under operational conditions, the rate limiting step has been shown to involve the concerted reaction of multiple holes (or oxidised equivalents);^{89,92} similar to the manganese calcium cubane cluster in PS II.^{136,137} As such, metal oxides require long-lived holes to oxidise water efficiently.^{79,131,138} Several strategies have been employed to increase hole lifetime in metal oxides, such as the use of surface co-catalysts (as will be discussed in *chapter 5*) and passivation layers that inhibit surface electron-hole recombination.¹⁷ However, one of the most promising strategies for extending charge carrier lifetime is to couple semiconductors with staggered band alignment, which promotes the spatial separation of charge. This has been shown to synergistically enhance the activity in a number of systems including anatase/rutile TiO₂, Cu₂O/TiO₂ and WO₃/BiVO₄.^{77,140,141} Using transient optical spectroscopy techniques herein, the enhancement in the performance of the WO₃/BiVO₄ heterojunction is demonstrated to be a direct result of fast electron transfer from BiVO₄ into WO₃, in agreement with previous reports.^{116,142} This leads to an overall decrease in recombination at timescales consequential to photoelectrochemical processes (*i.e.* water oxidation).

The most active phase of BiVO₄, (monoclinic scheelite) has a deep valence band ($\sim +2.5 V_{\text{RHE}}$) which provides a large thermodynamic driving force for the water oxidation reaction.^{31,67} However, as discussed in *chapter 1*, it is often argued that this material suffers from poor electron transport properties, which results in high recombination losses.^{43,67} Tungsten oxide (WO₃) is another frequently studied material for water oxidation. It possesses a wider indirect bandgap of 2.7 eV (*i.e.* can absorb $\sim 7\%$ of the solar spectrum), a deeper valence band ($\sim +3.2 V_{\text{RHE}}$) and can typically oxidise water at less anodic potentials. When held at the thermodynamic water oxidation potential ($1.23 V_{\text{RHE}}$), individual intrinsic BiVO₄ and WO₃ photoanodes typically show photocurrents in the region of $1 - 2 \text{ mA cm}^{-2}$ at 1 sun irradiance, significantly less than their theoretical limit (BiVO₄ $\sim 7.5 \text{ mA cm}^{-2}$; WO₃ $\sim 5.3 \text{ mA cm}^{-2}$).¹⁴³ Nevertheless, when these two materials are coupled together to form a WO₃/BiVO₄ junction, substantially higher photocurrents have been observed, in some cases approaching the theoretical limit for this system.⁷⁷

Although the WO₃/BiVO₄ junction has been shown to exhibit high water oxidation efficiencies, *in operando* studies of charge carrier behaviour that interrogate the system at the timescale of water oxidation is scarce in literature. Studies incorporating transient absorption spectroscopy have shown that electron transfer from BiVO₄ to WO₃ takes place on the ultra-fast timescale, enhancing charge carrier lifetime.^{116,142} However, simultaneous photoexcitation of both materials have also been shown to exacerbate interfacial recombination of holes in BiVO₄ and electrons in WO₃.^{142,144} To date, transient

absorption studies for this system typically have focussed on the ultra-fast timescales (fs-ns), when charge generation and trapping processes occur and do not provide insight into charge carrier dynamics under operational conditions (*i.e.* applied potential).^{116,142,144} As such, the precise role of this junction in inhibiting electron-hole recombination and promoting water oxidation remains unresolved.

4.2 In this chapter

In this chapter, the charge carrier dynamics in the $\text{WO}_3/\text{BiVO}_4$ junction during water oxidation is investigated using complementary transient absorption spectroscopy (TAS) and transient photocurrent (TPC) measurements. The results presented herein demonstrate that pre- μs electron transfer from BiVO_4 to WO_3 , results in a significant improvement in the yield of holes accumulated at the surface in the heterojunction, with respect to BiVO_4 alone. Moreover, anodic bias is found to substantially improve this electron transfer process, reducing recombination losses. These results thus shed new light on the role of this junction in facilitating synergistic improvements in water oxidation activity.

4.3 Experimental methods

BiVO_4 and WO_3 thin films were prepared using metal organic decomposition (MOD) and aerosol assisted chemical vapour deposition (AA-CVD), respectively. X-ray diffraction confirmed the formation of monoclinic scheelite BiVO_4 and monoclinic $\gamma\text{-WO}_3$ (*Figures 2.1a* and *2.2a* in *chapter 2*). The deposited materials were flat and dense, as confirmed by SEM imaging (*Figures 2.1b* and *2.2b* in *chapter 2*). The films were further characterised by UV-Visible absorption spectroscopy (*Figure 2.4* in *chapter 2*), with the band edge observed at ~ 500 nm for BiVO_4 and ~ 375 nm for WO_3 .

It is noted that the X-ray diffraction measurements reported in this chapter were conducted by Dr. Andreas Kafizas (Imperial College London, UK).

4.4 Results

4.4.1 Photoelectrochemical performance

The photoelectrochemical response of BiVO_4 and $\text{WO}_3/\text{BiVO}_4$ for water oxidation is shown in *Figure 4.1*. The planar, dense BiVO_4 photoanodes studied herein display a photoelectrochemical response that is strongly dependent on the film thickness. As can be seen in *Figure 4.1*, for front illumination of BiVO_4 photoanodes (see *Figure A4* in *appendix* for back illumination data), films that were ≤ 125 nm in thickness showed both a more positive onset potential and lower photocurrents when compared with thicknesses ≥ 175 nm. In contrast, when BiVO_4 was deposited on WO_3 , much higher photocurrents were observed even at low film thicknesses for both front and back illumination. The

photoelectrochemical response of the WO_3 photoanodes alone is negligible due to poor light harvesting and is presented in *Figure A4* in the *appendix* for comparison. The thickness dependence of the absorbed photon to current efficiency (APCE) for the films at 1.23 V_{RHE} under simulated 1 sun illumination are presented in *Figure 4.2a*, where key differences between BiVO_4 and $\text{WO}_3/\text{BiVO}_4$ can be observed.

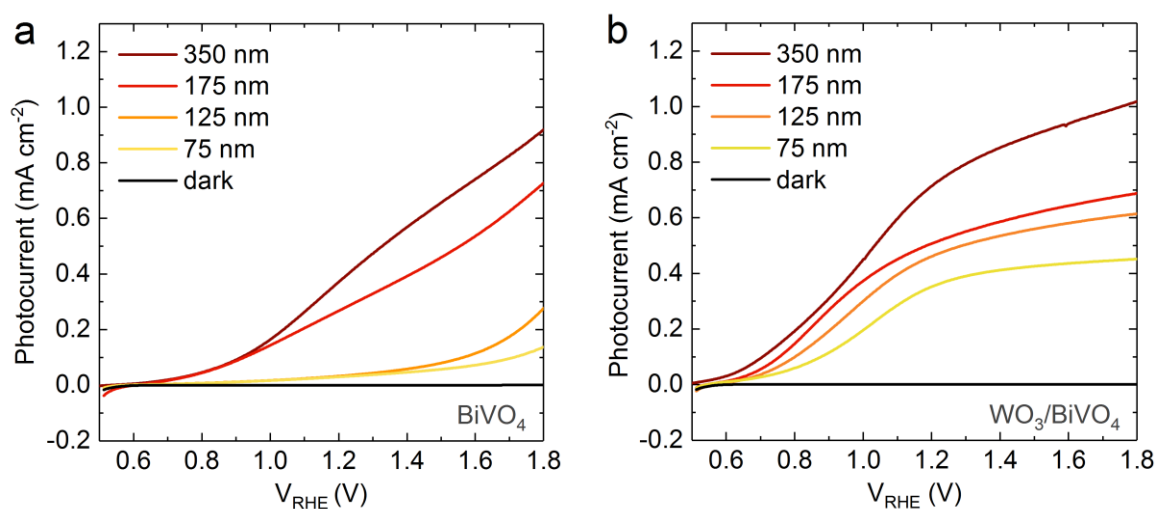


Figure 4.1| Effect of heterojunction on the photoelectrochemical performance. Photocurrent measurements of (a) BiVO_4 and (b) $\text{WO}_3/\text{BiVO}_4$ films of varying BiVO_4 thickness (and fixed WO_3 thickness of 200 nm), under front illumination (*i.e.* through BiVO_4 side) using simulated 1 sun irradiation, in 0.1 M phosphate buffer, pH 7.

Consistent with previous reports of BiVO_4 , back illumination generally performs better than front illumination due to poorer electron transport through the material in comparison to hole transport.⁴³ Although, the photocurrent improves with increasing film thickness, it is clear that at lower thicknesses, the performance is not limited by poor photon absorption (*Figure 4.2b*). This trend with thickness is recognised as a key signature characteristic of a “dead-layer effect” and also has been observed for other metal oxides such as hematite ($\alpha\text{-Fe}_2\text{O}_3$)¹⁴⁵ (where the material becomes more active once film thickness exceeds the inactive layer depth). Although the exact cause of the dead-layer remains unknown, it may arise from lattice mismatch at the semiconductor / FTO interface, which results in the formation of amorphous material close to the interface rich in trap states. The performance of BiVO_4 has been shown to improve with the addition of underlayers such as SnO_2 ,⁴³ which may explain why the presence of a WO_3 underlayer in the $\text{WO}_3/\text{BiVO}_4$ system shows substantial improvement in the activity of thin (≤ 125 nm) BiVO_4 layers (*Figure 4.2c*).

When the $\text{WO}_3/\text{BiVO}_4$ films are illuminated from the front, the photocurrent obtained is largely governed by the photon absorption, as shown in *Figure 4.2c* and is also visible in the thickness

independence of the APCEs shown in Figure 4.2a. However as observed in Figure 4.2a, when illuminated from the back, the APCE falls significantly from 85% to 40% when the BiVO₄ thickness increases from 75 nm to 350 nm. This is in stark contrast to bare BiVO₄ photoanodes, and is symptomatic of poor charge transport and the decrease in success of charge collection when photogenerated further from the WO₃/BiVO₄ interface. This may stem from the penetration depth of light and the resulting charge generation, *i.e.* considering the BiVO₄ thickness of 75 nm for the WO₃/BiVO₄ configuration, when the films are illuminated from the back, charge generation is likely to be closer to the WO₃/BiVO₄ interface, as opposed to the BiVO₄/electrolyte interface when illuminated from the front, resulting in back illumination performing significantly better than the alternative. However, this difference between the front and back illumination decreases with increasing BiVO₄ thickness as poor charge transport limits the performance.

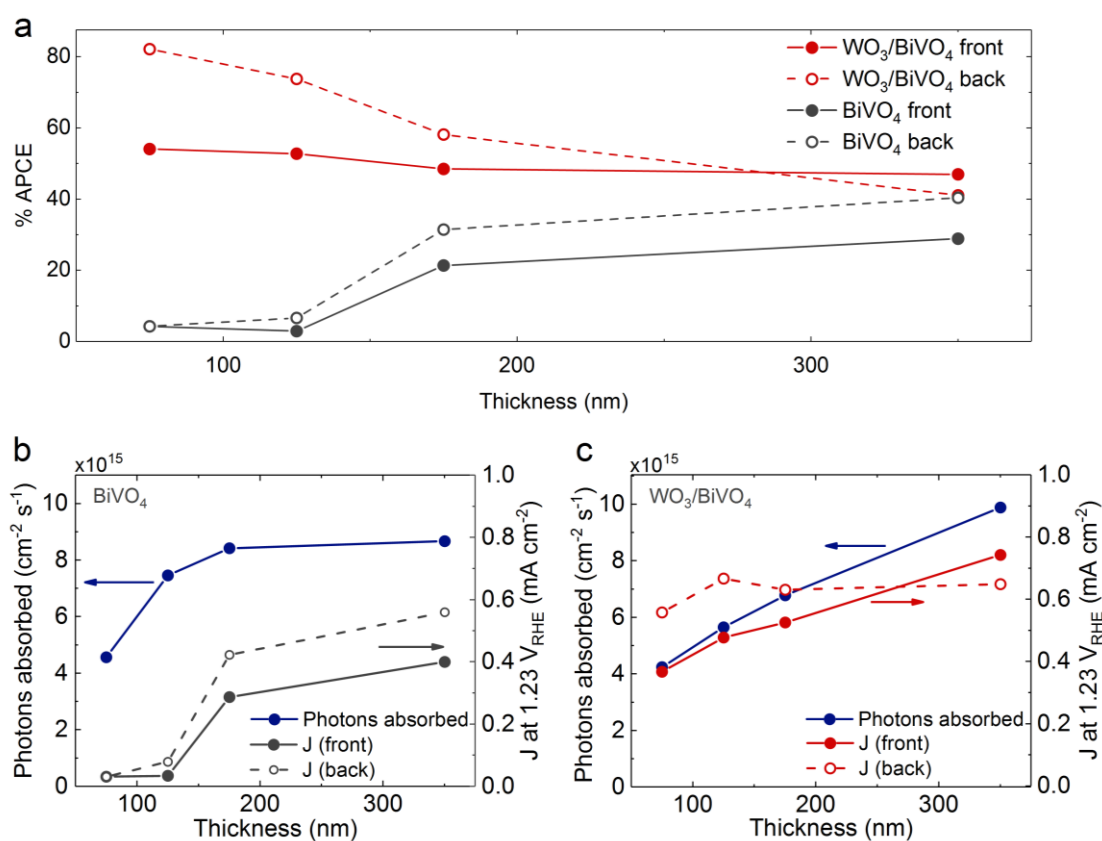


Figure 4.2 | Dependence of photoelectrochemical performance on the thickness of BiVO₄ layer for BiVO₄ and WO₃/BiVO₄ photoanodes. (a) The polychromatic %APCE of BiVO₄ (dark grey) and WO₃/BiVO₄ (red) as a function of BiVO₄ thickness, under simulated 1 sun illumination. Comparison of photons absorbed by the sample and the photocurrent obtained at 1.23 V_{RHE} for front (solid circles) and back illumination (open circles) under simulated 1 sun irradiation for (b) BiVO₄ and (c) WO₃/BiVO₄. All photocurrents were obtained using simulated 1 sun irradiation (Xe lamp), in 0.1 M phosphate buffer, pH 7.

As to why $\text{WO}_3/\text{BiVO}_4$ photoanodes exhibit higher photocurrents than BiVO_4 alone, further time-dependent spectroscopic studies were conducted (discussed in detail later), from which the fast timescale of electron transfer from BiVO_4 to WO_3 in the heterojunction suggest more effective spatial separation of charge compared to bare BiVO_4 , where electron extraction from FTO is slower. This leads to lower recombination losses in the heterojunction photoanodes, which manifest as an increase in photoelectrochemical performance, as opposed to bare BiVO_4 photoanodes.

4.4.2 Transient absorption spectra

As discussed in the previous chapters, TAS can be used to monitor the time-resolved behaviour of photogenerated charge, therefore it can be employed to observe if:

- (i) charge separation occurs across the $\text{WO}_3/\text{BiVO}_4$ interface
- (ii) charge separation results in enhanced charge carrier lifetimes

Previous TAS studies of BiVO_4 have shown that photogenerated holes in BiVO_4 give rise to a broad absorption spectrum, absorbing most strongly at ~ 550 nm.^{27,79,92} Due to the low absorption coefficient of photogenerated electrons in BiVO_4 , the signal arising from these species was not detected or probed over the range of wavelengths studied herein. *Figure 4.3a* shows the transient absorption spectra of BiVO_4 and $\text{WO}_3/\text{BiVO}_4$ under an applied bias of 1.23 V_{RHE} at 10 μs and 100 ms. Films were excited with front illumination (λ_{ex} : 355 nm) via the BiVO_4 side to ensure that light absorption and charge generation occurs predominantly within the BiVO_4 layer, to study the effect of electron transfer exclusively from BiVO_4 to WO_3 . According to the absorptance of each material (*Figure A3* in *appendix*), 85% of the light at 355 nm is absorbed by the 350 nm thick BiVO_4 layer, whereas 4% of light is absorbed by the 200 nm thick WO_3 layer underneath. Thus, for the TAS studies presented herein, a BiVO_4 thickness of 350 nm was chosen as a compromise between high light absorption within the BiVO_4 layer and good photoelectrochemical response. The observed trends in charge carrier dynamics were also confirmed using an excitation wavelength (λ_{ex} : 450 nm) at which the WO_3 layer is not photoexcited due to its wider bandgap (shown in *Figure 4.3b*), and exhibits analogous spectral shape to that observed when photoexcited with λ_{ex} : 355 nm. In addition, *Figure 4.2* indicates that there are clear differences in the performance of $\text{WO}_3/\text{BiVO}_4$ (for films of BiVO_4 thicknesses 75 – 125 nm) when illuminated from the front and back, photogenerating charges across both materials. Therefore, it would be interesting to study the illumination directional dependence of the charge carrier dynamics of these films. Furthermore, the influence of the WO_3 underlayer on hole trapping into $\text{V}_{\text{OV}}^{4+}$ states would also be interesting to monitor on the ultrafast timescales. However, as holes in WO_3 absorb most strongly at 500 nm and below,^{70,97} the overlap of signals between holes in WO_3 and

BiVO₄, and the trapped holes (V_{OV}^{5+}) monitored at 470 nm, can complicate signal assignments, and therefore these studies are not reported in this chapter.

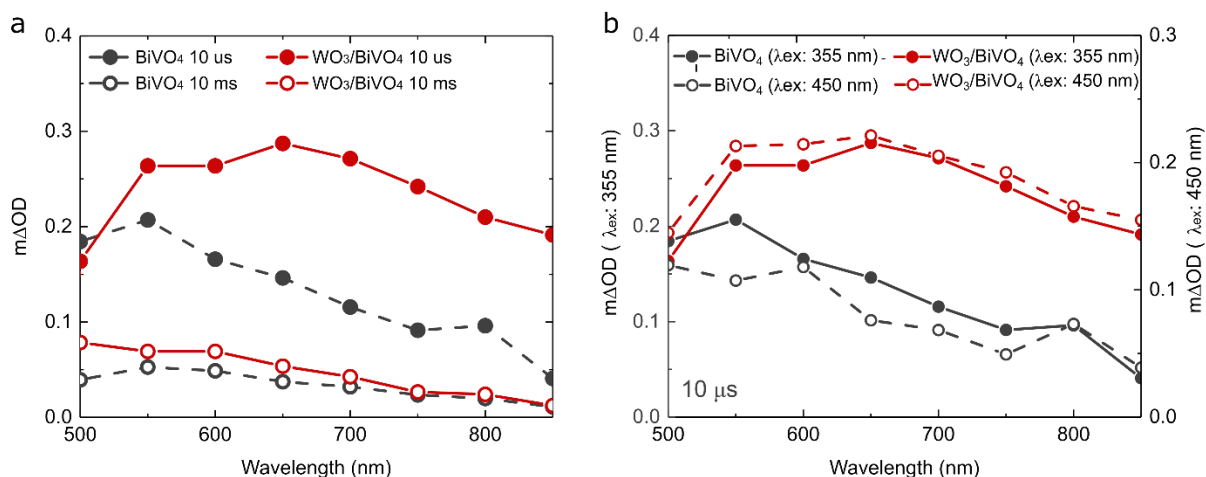


Figure 4.3| Charge transfer in WO₃/BiVO₄ photoanodes observed optically in the transient absorption spectra at 1.23 V_{RHE}. (a) Transient absorption spectra of BiVO₄ (grey) and WO₃/BiVO₄ (red) at 10 μs (solid) and 10 ms (open circles) under front illumination in 0.1 M phosphate buffer, with BiVO₄ film thickness of 350 nm, pump fluence: 500 μJ/cm². (b) TA spectra of BiVO₄ (grey) and WO₃/BiVO₄ (red) at 10 μs when excited with λ_{ex}: 355 nm (solid) and λ_{ex}: 450 nm (dashed).

The TAS spectra of BiVO₄ under anodic bias shows the characteristic peak at 550 nm (assigned to photogenerated holes in BiVO₄), however, the WO₃/BiVO₄ heterojunction shows a different spectral shape at early timescales, with an additional absorption feature at longer wavelengths, not present in bare BiVO₄. This feature disappears by 10 ms, following which the spectrum of the heterojunction is analogous to that of bare BiVO₄, but with a ~two-fold increase in amplitude at 500 nm (*i.e.* holes), consistent with prolonged hole lifetimes reported in another study.⁷⁴ Previous works have shown that photogenerated electrons in WO₃ present a broad transient absorption feature at around 800 nm, which extends into the near-infrared region.^{70,97,146} Given that this feature is also observed in the heterojunction when the excitation wavelength (λ_{ex}: 450 nm) selectively excites BiVO₄ (Figure 4.3b), this shows that at early timescales (microseconds), the heterojunction contains holes in BiVO₄ and electrons in WO₃. This indicates pre-μs electron transfer from BiVO₄ to WO₃, in agreement with previous ultra-fast studies.¹⁴² The electron signal in WO₃ will be discussed in forthcoming sections.

4.4.3 Transient absorption kinetics of surface holes

The effect of applied bias on the charge carrier dynamics was monitored in BiVO₄ and WO₃/BiVO₄. As mentioned earlier, the electron signal in WO₃ is broad, stretches into the NIR, which can be probed at 800 nm. Holes in BiVO₄ were probed at 500 nm herein, to minimise overlap with the electron absorption in WO₃. Figures 4.4a and b show the kinetic traces of the photogenerated holes in BiVO₄

and $\text{WO}_3/\text{BiVO}_4$ respectively, as a function of applied potential. While the lifetime and population of holes increase with increasing anodic bias in both systems, the increase is more substantial in the heterojunction system in comparison to bare BiVO_4 . Anodic bias results in the formation of a wider space charge layer at the semiconductor/electrolyte interface, thus increasing band bending that can facilitate greater hole accumulation at the surface. In contrast, in the presence of a hole scavenger (sodium sulfite), shown in *Figure 4.5*, hole accumulation in the heterojunction is significantly lower and is substantially less bias dependent, due to a more facile oxidation of sulfite in comparison to water. The biphasic nature of the hole decay dynamics observed in bare BiVO_4 , consistent with previous reports, consists of trap-mediated bimolecular recombination that dominates at earlier timescales ($< \mu\text{s}$ - ms) and water oxidation coupled with back electron-hole recombination that takes place over slower timescales (ms - s).

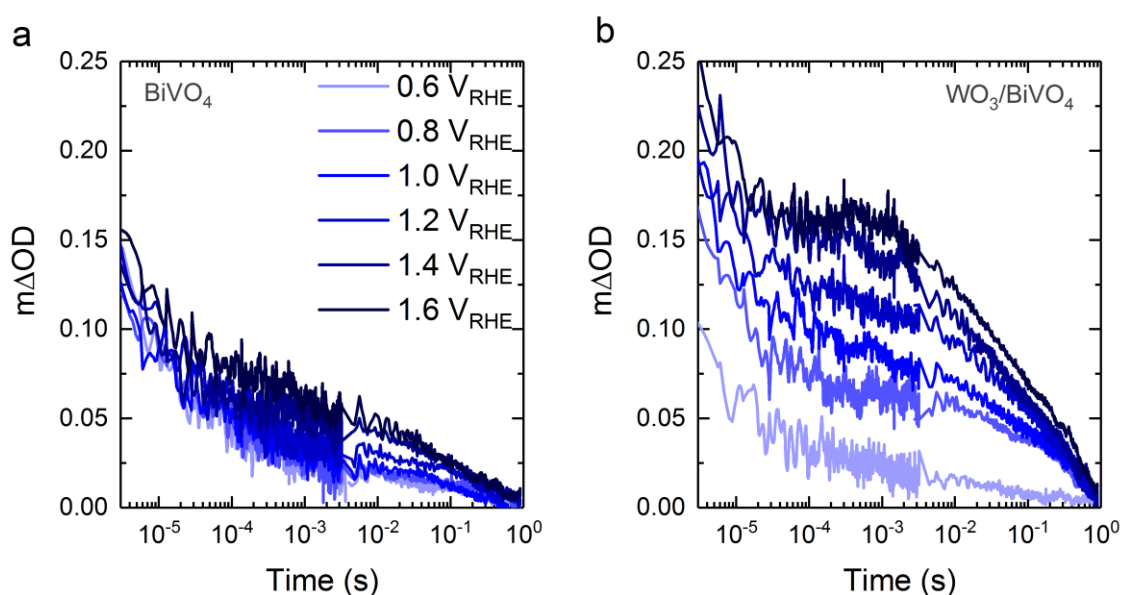


Figure 4.4 | Transient absorption kinetics traces of photogenerated holes in BiVO_4 and $\text{WO}_3/\text{BiVO}_4$ photoanodes. The films were excited at 355 nm under front illumination, with applied anodic bias ($0.2 \text{ V}_{\text{RHE}}$ interval) in 0.1 M phosphate buffer with BiVO_4 film thickness of 350 nm, pump fluence: $500 \mu\text{J}/\text{cm}^2$. TA decay traces of holes probed at 500 nm in (a) BiVO_4 and (b) $\text{WO}_3/\text{BiVO}_4$.

In bare BiVO_4 , at early timescales, bimolecular recombination, even with appreciable anodic bias, plays a significant role as observed in *Figure 4.3a*. However, this recombination is significantly suppressed in the heterojunction with increasing anodic bias, resulting in more substantial increase in hole population in BiVO_4 . The requirement for long-lived holes is a consequence of the slow kinetics of water oxidation on BiVO_4 (and metal oxides in general), which is on the order of $0.7\text{-}1 \text{ s}^{-1}$ on BiVO_4 under pulsed laser illumination.²⁷ These kinetics manifest as the slow decay phase from 0.1 ms to 1 s in *Figure 4.3*. No acceleration of this slow decay phase, assigned to water oxidation, is observed in the heterojunction over bare BiVO_4 , as the rate of catalysis is limited by the material in which holes

accumulate. On the other hand, in the heterojunction, a substantial improvement in carrier separation results in an increase in the population of long-lived holes, and an overall increase in water splitting activity.

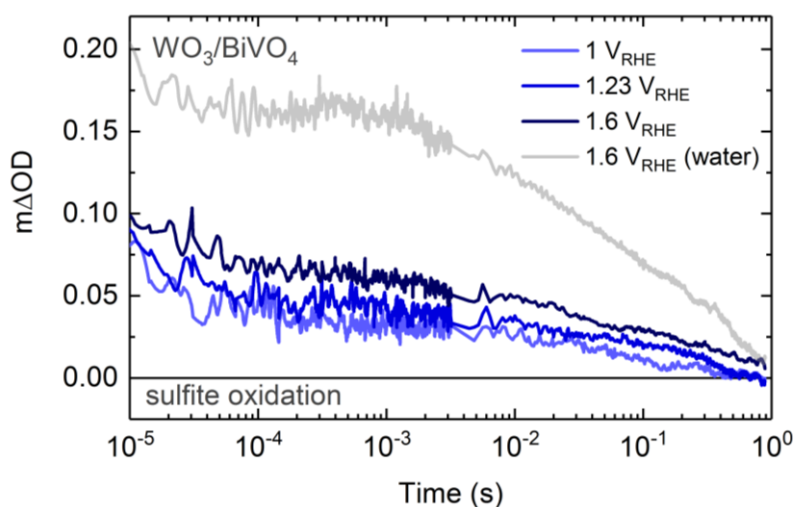


Figure 4.5 | Transient absorption kinetics traces of photogenerated holes probed at 500 nm in WO₃/BiVO₄ photoanodes for sulfite oxidation. The films were excited at 355 nm (pump fluence: 500 $\mu\text{J}/\text{cm}^2$) under front illumination, with applied anodic bias in 0.1 M Na₂SO₃ dissolved in 0.1 M phosphate buffer. The grey trace shows the equivalent kinetic trace at 1.6 V_{RHE} for the heterojunction for water oxidation.

4.4.4 Electron transfer, extraction and impact on performance

As discussed in previous chapters, transient photocurrent measurements can be used to monitor the charge extraction process from the photoanode following photoexcitation, and therefore allows direct probing of charge injection from the metal oxide to the back contact. Consequently, transient optical signal of electrons can be directly compared against the timescale of electron extraction. This is shown in *Figure 4.6a* where the transient absorption decay at 800 nm (*i.e.* electrons in WO₃) is plotted against the integrated transient photocurrent (*i.e.* charge extraction) from the photoanode at 1.23 V_{RHE}.

Firstly, focusing on the electron extraction from the photoanodes in *Figure 4.6a*, a five-fold increase in the number of electrons extracted is observed for the WO₃/BiVO₄ heterojunction in comparison to BiVO₄ alone, a direct consequence of effective charge separation suppressing bulk recombination losses in the heterojunction. In addition, the $t_{50\%}$ of electron extraction in the heterojunction (~ 1 ms) is an order of magnitude later than the bare BiVO₄ photoanode (~ 100 μs , grey trace). This slower extraction from the heterojunction can originate from the slower electron transport properties of WO₃ compared with BiVO₄ (*Figure 4.7*) which is consistent with previous report of electron transport in

WO₃ being the slowest amongst common metal oxides (*i.e.* BiVO₄, TiO₂, and α -Fe₂O₃) and heavily dependent upon the concentration and oxidation state of oxygen vacancies in the sample.¹⁴⁷

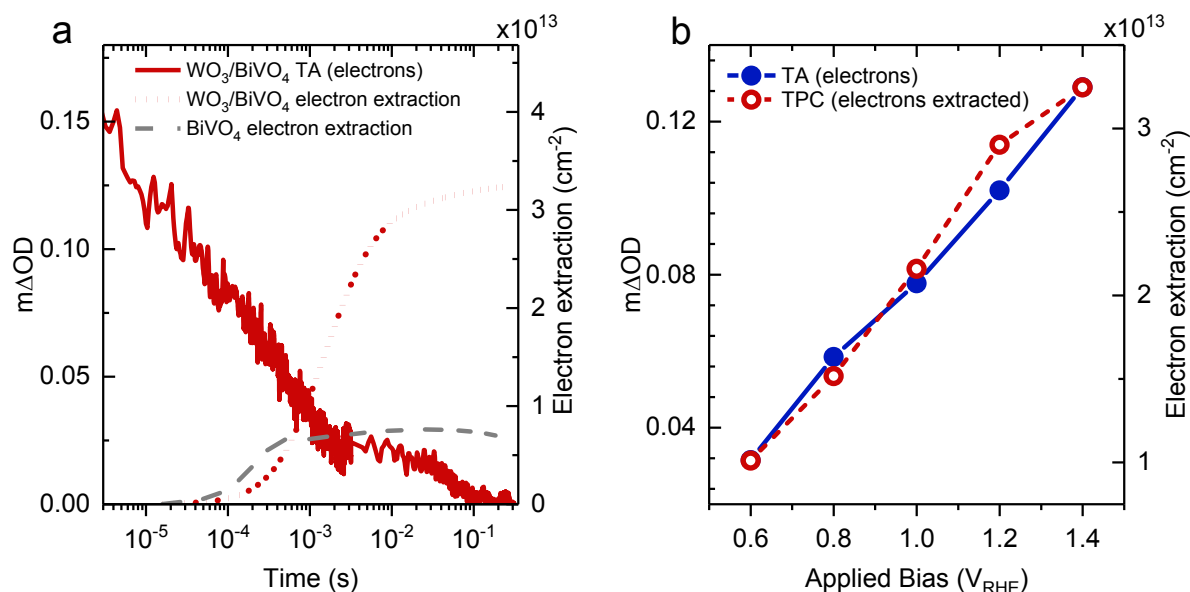


Figure 4.6 | Effect of applied potential on electron transfer and electron extraction in WO₃/BiVO₄ photoanodes. (a) TA trace of electrons in WO₃/BiVO₄ (red, solid line) at 1.23 V_{RHE} probed at 800 nm accompanied with the integrated transient photocurrent traces at the same bias for BiVO₄ (grey, dotted) and WO₃/BiVO₄ (red, dotted). (b) TA amplitude at 800 nm probing electrons in the WO₃/BiVO₄ system, at 50 μs (before the onset of charge extraction) (blue) compared with the total charge extracted from the WO₃/BiVO₄ photoanode (red).

Secondly, in the heterojunction, comparing the optical signal decay corresponding to the electrons transferred to WO₃ with the electron extraction in Figure 4.6a, it is observed that the optical signal decays prior to the onset of electron extraction (~50 μs). This indicates that a portion of electrons are lost at early timescales and not collected at timescales <50 μs. In addition, a similar decay of the optical signal is also observed (<50 μs) in the photogenerated hole kinetics of the heterojunction in Figure 4.4b, which can be tentatively assigned to the bimolecular recombination of electrons and holes at the WO₃/BiVO₄ interface before the onset of electron extraction. Additionally, most of the electron extraction for the heterojunction is completed by 10 ms, which is also consistent with the optical signal of electrons (Figure 4.3a), where the TA spectrum of the heterojunction at 10 ms is analogous in shape to that of bare BiVO₄ (*i.e.* holes accumulated at the surface of BiVO₄). The enhancement in the population of holes within BiVO₄ with increasing anodic bias due to improved charge transfer is also observed in the optical TA signal for electrons transferred to WO₃ (in Figure 4.6b). The bias dependence of the TA amplitude at 800 nm and the concomitant electron extraction shown in Figure 4.6b also strongly suggests i) that the electrons observed optically strongly correlates with the electrons that are extracted from the photoanode and ii) that charge separation across the WO₃/BiVO₄ improves with anodic potential.

In addition, the electron extraction profiles of $\text{WO}_3/\text{BiVO}_4$ photoanodes, shown in *Figure 4.8* exhibit greater bias dependence for water oxidation compared to sulfite oxidation, consistent with similar trends observed for the transient absorption kinetics of photogenerated holes (*Figure 4.5*). Again, this suggests faster transfer of holes to the electrolyte (due to more facile oxidation of sulfite compared to water), leading to an earlier turn off for recombination losses, and a greater yield of electron extraction. More importantly, it also indicates that spatial separation of charge across the heterojunction is insufficient, and further assistance from applied potential is needed to minimise recombination losses when charges (*i.e.* holes) are prone to accumulating due to the slower nature of water oxidation.

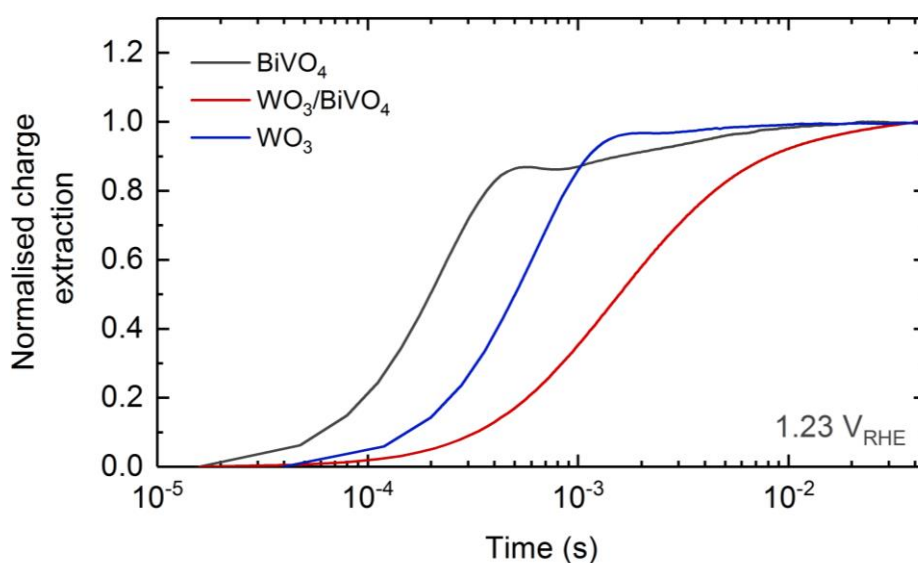


Figure 4.7| Normalised integrated transient photocurrent traces comparing the timescale of electron extraction for BiVO_4 , $\text{WO}_3/\text{BiVO}_4$ and WO_3 photoanodes. Traces taken under applied potential of $1.23 V_{\text{RHE}}$ in 0.1 M phosphate buffer, λ_{ex} : 355 nm (pump fluence: $500 \mu\text{J}/\text{cm}^2$), irradiated from the front.

4.5 Discussion

The results presented in this chapter show that the $\text{WO}_3/\text{BiVO}_4$ heterojunction exhibits higher water oxidation performance than bare BiVO_4 due to faster electron transfer from BiVO_4 to WO_3 than BiVO_4 to FTO. This results in a more effective charge separation that limits bimolecular recombination losses. The results also indicate that WO_3 functions as an effective underlayer, minimising charge carrier losses encountered at the BiVO_4/FTO interface. In bare BiVO_4 , it is observed from TPC measurements that electron injection into FTO begins from around 20 μs but the majority of this electron extraction is completed by 100 μs . However, in the heterojunction, TAS measurements show that electron transfer from BiVO_4 to WO_3 occurs $< \mu\text{s}$. This fast electron transfer from BiVO_4 to WO_3 minimises the recombination losses that can occur when electrons and holes reside within the same material.

Prolonging charge carrier lifetime through charge transfer and vectoral separation has evolved in nature over millions of years and is specifically employed in photosystem II (PS II) for driving water oxidation. Taking inspiration from PS II, where an assortment of processes such as light absorption, charge separation, and transfer occur successively, we can mimic this approach to maximise the efficiency of photoelectrodes for water splitting. By forming a staggered heterojunction like $\text{WO}_3/\text{BiVO}_4$, it is demonstrated how this system spatially separates photogenerated charge, and thus prolongs the lifetime and population of photogenerated holes that drive the kinetically limiting water oxidation reaction.

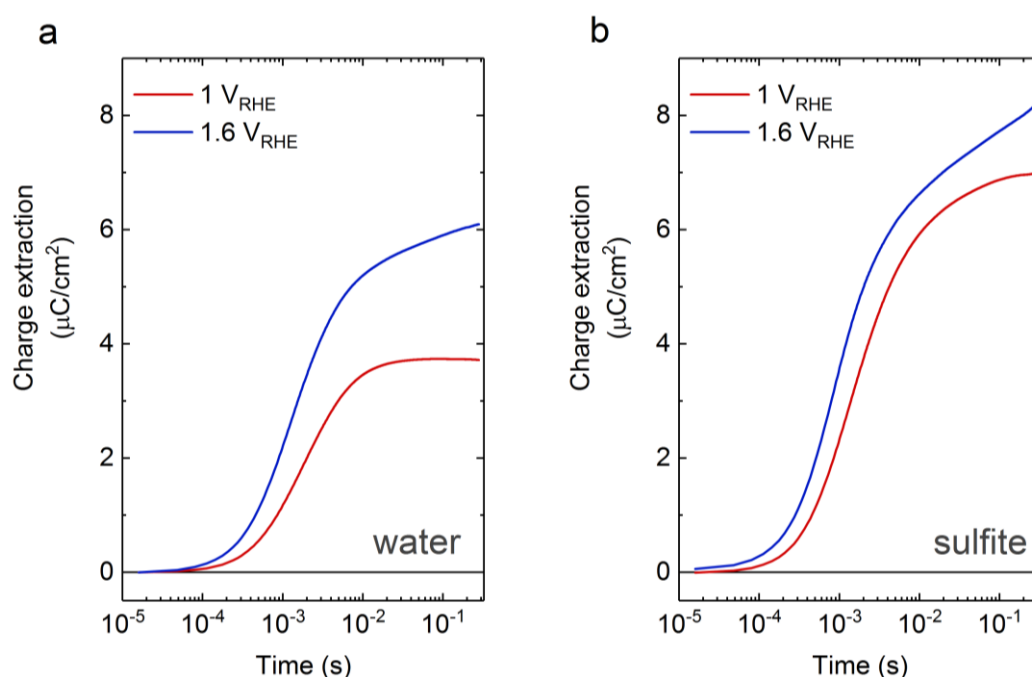


Figure 4.8| Integrated transient photocurrent traces of $\text{WO}_3/\text{BiVO}_4$ photoanodes for water and sulfite oxidation. Traces taken under applied potentials of 1 V_{RHE} and 1.6 V_{RHE} in 0.1M Na_2SO_3 dissolved in a solution of 0.1 M phosphate buffer, λ_{ex} : 355 nm (pump fluence: 500 $\mu\text{J}/\text{cm}^2$), irradiated from the front.

Hole lifetimes are found to improve with increasing anodic bias where the initial TA signal amplitude of the heterojunction is heavily dependent upon the bias applied. At potentials close to the photocurrent onset (0.6 V_{RHE}), the amplitude for holes in the heterojunction at 10 μs is lower than it is for bare BiVO_4 . This may be a result of recombination processes at the junction interface being predominant on the pre- μs timescale, which can be circumvented by increasing the anodic bias applied (and hence the band bending of BiVO_4 at the semiconductor/electrolyte interface) to favour charge separation. Although pre- μs carrier dynamics are not probed in this study, there have been other TAS studies of the charge carrier dynamics on the ultra-fast timescale for this heterojunction in the absence of applied bias.^{116,142,144} Their findings suggest the presence of loss mechanisms due to recombination across the interface of the materials following fast charge transfer to WO_3 .

Previous studies have shown that the typical conduction band positions of WO_3 and BiVO_4 are $+0.41 V_{\text{RHE}}$ and $+0.02 V_{\text{RHE}}$, whilst the valence band positions are expected to be around $+3.18 V_{\text{RHE}}$ and $+2.53 V_{\text{RHE}}$, respectively.⁷⁶ This forms a type II staggered heterojunction as shown in Scheme 1. Hence, there is a thermodynamic driving force for electrons generated in the conduction band of BiVO_4 to transfer to the conduction band of WO_3 . However, the bias dependent nature of the data presented herein show that low to modest bias ($\leq 0.6 V_{\text{RHE}}$) are required for charge separation to occur efficiently. For typical band alignments drawn for n-n type II heterojunctions, where bands are assumed to be pinned at the interface, Fermi level alignment would give rise to the formation of space charge layers at the interface that can hinder charge transfer (*i.e.* Schottky barrier). Therefore, there is scope for finding other combinations of semiconductors with staggered band alignments that can form a more favourable interface that precludes the need for applied bias to enhance charge separation. Furthermore, this should result in an earlier onset of photocurrent. Further studies of the exact nature of the alignment at the interface would shed further light into the need for anodic bias to facilitate charge separation in this system, but is beyond the scope of this study.

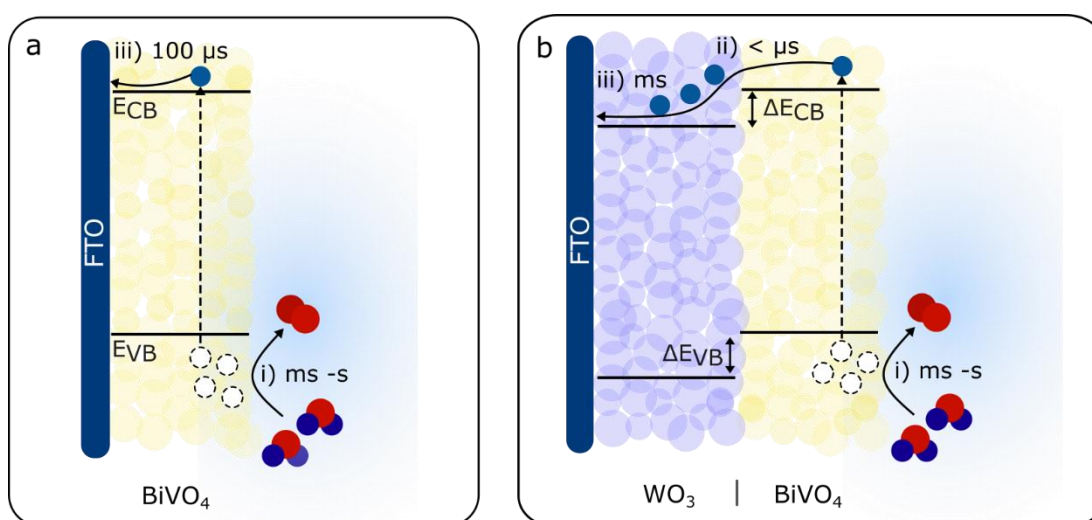


Figure 4.9 | Schematic representation of charge transfer processes in (a) BiVO_4 and (b) $\text{WO}_3/\text{BiVO}_4$. (i) Denotes holes reacting with water to form oxygen, (ii) is the electron transfer from BiVO_4 to WO_3 and (iii) is the electron transfer from the semiconductor to the FTO.

4.6 Conclusion

Overall, the results herein indicate that n-n type heterojunctions increases photocurrent by minimising bimolecular recombination, specifically at timescales that directly compete with water oxidation. As electrons are transferred to WO_3 on the pre-μs timescale, this significantly reduces the proportion of charge that undergo bimolecular recombination compared to bare BiVO_4 , for which charge injection into FTO lies on the ~20-100 μs timescale. On the other hand, slow charge transport

properties of WO_3 can give rise to interfacial recombination observed prior to charge extraction from the heterojunction photoanodes leaving scope for other materials to serve as better electron acceptor layers. The transient absorption studies show that the band alignment present in the $\text{WO}_3/\text{BiVO}_4$ heterojunction does not enhance charge lifetime alone, and requires anodic bias ($\geq 0.6 \text{ V}_{\text{RHE}}$) to increase the lifetime and population of holes that oxidise water on the ms-s timescale. Thus, demonstrating an effective example of how inorganic systems can be used to increase charge carrier lifetime, similar to photosynthetic systems, and compete with the slow kinetics of water oxidation.

Chapter 5 | Water oxidation on nickel/iron oxyhydroxide functionalised BiVO₄ photoanodes

In this chapter, spectroelectrochemical techniques are employed to analyse the catalytic water oxidation performance for a series of three nickel/iron oxyhydroxide electrocatalysts deposited on FTO, under neutral pH conditions. Similar electrochemical water oxidation performance is observed for the FeOOH, Ni(Fe)OOH and FeOOHNiOOH electrocatalysts studied, which is found to result from a balance between charge accumulation and water oxidation kinetics. Once incorporated onto BiVO₄ photoanodes to function as co-catalysts, a large enhancement in the water oxidation photoelectrochemical performance is observed in comparison to the un-modified BiVO₄. To understand the origin of this enhancement, the films were evaluated through time-resolved optical spectroscopic techniques, allowing comparison between the electrochemical and photoelectrochemical water oxidation. For all three catalysts, transient absorption data shows fast hole transfer from BiVO₄ to the catalyst (< 10 μs). This charge transfer is correlated with a suppression of recombination losses which results in remarkably enhanced water oxidation performance relative to un-functionalised BiVO₄.

The majority of the results presented in this chapter are included in the following publications:

“Water oxidation kinetics of mesoporous BiVO₄ photoanodes functionalised by nickel/iron oxyhydroxide electrocatalysts”

(Manuscript in preparation)

“Spectroelectrochemical study of water oxidation on nickel and iron oxyhydroxide electrocatalysts”

Francàs, L., Corby, S., Selim, S. *et al.* Spectroelectrochemical study of water oxidation on nickel and iron oxyhydroxide electrocatalysts. *Nat Commun* **10**, 5208 (2019) DOI: [10.1038/s41467-019-13061-0](https://doi.org/10.1038/s41467-019-13061-0)

5.1 Introduction

Photoelectrodes are often fabricated as mesoporous nanocrystalline films to increase the active surface area which can maximise contact of the semiconductor with the electrolyte to enhance charge transfer at the interface. This has successfully been demonstrated for mesoporous TiO_2 for applications in dye-sensitised solar cells (DSSCs).¹⁴⁸ For photoelectrochemical purposes, higher porosity also affords reduced path lengths for charge diffusion to the surface, *i.e.* photogenerated holes can have a greater access to the surface for water oxidation, which can in theory also reduce bulk recombination losses. This strategy has been proven effective for cauliflower-type structures of $\alpha\text{-Fe}_2\text{O}_3$, grown using atmospheric pressure – chemical vapour deposition (AP-CVD)^{149,150}. As discussed in *chapter 1*, under photoelectrochemical conditions, a long lifetime for photogenerated charges is a prerequisite when electrons or holes are required to drive catalytic processes at the surface. When the redox process is facile, *e.g.*: when charge transfer from semiconductor to electrolyte is fast, such as oxidation of substrates such as sulfite⁵² or methanol,⁹⁰ highly porous photoelectrodes tend to show high performance. However, for slow catalytic processes *e.g.* water oxidation, the same high performance is not always observed.^{52,80,151} As the particle sizes of nanoporous electrodes are often lower than the space-charge layer width, this can prevent the formation of an adequate band bending at the semiconductor/electrolyte interface which can prove to be an obstacle for effective charge separation.¹⁵² Therefore, in the absence of such adequate band bending, for kinetically challenging processes like water oxidation where charge transfer to the electrolyte is slow, the competition between charge transfer and recombination can be a limiting factor for overall photoelectrochemical performance. Several studies have suggested that this limitation of mesoporous photoelectrodes can be mitigated by the addition of a catalyst overlayer, if charge transfer from the semiconductor to the catalyst is faster than competing recombination pathways. This chapter focuses on addressing this kinetic competition for one, particularly high performing series of such electrodes, specifically mesoporous, nanocrystalline BiVO_4 with Fe/Ni oxyhydroxide catalyst overlayers.

Several earth abundant and inexpensive electrocatalysts have garnered extensive attention for water oxidation, such as cobalt based CoPi ,¹⁵³ and Co-Fe Prussian Blue.⁸⁰ In particular metal oxyhydroxide based catalysts such as Ni/FeOOH ^{154,155} have demonstrated excellent water oxidation performance in alkaline media, obtaining currents of 1 mA cm^{-2} at an overpotential of just $\sim 0.2 \text{ V}$.^{156–158} Inadvertent incorporation of Fe into the NiOOH lattice from electrolyte impurities have also been reported to enhance water oxidation performance.^{155,158,159} For this reason, NiOOH samples studied herein will be referred to as Ni(Fe)OOH . Several studies have investigated the catalytic water oxidation performance of Ni/Fe based oxyhydroxide catalysts studied herein. A recent study of Ni(Fe)OOH (low Fe incorporation) and FeOOH/NiOOH dual-layer electrocatalysts published by our group, have revealed

that the nature of species that accumulate under catalytic conditions to drive water oxidation at pH 13 are different in the two catalysts and is dependent upon the Fe content of the NiOOH.⁸⁴ Spectroelectrochemical data indicated that at low Fe contents, the accumulated species are most likely centred on Ni, whereas under high Fe contents present in the FeOOHNiOOH dual-layer catalyst, the species are more Fe dominant, and similar to that observed in FeOOH. This is consistent with previous reports of the performance of NiOOH catalysts being dependent upon the Fe content.^{154,160,161} However as these electrocatalysts exhibit their optimal performance under alkaline conditions, studies of water oxidation under neutral conditions is less readily available. As a result, the understanding of catalytic properties when they are incorporated onto BiVO₄ photoanodes, which operate under (near) neutral conditions for stability reasons, is limited.

Although the deposition of catalyst overlayers (referred to as co-catalysts from hereon in) on photoelectrodes have often demonstrated higher photoelectrochemical performance for oxidation in comparison to their undecorated photoelectrode counterparts,^{52,53,56,80} the origin of this enhancement is often unclear. Whilst such co-catalyst deposition has often been suggested to enhance water oxidation kinetics, where charges transferred to the catalyst drives the catalysis,^{52,56} detailed kinetic studies have shown that this performance enhancement can also arise from a myriad of factors. Co-catalyst overlayers can also lead to retarded recombination losses caused by favourable electric fields generated at the semiconductor/catalyst junction,^{78,79,162} as well as passivate surface defects which act as recombination centres.^{78,163} Distinguishing between these processes is not trivial however, which can often introduce difficulties in identifying the origin of performance enhancement.

Ni /Fe oxyhydroxide (referred to herein as MOOH, where M = Ni/Fe) electrocatalysts when coupled with mesoporous, nanocrystalline BiVO₄ exhibits photocurrents that ranks amongst the highest performing BiVO₄ photoanodes reported.^{52,53,56} Comparisons between BiVO₄/Ni(Fe)OOH and BiVO₄/FeOOH showed that the photoelectrode with FeOOH exhibits higher photocurrents in spite of NiOOH being reported as the more-active water oxidation electrocatalyst.^{52,161} This is attributed to FeOOH forming a better interface for charge transfer with BiVO₄ than NiOOH, and as such, the dual-layer catalyst BiVO₄/FeOOHNiOOH outperforms both FeOOH and NiOOH.⁵² Although the higher water photoelectrochemical performance is often attributed to faster water oxidation kinetics by the catalyst layers for these systems, studies directly comparing the electrochemical and photoelectrochemical catalysis by the MOOH and BiVO₄/MOOH systems under near-neutral conditions is scarce in literature, and therefore the origin of the enhancement remains unclear. To address this key issue, herein, transient optical and spectroelectrochemical techniques are utilised to compare the water oxidation and recombination kinetics of a series of Ni/Fe oxyhydroxide water

oxidation catalysts when used either as electrocatalysts or when functionalised on BiVO₄ photoanodes, under neutral electrolyte conditions.

5.2 In this chapter

In this chapter, using time-resolved and steady-state optical spectroscopy, key processes are probed to address: (i) the timescale of electrochemical water oxidation by MOOH catalysts at neutral pH, (ii) if charge transfer takes place from BiVO₄ to the MOOH electrocatalyst, and what timescale this occurs at and (iii) if the MOOH catalyst layer on BiVO₄ performs the water oxidation reaction in preference to the BiVO₄ surface in BiVO₄/MOOH photoanodes. The chapter is concluded by comparing between the performance of the electrocatalysts under neutral pH (optimal for BiVO₄) and alkaline pH (the optimal pH for electrocatalytic performance of these MOOH catalysts).

5.3 Experimental methods

All samples studied in this chapter were prepared and kindly provided by the group of Prof Kyoung-Shin Choi (University of Wisconsin-Madison, USA). The detailed experimental methods for sample preparation and characterisation information are outlined in *chapter 2*. Briefly, the electrocatalyst films were deposited on FTO using anodic deposition as reported previously.⁸⁴ The obtained thicknesses of the FeOOH, Ni(Fe)OOH and FeOOHNiOOH electrocatalyst films deposited on FTO were ~80 nm, ~80 nm and ~120 nm respectively (as determined by SEM⁸⁴). The latter was prepared using sequential deposition of FeOOH and NiOOH layers, with NiOOH being the top layer. The nanoporous BiVO₄ photoanodes employed herein were 450-500 nm thick. When each catalyst was deposited onto BiVO₄, the thickness of the catalyst layers were determined to be approximately ~8-10 nm. All presented studies of Ni(Fe)OOH and FeOOHNiOOH and their photoanode counterparts were obtained after the *in situ* regeneration of NiOOH from Ni(OH)₂, using an activation procedure, as the latter forms over time when the electrodes are not in use. Samples were activated using five consecutive linear sweep voltammetry (LSV) scans from the open-circuit potential to 2 V_{RHE}, which restored the grey colour of the films. The optical change in the spectra following NiOOH generation is shown in *Figure 5.1a*. This activation process generates the precatalytic species, termed MOOH(+) from hereon in, shown in *Figure 5.1a*, and is in accordance with previous reports.^{161,164,165}

It is noted that Dr. Laia Francas (Imperial College London) and Dr. Sacha Corby (Imperial College London) contributed to obtaining the experimental data for the chapter. Sample preparations and characterisation (SEM analysis) were conducted by the group of Professor Kyoung-Shin Choi (University of Wisconsin-Madison, USA).

5.4 Results

5.4.1 Electrocatalytic properties of Ni/Fe oxyhydroxide catalysts

Before studying the origin of the enhanced performance of BiVO_4 photoanodes when surface decorated with MOOH based catalysts (FeOOH , FeOOHNiOOH and Ni(Fe)OOH), the optical and kinetic characteristics of the electrocatalysts were first studied electrochemically on FTO. Comparison of the electrochemical performance of these electrocatalysts under pH 7 and 13 is also discussed later.

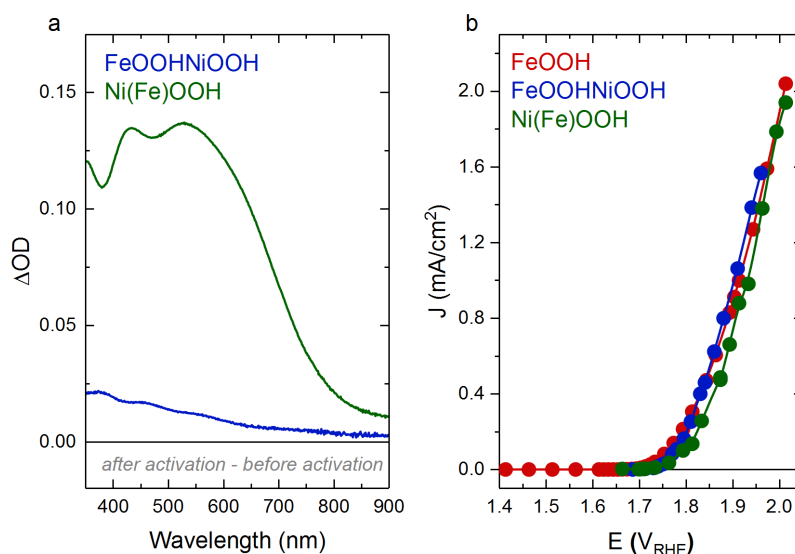


Figure 5.1 | Electrochemical performance of FeOOH , FeOOHNiOOH and Ni(Fe)OOH catalysts. (a) The difference UV-Vis absorbance spectra ($\text{OD}_{\text{After activation}} - \text{OD}_{\text{Before activation}}$) of FeOOHNiOOH and Ni(Fe)OOH catalysts, showing the spectra of the MOOH(+) species generated after sample activation. The change in the optical spectrum upon activation for FeOOH was negligible, therefore it is not included here. (b) The steady-state $J - V$ curves of the electrocatalysts. All measurements were taken in 0.1 M phosphate buffer (pH 7). The steady-state currents were obtained at different applied potentials under atmospheric conditions. The FeOOH and Ni(Fe)OOH films were ~ 80 nm thick, and the FeOOHNiOOH film was ~ 120 nm thick.

As mentioned in *section 5.3*, the electrocatalyst samples containing Ni requires an oxidative activation process, to convert Ni(OH)_2 to NiOOH for both Ni(Fe)OOH and FeOOHNiOOH . Following sample activation, the steady-state currents under operational conditions are shown in *Figure 5.1b*, from which it can be seen that all three electrocatalysts exhibit similar electrocatalytic performance under neutral conditions. However, the similar overall performance under pH 7 differs from that observed under alkaline media (pH 13), where the catalytic onset potential for FeOOH is positively shifted by ~ 70 mV compared with Ni(Fe)OOH and FeOOHNiOOH .⁸⁴

In spectroelectrochemical (SEC) measurements, when potentials greater than the catalytic onset are applied, corresponding to electrocatalytic water oxidation conditions, the growth of new spectral

features can be observed for each of the catalysts, as shown in *Figure 5.2*. These spectral features are assigned to the generation of oxidised states that accumulate under water oxidation catalysis, referred to as MOOH(++) from hereon in. As can be observed in *Figure 5.2a* and *b*, the spectra of the FeOOH(++) and the FeOOHNiOOH(++) species are almost indistinguishable, with an absorption maximum at 400 – 425 nm, suggestive of the similar nature of these oxidised states. In contrast, the Ni(Fe)OOH(++) species shown in *Figure 5.2c* exhibits a peak centred at ~650 nm, indicative of a different nature of oxidised state that forms in Ni(Fe)OOH catalysts under water oxidation conditions. A similar trend for the respective spectral features of MOOH(+) and MOOH(++) species of these three catalysts, is also present at pH 13.⁸⁴ It is worth noting that the Ni(Fe)OOH samples were found to be relatively unstable when potentials greater than 2 V_{RHE} were applied, leading to a loss in optical signal and performance (see *section A.8* in *appendix*). This has previously been associated with the formation of NiO₂, which is less conductive and leads to a loss in performance.¹⁶⁶

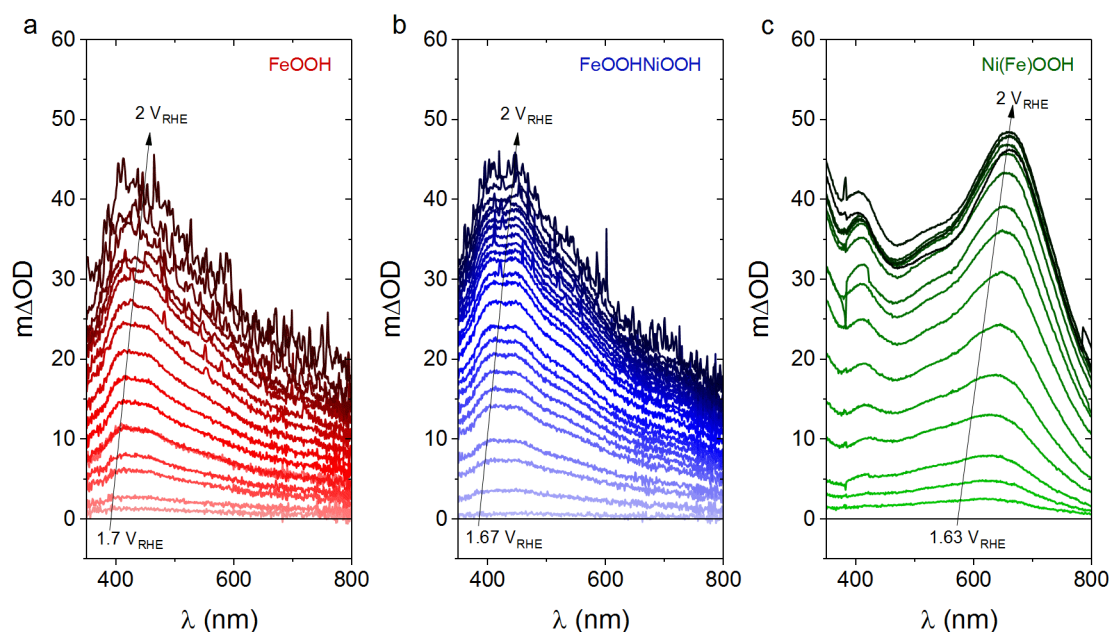


Figure 5.2 | Difference UV-Vis absorption spectra showing the spectra of the MOOH(++) species of the electrocatalysts obtained under electrochemical water oxidation conditions at different applied potentials. The spectra were subtracted from corresponding spectrum at the catalytic onset potential for each catalyst: (a) FeOOH (V_{onset} : 1.68 V_{RHE}), (b) FeOOHNiOOH (V_{onset} : 1.66 V_{RHE}) and (c) Ni(Fe)OOH (V_{onset} : 1.61 V_{RHE}). All spectra were taken in 0.1 M phosphate buffer (pH 7).

To allow quantitative comparison of the oxidation of these electrocatalysts and the associated water oxidation kinetics, the extinction coefficients (ϵ) of the (++) oxidised species for each of the catalysts were estimated using step-potential spectroelectrochemistry (SP-SEC), shown in *Figure 5.3* (see *chapter 2, section 2.8.1* for description of the method). Extinction coefficient (ϵ) values of 3500 and 3100 M⁻¹ cm⁻¹ were obtained at wavelengths of 550 nm for FeOOH and FeOOHNiOOH, and a value of

$3100 \text{ M}^{-1} \text{ cm}^{-1}$ was obtained at 650 nm for Ni(Fe)OOH. Using the estimated values of ϵ for each of the samples, the optical signal (ΔOD) shown in *Figure 5.2* can be correlated with the concentration of accumulated MOOH(++) species as a function of applied potential. When combined with current densities, these data yield kinetic information on the water oxidation process, allowing the estimation of reaction time (τ) or turn over frequency (TOF) for O_2 generation, as a function of MOOH(++) species. These analyses have been described in *section 2.9, chapter 2* and has been reported previously.⁸⁴ The water oxidation kinetic data are plotted as a function of MOOH(++) accumulated species (*Figure 5.4a*) and also as a function of applied potential (*Figure 5.4b*).

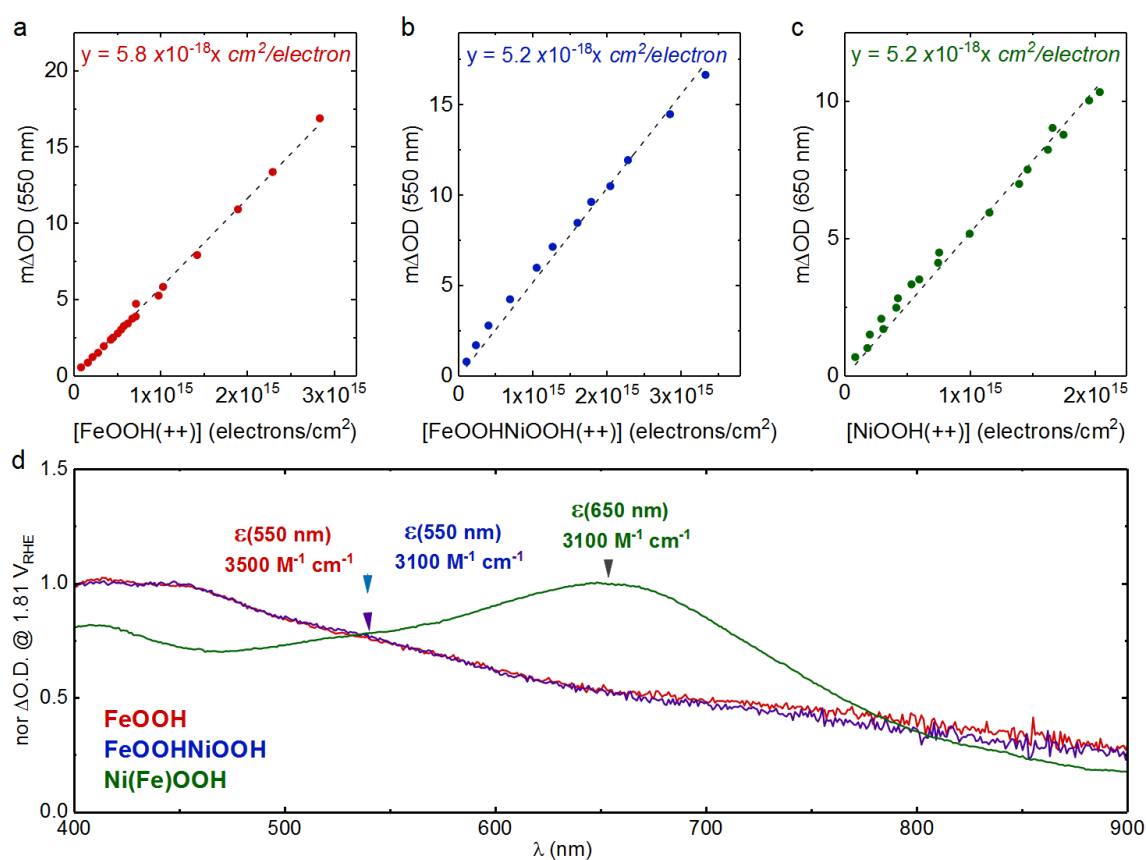


Figure 5. 3 | Estimation of the extinction coefficients of the MOOH(++) species for the catalysts. The extinction coefficients were estimated using the method outlined in *chapter 2, section 2.8.1*, obtained under electrochemical water oxidation conditions. The onset potential used for each catalysts were: (a) FeOOH (V_{onset} : $1.71 \text{ V}_{\text{RHE}}$), (b) FeOOHNiOOH (V_{onset} : $1.61 \text{ V}_{\text{RHE}}$) and (c) Ni(Fe)OOH (V_{onset} : $1.68 \text{ V}_{\text{RHE}}$). (d) The estimated extinction coefficients are shown for each catalyst at the wavelength at which they were determined. All measurements were taken in 0.1 M phosphate buffer (pH 7). Same colours used in (a), (b), (c) and (d).

As can be observed in *Figure 5.4a* (empty circles, bottom panel), the concentration of the MOOH(++) species increases with the applied potential for each of the catalysts, resulting in an acceleration of the water oxidation time constant by two orders of magnitude (solid circles, top panel). For a given

potential, it is also observed that Ni(Fe)OOH accumulates more MOOH(++) species than FeOOH and FeOOHNiOOH. Whilst it is apparent that both FeOOH and FeOOHNiOOH exhibit similar reaction time constants, Ni(Fe)OOH(++) states oxidise water ~an order of magnitude more slowly, when compared at equivalent concentrations of MOOH(++) species. The slower water oxidation kinetics of Ni(Fe)OOH(++) is also reflected in the plot of TOF (s^{-1}) vs applied potential (*Figure 5.4b*) which shows that at a given potential, FeOOH(++) and FeOOHNiOOH(++) both oxidise water at a similar rate, whereas the TOF (s^{-1}) for Ni(Fe)OOH(++) is approximately halved. Overall, while Ni(Fe)OOH(++) is able to accumulate a greater concentration of MOOH(++) species than FeOOH and FeOOHNiOOH, this is offset by the slower water oxidation kinetics. This manifests as an overall, similar electrocatalytic performance for water oxidation of all three electrocatalysts, as shown in *Figure 5.1b*. These trends are markedly different to those observed under pH 13 where Ni(Fe)OOH shows the fastest water oxidation kinetics amongst the three, and accumulates fewer Ni(Fe)OOH(++) species under catalytic conditions. These differences can arise from different mechanisms of oxygen evolution reactions operating under different pH conditions, as discussed further in *section 5.5* below.^{154,160,164,166–168}

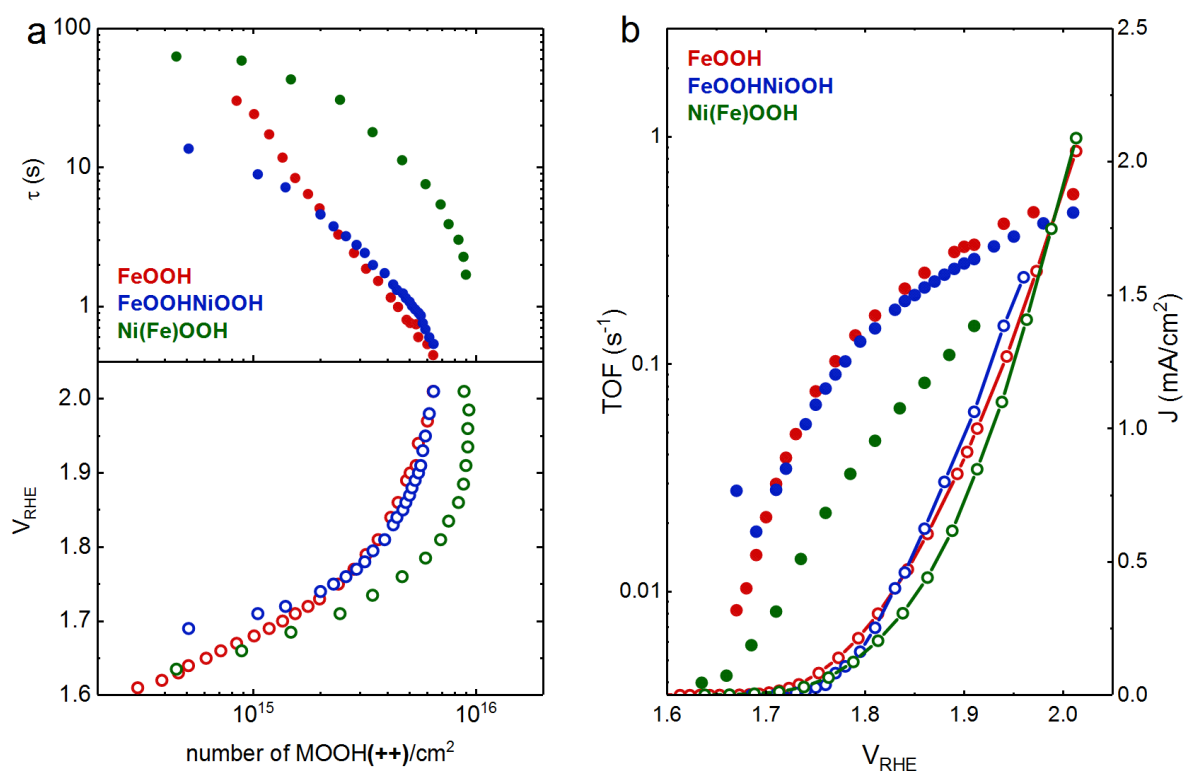


Figure 5.4 | Kinetics of water oxidation of the electrocatalysts under electrochemical conditions. (a) Water oxidation reaction time constants (τ , solid circles, top panel) and the applied potential (bottom panel) plotted against the number of accumulated MOOH(++) species. (b) The TOF for O₂ generation (solid circles, left axis) against the applied potential plotted together with the current density (open circles, right axis). Same colours used in (a) and (b). All measurements were taken in 0.1 M phosphate buffer (pH 7). TOF and Tau were estimated using *equations 2.15* and *2.16*.

5.4.2 Photoelectrochemical water oxidation of Ni/Fe oxyhydroxide functionalised BiVO₄ photoanodes

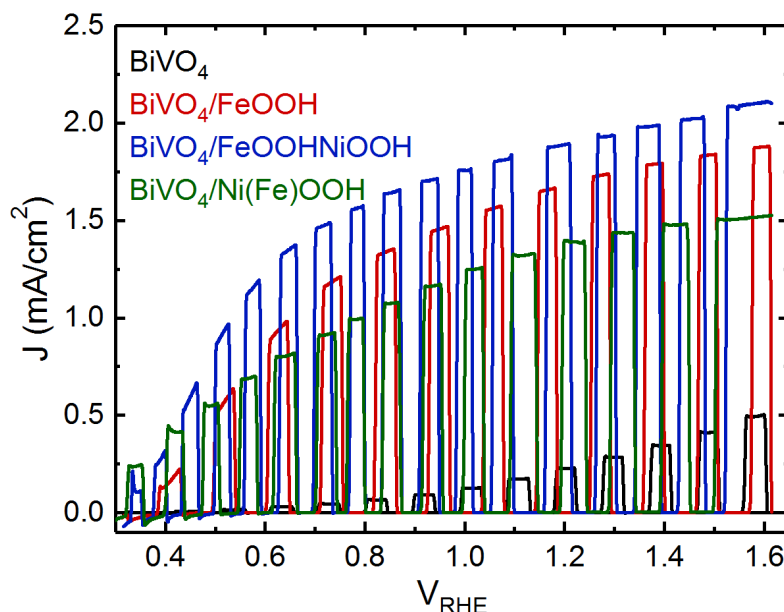


Figure 5.5|Photoelectrochemical performance of BiVO₄ and catalyst functionalised BiVO₄ photoanodes. Linear sweep voltammetry (LSV) under chopped light (1 sun equivalent, illuminated with 365 nm LED, back irradiation). All LSVs were recorded using a scan rate of 10 mV/s, in 0.1 M phosphate buffer (pH 7).

When the FeOOH, FeOOHNiOOH and Ni(Fe)OOH electrocatalysts are deposited on nanoporous BiVO₄ electrodes, a significant enhancement in the photoelectrochemical water oxidation performance is observed for the BiVO₄/MOOH photoanodes in comparison to the un-modified BiVO₄ counterpart. Analogous enhancements in other semiconductor / co-catalyst photoanodes have often been attributed to improved water oxidation kinetics due to faster kinetics of water oxidation by the catalyst layer.⁵² The poor performance of the un-modified mesoporous BiVO₄ typically results from poor charge separation and high charge recombination losses as discussed in *section 5.1* and often attributed to poor water oxidation catalysis on the BiVO₄ surface.^{31,52} The enhancement observed herein is consistent with that reported previously for this BiVO₄ / MOOH combination^{52,56} and is much greater than that typically found when electrocatalysts (e.g. CoPi) are deposited on dense planar BiVO₄ electrodes.^{78,79} Despite the similar electrochemical performance shown in *Figure 5.1b*, when these three electrocatalysts are deposited on BiVO₄ photoanodes, the same trend is not reflected in their photoelectrochemical performance (shown in *Figure 5.5*). The MOOH decorated BiVO₄ photoanodes exhibits the best photocurrents in the order: BiVO₄/FeOOHNiOOH, followed by BiVO₄/FeOOH and BiVO₄/Ni(Fe)OOH. The lower performance of the BiVO₄/Ni(Fe)OOH photoanode, compared to its counterparts could result from the slower water oxidation kinetics of the Ni(Fe)OOH(++) species, as

discussed in section 5.4.1. However, the difference in performance of the $\text{BiVO}_4/\text{FeOOH}$ and the $\text{BiVO}_4/\text{FeOOHNiOOH}$ photoanodes is surprising, since electrocatalytically, the two electrocatalysts exhibit similar currents. In order to unravel the origin of the enhancement in photoelectrochemical water oxidation performance upon the incorporation of MOOH catalysts onto BiVO_4 , two different time-resolved optical and electrochemical techniques are employed: transient absorption spectroscopy (TAS) and spectroelectrochemical photo-induced absorption spectroscopy (SEC-PIAS).

5.4.3 Charge transfer in $\text{BiVO}_4/\text{MOOH}$ photoanodes

As discussed in previous chapters, TAS can be employed to determine the fate of the photogenerated charge generated, and has been employed herein to investigate if charge transfer occurs following bandgap excitation of BiVO_4 , under an applied potential of $1.4 V_{\text{RHE}}$. Figure 5.6 presents the TAS spectra for BiVO_4 (a), $\text{BiVO}_4/\text{Ni(Fe)OOH}$ (b), $\text{BiVO}_4/\text{FeOOH}$ (c) and $\text{BiVO}_4/\text{FeOOHNiOOH}$ (d). The data for BiVO_4 (Figure 5.6a) are similar to that reported previously, and are associated with holes accumulated at the surface. The optical signal observed at shorter wavelengths (~ 460 nm) across all BiVO_4 and $\text{BiVO}_4/\text{MOOH}$ photoanodes presented in Figure 5.6, is dominated by the transient bleach and is indicative of electron trapping in oxygen vacancies as discussed previously in chapter 3, and reported previously.¹⁶⁹ As electrons from the conduction band trap into the oxidised oxygen vacancy states (V_{OV}^{5+}), this manifests as a transient bleach for all the combinations of BiVO_4 and $\text{BiVO}_4/\text{MOOH}$ studied herein. The recovery of the bleach in the optical signal is concomitant with the electron extraction from the photoanodes (as previously shown in Figure 3.10), upon which the optical signal for BiVO_4 holes or $\text{MOOH}(++)$ species can be observed.

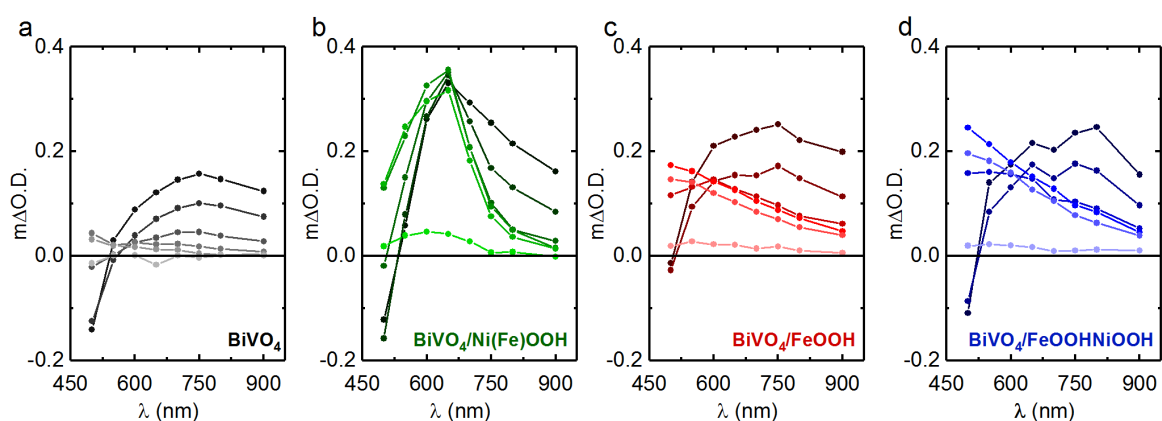


Figure 5.6 | Transient absorption spectra of BiVO_4 and catalyst functionalised BiVO_4 photoanodes. Spectra shown for (a) BiVO_4 , (b) $\text{BiVO}_4/\text{Ni(Fe)OOH}$, (c) $\text{BiVO}_4/\text{FeOOH}$ and (d) $\text{BiVO}_4/\text{FeOOHNiOOH}$. The dark to light colours represent spectra at $10 \mu\text{s} - 100 \mu\text{s} - 1 \text{ms} - 10 \text{ms} - 100 \text{ms} - 1 \text{s}$. All spectra were recorded at an applied potential of $1.4 V_{\text{RHE}}$ using 355 nm excitation ($300 \mu\text{J}/\text{cm}^2$), in 0.1 M phosphate buffer ($\text{pH } 7$).

In the case of $\text{BiVO}_4/\text{Ni(Fe)OOH}$ (Figure 5.6b), a peak at 650 nm can be observed on the 10 μs TA spectrum onwards, which is reminiscent of the Ni(Fe)OOH(++) species observed under electrocatalytic conditions shown in Figure 5.2c. The similarity of the spectral feature at 650 nm, obtained for the Ni(Fe)OOH electrocatalyst samples and the $\text{BiVO}_4/\text{Ni(Fe)OOH}$ photoanodes upon photoexcitation suggests that both electrical and optical oxidation (via BiVO_4) generates similar Ni(Fe)OOH(++) species. The observation of this spectral feature in the spectrum obtained at 10 μs is indicative of fast hole transfer from BiVO_4 to the MOOH catalyst, that occurs within the time resolution of the measurements ($< 10 \mu\text{s}$). The spectral shape in Figure 5.6b is clearly distinct from un-modified BiVO_4 (Figure 5.6a), at all timescales, indicating that holes predominantly reside in the Ni(Fe)OOH catalyst layer over the timescales studied herein. Comparison of the kinetic traces presented in Figure 5.7, shows that Ni(Fe)OOH(++) species have a much longer lifetime than the holes in BiVO_4 . Following hole transfer from BiVO_4 to the Ni(Fe)OOH layer, the accumulated Ni(Fe)OOH(++) species are spatially separated from photogenerated electrons in BiVO_4 and are thus prevented from recombination, unlike un-modified BiVO_4 . Analogous conclusions can be drawn for the cases of $\text{BiVO}_4/\text{FeOOH}$ and $\text{BiVO}_4/\text{FeOOHNiOOH}$, where the spectral profiles of MOOH(++) species are also observed in the TA spectra (millisecond onwards), although it is less clear than the case of $\text{BiVO}_4/\text{Ni(Fe)OOH}$, due to the similarity in the spectral signature of holes in BiVO_4 and MOOH(++) species in the FeOOH and FeOOHNiOOH within the probed region. In addition, the optical signature of MOOH(++) species for FeOOH and FeOOHNiOOH at early timescales also overlaps with the transient bleach observed (μs – ms) due to electron trapping, further obscuring the detection of charge transfer at early timescales for these two cases. Nonetheless, all three catalysts functionalised samples exhibit much longer lived signals than BiVO_4 alone (as seen in the TA spectra in Figure 5.6), indicative of catalyst deposition resulting in a substantial extension of the lifetime of photogenerated charges.

At early timescales (between 10 μs and 1 ms), an absorption tail at longer wavelengths ($\sim 700 - 900$ nm) is present in all samples (Figure 5.6). As this spectral signal is also present in the un-modified BiVO_4 photoanode, it can be indicative of photogenerated charges within BiVO_4 . In the case of the catalyst modified samples ($\text{BiVO}_4/\text{MOOH}$), this tail absorption decays by ~ 1 ms without any significant concomitant change in the signal observed for the MOOH(++) species, most clearly visible for the case of $\text{BiVO}_4/\text{Ni(Fe)OOH}$ (Figure 5.6b). Since the extinction coefficient of the MOOH(++) species are $\sim 7-8$ times larger than the hole extinction coefficient of BiVO_4 ($420 \text{ M}^{-1} \text{ cm}^{-1}$)⁷⁹, any further hole transfer from BiVO_4 to the catalyst layer within 10 μs and 1 ms would be expected to give rise to a much larger signal observed for the MOOH(++) species. Since no increase in signal is observed, this may be indicative of recombination of photogenerated species in BiVO_4 that have not transferred to the catalyst layer by $\sim 10 \mu\text{s}$.

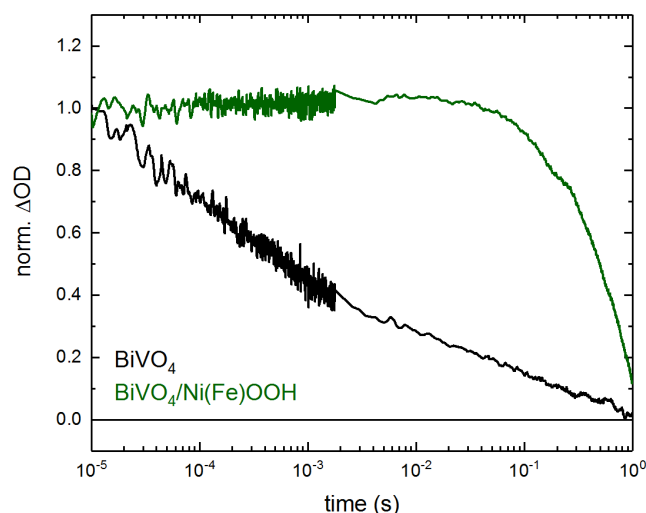


Figure 5.7 | Normalised transient absorption kinetics of BiVO_4 (550 nm, h^+) and $\text{BiVO}_4/\text{Ni(Fe)OOH}$ (650 nm, $\text{MOOH}(++)$). Kinetics were recorded at an applied potential of 1.4 V_{RHE} using 355 nm excitation ($300 \mu\text{J}/\text{cm}^2$), in 0.1 M phosphate buffer (pH 7).

As discussed previously, it is intriguing that the FeOOHNiOOH functionalised BiVO_4 photoanode performs better than the FeOOH counterpart, despite exhibiting almost identical kinetics for water oxidation under electrocatalytic conditions. From the TA spectra, it appears that the signal amplitude for $\text{BiVO}_4/\text{FeOOHNiOOH}$ is larger than it is for $\text{BiVO}_4/\text{FeOOH}$. Taking the respective extinction coefficients of the $\text{MOOH}(++)$ species into consideration, this would indicate that a greater amount of holes successfully transfer from BiVO_4 to FeOOHNiOOH in comparison to FeOOH . This could potentially be due to a more favourable interface for charge transfer between the co-catalyst and BiVO_4 in presence of NiOOH for the mixed co-catalyst, although a deeper understanding of the interface is beyond the scope of the spectroscopic measurements obtained herein.

To examine the photoelectrochemical processes under steady state conditions, spectroelectrochemical photoinduced absorption spectroscopy (SEC-PIAS) was employed. Unfortunately, instability of $\text{BiVO}_4/\text{Ni(Fe)OOH}$ samples under oxidative conditions over prolonged periods of time required for SEC-PIAS measurements, precludes them from these analyses. The normalised SEC-PIAS spectra of BiVO_4 , $\text{BiVO}_4/\text{FeOOH}$ and $\text{BiVO}_4/\text{FeOOHNiOOH}$ under an applied potential of 1.4 V_{RHE} are shown in *Figure 5.8*, along with the normalised spectra of the respective $\text{MOOH}(++)$ species obtained under electrochemical conditions. The resemblance of the spectral shapes indicate that similar species accumulate under the two catalytic conditions, which in conjunction with the TAS data (*Figure 5.6*), further confirms that photoexcitation of BiVO_4 leads to the oxidation of the catalyst, also under steady-state PEC conditions.

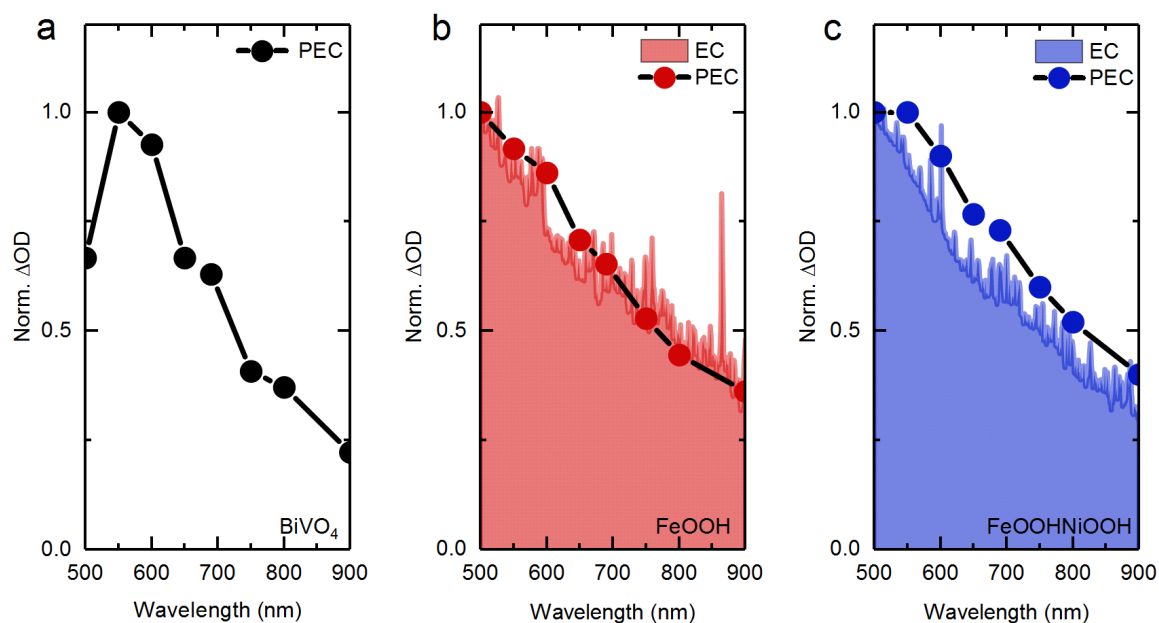


Figure 5.8|Comparison of normalised spectra of MOOH(++) species under electrochemical and photoelectrochemical conditions. (a) The SEC-PIAS spectrum of BiVO_4 . (b) The SEC spectrum of FeOOH electrocatalyst (red, shaded) and the SEC-PIAS spectrum of $\text{BiVO}_4/\text{FeOOH}$ (solid red circle, black line). (c) The SEC spectrum of FeOOHNiOOH electrocatalyst (blue, shaded) and the SEC-PIAS spectrum of $\text{BiVO}_4/\text{FeOOHNiOOH}$ (solid blue circle, black line). All SEC spectra under electrochemical conditions were obtained under an applied potential of $2 V_{\text{RHE}}$, and all SEC-PIAS were obtained under 1 sun equivalent illumination (365 nm LED) under $1.4 V_{\text{RHE}}$. All measurements were taken in 0.1 M phosphate buffer (pH 7).

Under steady-state conditions, the photoelectrochemical performance of BiVO_4 and $\text{BiVO}_4/\text{MOOH}$ photoelectrodes can be compared with the electrochemical performance of the MOOH electrocatalysts using SEC-PIAS and SP-SEC, respectively. The optical signals obtained through SEC-PIAS and SP-SEC for the photoanodes and electrocatalyst electrodes, under catalytic conditions, were converted to the amount of oxidising equivalents for water oxidation, *i.e.* holes in BiVO_4 and MOOH(++) species in the case of the catalysts. This is based upon the assumption that under steady-state conditions, holes are transferred from BiVO_4 to the catalyst layer, thus generating MOOH(++) species in the $\text{BiVO}_4/\text{MOOH}$ photoanodes (as indicated by the SEC-PIAS spectra shown in *Figure 5.8*). By relating the optical signal to the concomitant current transient signals, kinetic information associated with the water oxidation reaction were determined using equation 2.14 (kinetic analysis description is outlined in *section 2.9, chapter 2*).

Firstly, from *Figure 5.9a*, it is observed that whilst photogenerated holes in BiVO_4 follow a reaction order (β) of 3 for water oxidation, consistent with previous reports,^{23,92} both FeOOH and FeOOHNiOOH operate with a β of ~ 2 under both photoelectrochemical and electrochemical conditions at pH 7. A reaction order of ~ 2 for these electrocatalysts differ from that observed under alkaline conditions (β

~ 4 at pH 13),⁸⁴ and is discussed further later. Differences in β between BiVO_4 and $\text{BiVO}_4/\text{MOOH}$ photoanodes indicate differences in reaction mechanism between water oxidation driven directly by photogenerated holes in BiVO_4 and by $\text{MOOH}(++)$ species in the catalyst layer. In addition, similar reaction orders obtained for the MOOH electrocatalysts and the photoanodes functionalised with the electrocatalysts further indicates that water oxidation predominantly takes place via $\text{MOOH}(++)$ states in the $\text{BiVO}_4/\text{MOOH}$ photoanodes studied herein, which are generated following hole transfer from BiVO_4 . This is also in agreement with the observation that hole transfer from BiVO_4 to the catalyst is relatively fast ($< \mu\text{s}$) as seen in the TAS spectra (*Figure 5.6*). The differences in the number of $\text{MOOH}(++)$ species accumulated under photoelectrochemical and electrochemical conditions could result from a range of influencing factors to draw meaningful comparisons. For instance, differences in surface roughness of the electrocatalyst electrodes and photoelectrodes can lead to deviations in the estimated number of $\text{MOOH}(++)/\text{cm}^2$ per geometric area and when corrected for the real surface area. To determine the actual surface area however, further experiments would be required to determine the roughness factors of the respective electrodes. Furthermore the differing thickness of the electrocatalysts deposited on FTO (~ 80 nm) and on BiVO_4 (~ 8 -10 nm) may result in the formation of some unreactive $\text{MOOH}(++)$ in the bulk of the MOOH/FTO samples, resulting in deviations in the amount of $\text{MOOH}(++)$ observed under PEC conditions. Accounting for all the aforementioned factors is not trivial, however the agreement in the density of $\text{MOOH}(++)$ species observed under EC and PEC conditions (within an order of magnitude) can be considered to be within experimental error.

Secondly, *Figure 5.9b* compares the time constants (τ) for water oxidation under PEC and EC conditions by BiVO_4 and the catalyst, which reveals that under an equivalent number of oxidising equivalents, PEC water oxidation for these systems is an order of magnitude faster than EC water oxidation. Although the density of $\text{MOOH}(++)$ species observed under electrocatalytic conditions and the resulting estimations of τ may well be an overestimate for the aforementioned reasons, the τ values calculated for the PEC systems suggest that water oxidation occurs on a similar timescale on BiVO_4 and on the electrocatalysts. Therefore no significant advantage in the kinetics of water oxidation is gained by depositing the FeOOH and $\text{FeOOH}/\text{NiOOH}$ catalysts studied herein. However, these results indicate that these systems benefit from fast charge transfer from BiVO_4 to the catalyst layer, thereby minimising recombination losses.

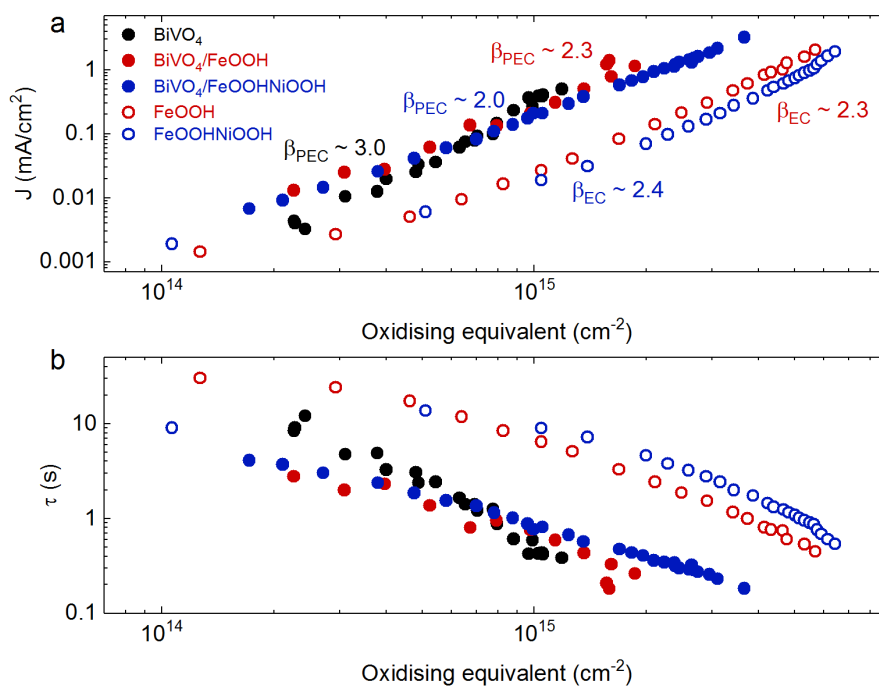


Figure 5.9 | Comparison of kinetics under electrochemical and photoelectrochemical conditions. (a) The density of oxidising equivalents (h^+ for BiVO_4 , or $\text{MOOH}(++)$ species for catalysts) under catalytic conditions against the photocurrent obtained. The reaction orders (β) for the respective electrochemical and photoelectrochemical water oxidation reactions are also shown (determined from the slope). (b) The density of oxidising equivalents plotted against the water reaction time constants (τ) under (photo)electrochemical conditions. Same colours used in (a) and (b). All measurements were taken in 0.1 M phosphate buffer. The reported extinction coefficient of $420 \text{ M}^{-1} \text{ cm}^{-1}$ was used for holes in BiVO_4 ⁷⁹ and the values of $3500 \text{ M}^{-1} \text{ cm}^{-1}$ and $3100 \text{ M}^{-1} \text{ cm}^{-1}$ were used for $\text{MOOH}(++)$ species in FeOOH and FeOOHNiOOH , respectively (as estimated in Figure 5.3).

5.5 Discussion

The electrocatalysts explored in this chapter are studied under neutral conditions as they are the conditions under which BiVO_4 is considered stable. Overall, it is observed that all three electrocatalysts exhibit similar electrochemical water oxidation performance, which is governed by the accumulation of charge in the catalyst and the kinetics by which they react. When deposited on mesoporous BiVO_4 electrodes to function as co-catalysts, they induce remarkable enhancement in the PEC water oxidation performance of the BiVO_4 photoanodes.

The spectroscopic signatures of the $\text{MOOH}(++)$ species detected for the FeOOH , FeOOHNiOOH and Ni(Fe)OOH catalysts under electrochemical water oxidation conditions are analogous to those detected under pH 13 (where they exhibit their optimum performance).⁸⁴ Comparisons of rate law analyses shown in Figure 5.9 at pH 7 with that reported previously⁸⁴ for the same set of electrocatalysts at pH 13 indicate differences in reaction mechanism when operating under the two electrolyte pH conditions. At pH 13, reaction orders (β) of 4 are observed – meaning four equivalents

of MOOH(++) species accumulate under steady state conditions to overcome the rate-limiting step (RLS) of the catalytic cycle, which then proceed to undergo water oxidation and liberate O₂.⁸⁴ In contrast, a β of 2 is detected for both FeOOH and FeOOHNiOOH under neutral conditions (*Figure 5.9a*). In addition, the trends in behaviour between the catalysts also differ considerably, for instance, under pH 7 the activity of the electrocatalysts (measured by TOF (s⁻¹)) follows the order FeOOH ~ FeOOHNiOOH > Ni(Fe)OOH, whereas this doesn't hold true under pH 13 where FeOOH displays the lowest activity of the three electrocatalysts. This is also observed in the J – V curves in *Figures 5.10a* and *b*. A comparison of the reaction time constant (τ) for the same electrocatalysts under pH 7 and pH 13 are shown in *Figure 5.10c* and *d*. At pH 13, Ni(Fe)OOH exhibits the fastest kinetics of the three - in stark contrast to pH 7, but is limited by the lower number of MOOH(++) species it is able to accumulate at any given potential in comparison to the other two electrocatalysts.⁸⁴ This pH dependence of catalyst activity is also consistent with previous reports, *i.e.* deprotonation of Ni(Fe)OOH is often considered to play a crucial role in the activity towards water oxidation.^{166,167} Therefore, reactivity of catalysts under different pH conditions must be considered when they are incorporated on photoelectrodes that are limited by the pH in which they operate.

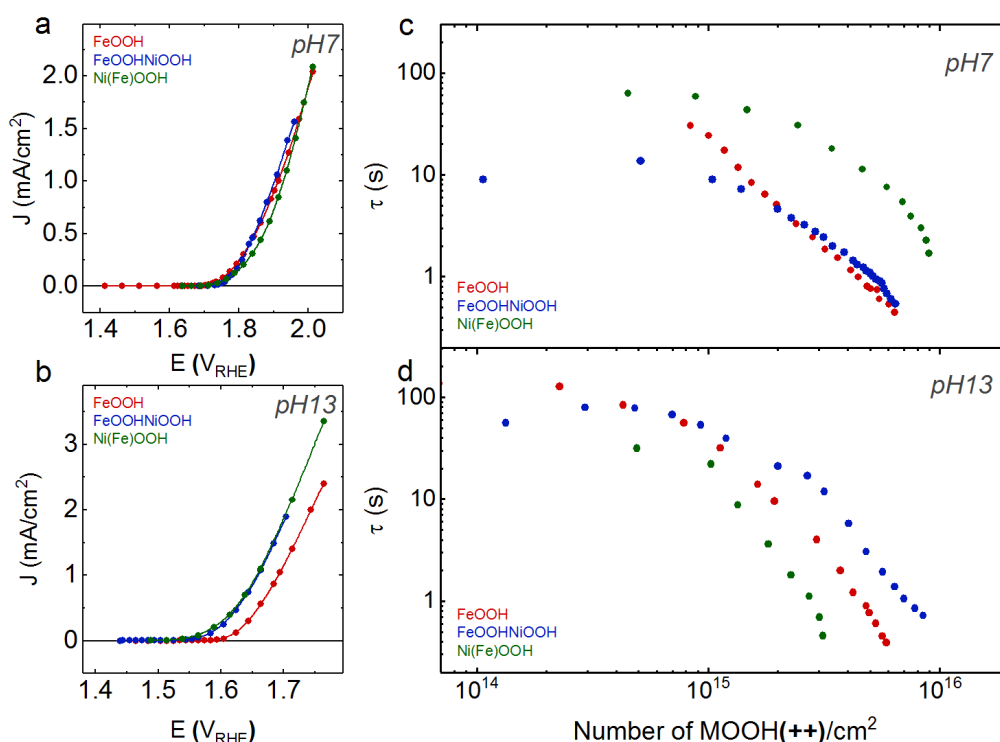


Figure 5.10 | Comparison of electrochemical water oxidation kinetics for the same electrocatalysts under pH7 and pH 13. J – V characteristics of the electrocatalysts at (a) pH 7 and (b) pH 13. The water oxidation time constants (τ) plotted against the number of accumulated MOOH(++) species at (c) pH 7 and (d) pH 13. pH 7 measurements were taken in 0.1 M phosphate buffer, whilst pH 13 data were obtained in 0.1 M NaOH solution. pH 13 data were taken from the referenced publication.⁸⁴

It is also striking that the most popular catalysts for water oxidation display time constants on the order of seconds, *i.e.* Co-Fe based prussian blue.¹⁷⁰ Even the popular Ni(Fe)OOH catalysts investigated under the optimal alkaline conditions, operate with time constants⁸⁴ which are comparable to water oxidation by metal oxides such BiVO₄.²³ Therefore it appears that the significant enhancement in photoelectrochemical performance of BiVO₄ photoanodes decorated with these co-catalysts do not originate from faster kinetics of water oxidation, rather, it is most likely due to fast hole transfer from BiVO₄ to the catalyst layer which spatially separates charges, effectively minimising recombination losses. This is however, markedly different to CoPi, which exhibits water oxidation time constants (τ) that are two – three orders of magnitude larger than what is observed for BiVO₄ alone, where the enhancement in performance is attributed to increase in band-bending that drives charge separation.^{79,171} In the case of CoPi, it is observed that the amount of charge accumulated in CoPi under PEC conditions (when incorporated on BiVO₄) is significantly lower than that is observed under electrochemical water oxidation conditions at matched current densities, by two orders of magnitude.⁷⁹ Therefore, it is concluded that the amount of charge that accumulates in CoPi from BiVO₄ is insufficient to drive water oxidation. This conclusion is also supported by intensity-modulated photocurrent spectroscopy (IMPS) studies which indicate that CoPi mainly serves to passivate surface defects, with no significant enhancement of water oxidation kinetics when deposited on BiVO₄ or α -Fe₂O₃.^{78,172} However, as conflicting studies based on dual working electrode measurements which assign water oxidation to the CoPi catalyst overlayers also have been reported,⁸¹ this makes the role of CoPi as co-catalyst overlayers on semiconductor photoelectrodes, difficult to determine. For the case of the MOOH electrocatalysts studied herein, although a slight discrepancy in the amount of MOOH(++) species is also observed for the FeOOH and FeOOHNiOOH electrodes studied, this difference (within an order of magnitude) is less dramatic than the case of CoPi,⁷⁹ and is more similar to the case of RuO_x catalysts operating as electrocatalysts and co-catalysts on photoelectrochemical systems.⁸⁷ The charge transfer observed from BiVO₄ to the catalyst layer to generate MOOH(++) species is seen both in the transient absorption spectra and the photo-induced spectra under steady-state conditions. Additionally, as the reaction order for water oxidation for BiVO₄/MOOH photoanodes also differ from that of BiVO₄ photoanodes, it strongly indicates that water oxidation in the catalyst decorated photoanodes studied herein is driven via MOOH(++) species accumulated in the catalyst layer.

5.6 Conclusion

In this chapter, the electrochemical and photoelectrochemical performance of FeOOH, FeOOHNiOOH and Ni(Fe)OOH catalysts are studied as standalone catalysts and also when incorporated on the surface of BiVO₄ photoanodes. Whilst electrochemically, all three electrocatalysts demonstrate similar

water oxidation performance, FeOOH and FeOOHNiOOH exhibit faster kinetics for water oxidation in comparison to Ni(Fe)OOH. However, Ni(Fe)OOH is able to accumulate a larger concentration of species compared to the other two at any given potential under catalytic condition, which overall results in comparable water oxidation electrochemical performance. Once incorporated as co-catalysts on the surface of mesoporous BiVO₄ photoelectrodes, significant improvements in the photoelectrochemical water oxidation performance are observed with respect to un-modified BiVO₄. However, no significant enhancement in water oxidation kinetics is observed for the BiVO₄/MOOH photoanodes. Rather, the enhancement in performance most likely results from fast charge transfer (<μs) from BiVO₄ to the catalyst layer, thus minimising recombination losses. This is illustrated in *Figure 5.11*. Significant differences in the operation of the catalysts are also highlighted between neutral conditions (when incorporated onto BiVO₄) and under alkaline conditions where these MOOH electrocatalysts exhibit their optimal water oxidation performance.

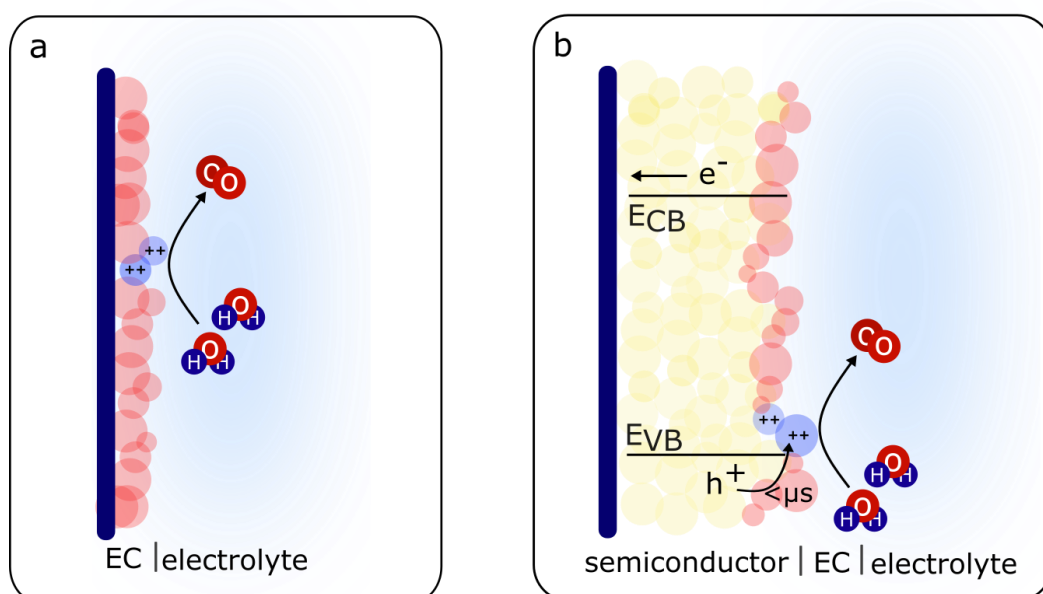


Figure 5.11 | Schematic illustration of electrochemical and photoelectrochemical water oxidation in MOOH electrodes and BiVO₄/MOOH photoelectrodes. (a) The electrochemically generated MOOH(++) species (blue spheres) in the activated electrocatalyst accumulate and drive water oxidation. (b) The photogenerated holes in the BiVO₄ transfer to the activated catalyst, generating MOOH(++) species (blue spheres) which then drive water oxidation. The electrons in the conduction band are collected at the back contact.

Chapter 6 | Concluding remarks

6.1 Concluding remarks

The primary focus of this thesis has been to gain insight into the charge carrier dynamics of BiVO_4 , and to understand how these processes impact upon photoelectrochemical water oxidation. Using transient absorption spectroscopy, dynamics of photogenerated charge were monitored from the timescale of charge generation to water oxidation (fs – s). By combining this with transient photocurrent measurements, and steady – state absorption spectroscopic techniques under operational conditions, such as light-induced and step-potential spectroelectrochemistry, the processes that govern photoelectrochemical water oxidation were investigated.

In *chapter 3*, the role of charge carrier trapping in electronic states close to the conduction band edge, *i.e.* in $\text{V}^{4+}/\text{V}^{5+}$ states associated with oxygen vacancies, were investigated. In the bulk, occupied states (V^{4+}) were found to function as centres for a fast, strongly exothermic hole-trapping process (fs), with the resultant trapped holes being energetically unable to drive water oxidation. In contrast, electron-trapping into unoccupied states (V^{5+}), which occurs predominantly within the space-charge layer (< μs – s), were found to be reversible. These trapped electrons were subsequently observed to undergo a thermally activated charge extraction (ms), with an activation energy of ~ 0.2 eV, which was consistent with the higher photoelectrochemical water oxidation performance observed at elevated temperatures.

The role of staggered (type II) heterojunctions in enhancing the photoelectrochemical water oxidation performance for $\text{WO}_3/\text{BiVO}_4$ was then investigated in *chapter 4*. Transient absorption studies indicated that charge separation, *i.e.* electron transfer from BiVO_4 to WO_3 , occurred pre- μs , whilst photogenerated holes resided within BiVO_4 . The success of spatial separation of charge to inhibit recombination losses was found to be dependent upon the applied potential, with anodic potentials significantly retarding recombination on the μs – ms timescale, resulting in a higher yield of holes that are able to participate in water oxidation.

In *chapter 5*, electrochemical water oxidation by FeOOH , Ni(Fe)OOH , and FeOOHNiOOH electrocatalysts, operating under neutral conditions were investigated. Using spectroelectrochemical techniques, the spectroscopic signatures of species that accumulate under water oxidation conditions were identified, and the respective kinetics of water oxidation by these species were determined for each catalyst. These electrocatalysts exhibit their optimum performance under alkaline conditions, which diminishes as the pH progresses towards neutral conditions. It is observed that the mechanism by which these catalysts operate under neutral and alkaline conditions are different, with the pH also

affecting the trends in reactivity between the three catalysts. Once incorporated as co-catalysts on BiVO₄ photoelectrodes, the photoelectrochemical performance of the catalyst-incorporated photoelectrodes were found to significantly exceed that of unmodified BiVO₄ under neutral conditions. The most likely origin of this enhancement was observed to result from fast charge transfer from BiVO₄ to the catalyst layers which occurred pre – μ s. However no significant enhancement in water oxidation kinetics by the catalyst was observed in comparison to unmodified BiVO₄.

6.2 Future Work

The results obtained in this thesis can be supplemented with further work that can help address questions that came to light during the course of investigations. In *chapter 3*, the electronic occupancy of the oxygen vacancies were modulated *in situ* using electrical bias, thermal perturbations, and photogenerated charge carrier trapping. The observed 470 nm optical feature that is observed to correlate to with the electronic occupancy of V^{4+/5+} states in this work, has also been reported previously to correlate with bandgap shifting and broadening. Therefore, the exact nature of the optical transition associated with the 470 nm feature remains unclear. Computational modelling of how changes in electronic density can affect band edges and the observed optical transitions can aid the assignment of spectroscopically observed features. In addition, in lieu of altering the electronic occupancy of defect states *in situ*, studying samples of varying concentrations of chemical defects that are altered synthetically can shed further light into how structural defects affect photoelectrochemical performance.

In *chapter 4*, it is found that charge separation is aided by positive applied bias. Computational studies modelling the interface of the two semiconductors under operational conditions can help elucidate the nature of band alignment under applied potentials, and help identify if the presence of energetic barriers to charge transfer limits the photoelectrochemical water oxidation efficiencies.

The electrochemical and photoelectrochemical function of electrocatalysts studied in *chapter 5* were directly compared when deposited on FTO, and when incorporated onto BiVO₄ photoelectrodes. However, the differing roughness factors of the two substrates can make comparisons of the exact density of surface holes (or oxidising equivalents), difficult. Therefore, it can be useful to determine the active roughness factors of the individual electrocatalyst electrodes and BiVO₄/MOOH photoelectrodes. Further work is currently ongoing to determine the “active” surface area of mesoporous electrodes, which can differ significantly from the surface area determined using techniques such as Brunauer-Emmet-Teller (BET). Additionally, the bias dependence of the charge transfer processes between BiVO₄ and the MOOH electrocatalysts would also shed light into the role of the electrocatalysts in suppressing surface recombination losses.

References |

- 1 IEA, *World energy balances: An Overview*, 2019.
- 2 IEA, *Global Energy & CO₂ Status Report 2019*, 2019.
- 3 D. Lüthi, M. Le Floch, B. Bereiter, T. Blunier, J. M. Barnola, U. Siegenthaler, D. Raynaud, J. Jouzel, H. Fischer, K. Kawamura and T. F. Stocker, *Nature*, 2008, **453**, 379–382.
- 4 IEA, *World Energy Outlook 2019*, 2019.
- 5 IPCC, *Global warming of 1.5 ° C*, 2018.
- 6 NASA/GISS, Global Land-Ocean temperature index, <https://climate.nasa.gov/vital-signs/global-temperature/>, (accessed 31 January 2020).
- 7 World Bank national accounts data, and OECD National Accounts data files, <https://data.worldbank.org/indicator/NY.GDP.PCAP.CD?end=2018&start=1990>.
- 8 U. Nations, *UN Framework Convention on Climate Change*, 2010.
- 9 U. Nations, *Paris Agreement*, 2015.
- 10 IEA, *World Energy Model*, 2019.
- 11 P. Tans, Trends in Atmospheric Carbon Dioxide, <http://www.esrl.noaa.gov/gmd/ccgg/trends/global.html> <http://www.esrl.noaa.gov/gmd/ccgg/trends/weekly.html>, (accessed 31 January 2020).
- 12 IPCC, *Renewable energy sources and climate change mitigation: Special report of the intergovernmental panel on climate change*, 2012.
- 13 J. M. Ogden, *Annu. Rev. Energy Environ.*, 1999, **24**, 227–279.
- 14 S. T. Wismann, J. S. Engbæk, S. B. Vendelbo, F. B. Bendixen, W. L. Eriksen, K. Aasberg-Petersen, C. Frandsen, I. Chorkendorff and P. M. Mortensen, *Science*, 2019, **364**, 756–759.
- 15 C. H. Christensen, T. Johannessen, R. Z. Sørensen and J. K. Nørskov, *Catal. Today*, 2006, **111**, 140–144.
- 16 CCC, *Net Zero - The UK's contribution to stopping global warming*, 2019.
- 17 CCC, *Hydrogen in a low-carbon economy*, 2018.
- 18 HyDeploy, *HyDeploy Project*, 2018.
- 19 A. Kafizas, R. Godin and J. R. Durrant, *Semicond. Semimetals*, 2017, **97**, 3–46.
- 20 J. R. Bolton, S. J. Strickler and J. S. Connolly, *Nature*, 1985, **316**, 495–500.
- 21 A. J. Cowan and J. R. Durrant, *Chem. Soc. Rev.*, 2013, **42**, 2281–2293.
- 22 C. Lohaus, A. Klein and W. Jaegermann, *Nat. Commun.*, 2018, **9**, 1–7.
- 23 C. A. Mesa, L. Francàs, K. R. Yang, P. Garrido-Barros, E. Pastor, Y. Ma, A. Kafizas, T. E. Rosser, M. T. Mayer, E. Reisner, M. Grätzel, V. S. Batista and J. R. Durrant, *Nat. Chem.*, , DOI:10.1038/s41557-019-0347-1.

- 24 R. Van De Krol and M. Grätzel, *Photoelectrochemical Hydrogen Production*, Springer US, Boston, MA, 2012, vol. 102.
- 25 R. Godin, A. Kafizas and J. R. Durrant, *Curr. Opin. Electrochem.*, 2017, **2**, 136–143.
- 26 F. Le Formal, K. Sivula and M. Grätzel, *J. Phys. Chem. C*, 2012, **116**, 26707–26720.
- 27 Y. Ma, S. R. Pendlebury, A. Reynal, F. Le Formal and J. R. Durrant, *Chem. Sci.*, 2014, **5**, 2964–2973.
- 28 F. Le Formal, S. R. Pendlebury, M. Cornuz, S. D. Tilley, M. Grätzel and J. R. Durrant, *J. Am. Chem. Soc.*, 2014, **136**, 2564–2574.
- 29 ASTM, .
- 30 T. E. Rosser, M. A. Gross, Y. H. Lai and E. Reisner, *Chem. Sci.*, 2016, **7**, 4024–4035.
- 31 Y. Park, K. J. McDonald and K.-S. Choi, *Chem. Soc. Rev.*, 2013, **42**, 2321–2337.
- 32 S. Tokunaga, H. Kato and A. Kudo, *Chem. Mater.*, 2001, **13**, 4624–4628.
- 33 A. Walsh, Y. Yan, M. N. Huda, M. M. Al-Jassim and S.-H. H. Wei, *Chem. Mater.*, 2009, **21**, 547–551.
- 34 J. K. Cooper, S. Gul, F. M. Toma, L. Chen, P.-A. Glans, J. Guo, J. W. Ager, J. Yano and I. D. Sharp, *Chem. Mater.*, 2014, **26**, 5365–5373.
- 35 D. J. Payne, M. D. M. Robinson, R. G. Egdell, A. Walsh, J. McNulty, K. E. Smith and L. F. J. Piper, *Appl. Phys. Lett.*, 2011, **98**, 1–4.
- 36 J. Ma and L. W. Wang, *Appl. Phys. Lett.*, 2014, **105**, 1–5.
- 37 Z. Zhao, Z. Li and Z. Zou, *Phys. Chem. Chem. Phys.*, 2011, **13**, 4746–4753.
- 38 J. K. Cooper, S. Gul, F. M. Toma, L. Chen, Y. S. Liu, J. Guo, J. W. Ager, J. Yano and I. D. Sharp, *J. Phys. Chem. C*, 2015, **119**, 2969–2974.
- 39 J. W. Jang, D. Friedrich, S. Müller, M. Lamers, H. Hempel, S. Lardhi, Z. Cao, M. Harb, L. Cavallo, R. Heller, R. Eichberger, R. van de Krol and F. F. Abdi, *Adv. Energy Mater.*, 2017, **7**, 1–11.
- 40 A. J. E. E. Rettie, H. C. Lee, L. G. Marshall, J.-F. Lin, C. Capan, J. Lindemuth, J. S. McCloy, J. Zhou, A. J. Bard and C. B. Mullins, *J. Am. Chem. Soc.*, 2013, **135**, 11389–11396.
- 41 P. Salvador, *J. Appl. Phys.*, 1984, **55**, 2977–2985.
- 42 J. H. Kennedy and K. W. Frese, *J. Electrochem. Soc.*, 1978, **125**, 709–714.
- 43 Y. Liang, T. Tsubota, L. P. A. Mooij and R. van de Krol, *J. Phys. Chem. C*, 2011, **115**, 17594–17598.
- 44 M. Ziwritsch, S. Müller, H. Hempel, T. Unold, F. F. Abdi, R. Van De Krol, D. Friedrich and R. Eichberger, *ACS Energy Lett.*, 2016, **1**, 888–894.
- 45 F. F. Abdi, T. J. Savenije, M. M. May, B. Dam and R. Van De Krol, *J. Phys. Chem. Lett.*, 2013, **4**, 2752–2757.
- 46 E. Pastor, J. Park, L. Steier, S. Kim, M. Grätzel, J. R. Durrant, A. Walsh and A. A. Bakulin, *Nat.*

- Commun.*, 2019, **10**, 3962.
- 47 L. M. Carneiro, S. K. Cushing, C. Liu, Y. Su, P. Yang, A. P. P. Alivisatos and S. R. Leone, *Nat. Mater.*, 2017, **16**, 819.
 - 48 S. Lany, *J. Phys. Condens. Matter*, 2015, **27**, 283203.
 - 49 A. J. E. Rettie, W. D. Chemelewski, J. Lindemuth, J. S. McCloy, L. G. Marshall, J. Zhou, D. Emin and C. B. Mullins, *Appl. Phys. Lett.*, 2015, **106**, 022106.
 - 50 A. J. E. Rettie, W. D. Chemelewski, D. Emin and C. B. Mullins, *J. Phys. Chem. Lett.*, 2016, **7**, 471–479.
 - 51 H. Seo, Y. Ping and G. Galli, *Chem. Mater.*, 2018, **30**, 7793–7802.
 - 52 T. W. Kim and K.-S. Choi, *Science*, 2014, **343**, 990–994.
 - 53 D. K. Lee, D. Lee, M. A. Lumley and K. S. Choi, *Chem. Soc. Rev.*, 2019, **48**, 2126–2157.
 - 54 D. K. Lee and K.-S. Choi, *Nat. Energy*, , DOI:10.1038/s41560-017-0057-0.
 - 55 Y. Kuang, Q. Jia, G. Ma, T. Hisatomi, T. Minegishi, H. Nishiyama, M. Nakabayashi, N. Shibata, T. Yamada, A. Kudo and K. Domen, *Nat. Energy*, 2017, **2**, 1–3.
 - 56 S. Wang, P. Chen, Y. Bai, J. H. Yun, G. Liu and L. Wang, *Adv. Mater.*, 2018, **30**, 1–7.
 - 57 M. Favaro, F. F. Abdi, M. Lamers, E. J. Crumlin, Z. Liu, R. van de Krol and D. E. Starr, *J. Phys. Chem. B*, 2018, **122**, 801–809.
 - 58 L. Han, F. F. Abdi, R. Van De Krol, R. Liu, Z. Huang, H. J. Lewerenz, B. Dam, M. Zeman and A. H. M. Smets, *ChemSusChem*, 2014, **7**, 2832–2838.
 - 59 Y. Kuang, Q. Jia, H. Nishiyama, T. Yamada, A. Kudo and K. Domen, *Adv. Energy Mater.*, 2016, **6**, 2–8.
 - 60 J. H. Kim, J.-W. Jang, Y. H. Jo, F. F. Abdi, Y. H. Lee, R. van de Krol and J. S. Lee, *Nat. Commun.*, 2016, **7**, 13380.
 - 61 Y. Qiu, W. Liu, W. Chen, G. Zhou, P. C. Hsu, R. Zhang, Z. Liang, S. Fan, Y. Zhang and Y. Cui, *Sci. Adv.*, , DOI:10.1126/sciadv.1501764.
 - 62 S. Xiao, C. Hu, H. Lin, X. Meng, Y. Bai, T. Zhang, Y. Yang, Y. Qu, K. Yan, J. Xu, Y. Qiu and S. Yang, *J. Mater. Chem. A*, 2017, **5**, 19091–19097.
 - 63 H. S. Park, K. E. Kweon, H. Ye, E. Paek, G. S. Hwang and A. J. Bard, *J. Phys. Chem. C*, 2011, **115**, 17870–17879.
 - 64 C. Jiang, R. Wang and B. A. Parkinson, *ACS Comb. Sci.*, 2013, **15**, 639–645.
 - 65 K. P. S. Parmar, H. J. Kang, A. Bist, P. Dua, J. S. Jang and J. S. Lee, *ChemSusChem*, 2012, **5**, 1926–1934.
 - 66 S. P. Berglund, A. J. E. Rettie, S. Hoang and C. B. Mullins, *Phys. Chem. Chem. Phys.*, 2012, **14**, 7065.

- 67 F. F. Abdi, L. Han, A. H. M. Smets, M. Zeman, B. Dam and R. van de Krol, *Nat. Commun.*, 2013, **4**, 2195.
- 68 J. K. Cooper, S. B. Scott, Y. Ling, J. Yang, S. Hao, Y. Li, F. M. Toma, M. Stutzmann, K. V. Lakshmi and I. D. Sharp, *Chem. Mater.*, 2016, **28**, 5761–5771.
- 69 G. Wang, Y. Ling, X. Lu, F. Qian, Y. Tong, J. Z. Zhang, V. Lordi, C. Rocha Leao and Y. Li, *J. Phys. Chem. C*, 2013, **117**, 10957–10964.
- 70 M. Sachs, J. Park, E. Pastor, A. Kafizas, A. A. Wilson, L. Francàs, S. Gul, M. Ling, C. Blackman, J. Yano, A. Walsh and J. R. Durrant, *Chem. Sci.*, 2019, **10**, 5667–5677.
- 71 J. M. Wu, Y. Chen, L. Pan, P. Wang, Y. Cui, D. C. Kong, L. Wang, X. Zhang and J. J. Zou, *Appl. Catal. B Environ.*, 2018, **221**, 187–195.
- 72 S. R. Pendlebury, X. Wang, F. Le Formal, M. Cornuz, A. Kafizas, S. D. Tilley, M. Grätzel and J. R. Durrant, *J. Am. Chem. Soc.*, 2014, **136**, 9854–9857.
- 73 M. Barroso, S. R. Pendlebury, A. J. Cowan and J. R. Durrant, *Chem. Sci.*, 2013, **4**, 2724.
- 74 A. Loiudice, J. K. Cooper, L. H. Hess, T. M. Mattox, I. D. Sharp and R. Buonsanti, *Nano Lett.*, 2015, **15**, 7347–7354.
- 75 X. Shi, I. Herraiz-Cardona, L. Bertoluzzi, P. Lopez-Varo, J. Bisquert, J. H. Park and S. Gimenez, *Phys. Chem. Chem. Phys.*, 2016, **18**, 9255–9261.
- 76 S. J. Hong, S. Lee, J. S. Jang and J. S. Lee, *Energy Environ. Sci.*, 2011, **4**, 1781.
- 77 Y. Pihosh, I. Turkevych, K. Mawatari, J. Uemura, Y. Kazoe, S. Kosar, K. Makita, T. Sugaya, T. Matsui, D. Fujita, M. Tosa, M. Kondo and T. Kitamori, *Sci. Rep.*, 2015, **5**, 11141.
- 78 C. Zachäus, F. F. Abdi, L. M. Peter and R. van de Krol, *Chem. Sci.*, 2017, **8**, 3712–3719.
- 79 Y. Ma, A. Kafizas, S. R. Pendlebury, F. Le Formal and J. R. Durrant, *Adv. Funct. Mater.*, 2016, **26**, 4951–4960.
- 80 F. S. Hegner, I. Herraiz-Cardona, D. Cardenas-Morcoso, N. López, J. R. Galán-Mascarós and S. Gimenez, *ACS Appl. Mater. Interfaces*, 2017, **9**, 37671–37681.
- 81 F. A. L. Laskowski, M. R. Nellist, J. Qiu and S. W. Boettcher, *J. Am. Chem. Soc.*, 2019, **141**, 1394–1405.
- 82 A. Kafizas, L. Francàs, C. Sotelo-Vazquez, M. Ling, Y. Li, E. Glover, L. McCafferty, C. Blackman, J. Darr and I. Parkin, *J. Phys. Chem. C*, 2017, **121**, 5983–5993.
- 83 S. Selim, L. Francàs, M. García-Tecedor, S. Corby, C. Blackman, S. Gimenez, J. R. Durrant and A. Kafizas, *Chem. Sci.*, 2019, **10**, 2643–2652.
- 84 L. Francàs, S. Corby, S. Selim, D. Lee, C. A. Mesa, R. Godin, E. Pastor, I. E. L. Stephens, K. S. Choi and J. R. Durrant, *Nat. Commun.*, 2019, **10**, 1–10.
- 85 G. Porter and R. G. W. Norrish, *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.*, 1950, **200**, 284–

- 300.
- 86 A. A. Bakulin, A. Rao, V. G. Pavelyev, P. H. M. van Loosdrecht, M. S. Pshenichnikov, D. Niedzialek, J. Cornil, D. Beljonne and R. H. Friend, *Science*, 2012, **335**, 1340–1344.
 - 87 E. Pastor, F. Le Formal, M. T. Mayer, S. D. Tilley, L. Francàs, C. A. Mesa, M. Grätzel and J. R. Durrant, *Nat. Commun.*, 2017, **8**, 14280.
 - 88 Y. Ma, C. A. Mesa, E. Pastor, A. Kafizas, L. Francàs, F. Le Formal, S. R. Pendlebury and J. R. Durrant, *ACS Energy Lett.*, 2016, **1**, 618–623.
 - 89 F. Le Formal, E. Pastor, S. D. Tilley, C. A. Mesa, S. R. Pendlebury, M. Grätzel and J. R. Durrant, *J. Am. Chem. Soc.*, 2015, **137**, 6629–37.
 - 90 C. A. Mesa, A. Kafizas, L. Francàs, S. R. Pendlebury, E. Pastor, Y. Ma, F. Le Formal, M. T. Mayer, M. Grätzel and J. R. Durrant, *J. Am. Chem. Soc.*, 2017, **139**, 11537–11543.
 - 91 A. Kafizas, Y. Ma, E. Pastor, S. R. Pendlebury, C. Mesa, L. Francàs, F. Le Formal, N. Noor, M. Ling, C. Sotelo-Vazquez, C. J. Carmalt, I. P. Parkin and J. R. Durrant, *ACS Catal.*, 2017, **7**, 4896–4903.
 - 92 Y. Ma, C. A. Mesa, E. Pastor, A. Kafizas, L. Francàs, F. Le Formal, S. R. Pendlebury and J. R. Durrant, *ACS Energy Lett.*, 2016, **1**, 618–623.
 - 93 B. Lamm, B. J. Trzeźniewski, H. Döscher, W. A. Smith and M. Stefik, *ACS Energy Lett.*, 2018, **3**, 112–124.
 - 94 F. S. Hegner, D. Forrer, J. R. Galán-Mascarós, N. López and A. Selloni, *J. Phys. Chem. Lett.*, 2019, 6672–6678.
 - 95 S. Wang, P. Chen, J. H. Yun, Y. Hu and L. Wang, *Angew. Chemie - Int. Ed.*, 2017, **56**, 8500–8504.
 - 96 Y. Zhang, Y. Guo, H. Duan, H. Li, C. Sun and H. Liu, *Phys. Chem. Chem. Phys.*, 2014, **16**, 24519–24526.
 - 97 S. Corby, L. Francàs, S. Selim, M. Sachs, C. Blackman, A. Kafizas and J. R. Durrant, *J. Am. Chem. Soc.*, 2018, **140**, 16168–16177.
 - 98 Y. Yuan, Y. Huang, F. Ma, Z. Zhang and X. Wei, *J. Mater. Sci.*, 2017, **52**, 8546–8555.
 - 99 A. Grimaud, O. Diaz-Morales, B. Han, W. T. Hong, Y. L. Lee, L. Giordano, K. A. Stoerzinger, M. T. M. Koper and Y. Shao-Horn, *Nat. Chem.*, 2017, **9**, 457–465.
 - 100 J. Wang, Z. Wang, B. Huang, Y. Ma, Y. Liu, X. Qin, X. Zhang and Y. Dai, *ACS Appl. Mater. Interfaces*, 2012, **4**, 4024–4030.
 - 101 F. B. Erik Wahlström, Ebbe Kruse Vestergaard, Renald Schaub, Anders Rønnau, Majken Vestergaard, Erik Lægsgaard, Ivan Stensgaard, E. Wahlström, E. K. Vestergaard, R. Schaub, A. Rønnau, M. Vestergaard, E. Lægsgaard, I. Stensgaard and F. Besenbacher, *Science*, 2004, **303**, 511 LP-513.
 - 102 D. D. Qin, T. Wang, Y. M. Song and C. L. Tao, *Dalt. Trans.*, 2014, **43**, 7691–7694.

- 103 T. W. Kim, Y. Ping, G. A. Galli and K. S. Choi, *Nat. Commun.*, 2015, **6**, 1–10.
- 104 W.-J. Yin, S.-H. Wei, M. M. Al-Jassim, J. Turner and Y. Yan, *Phys. Rev. B*, 2011, **83**, 155102.
- 105 Z. Wang, X. Mao, P. Chen, M. Xiao, S. A. Monny, S. Wang, M. Konarova, A. Du and L. Wang, *Angew. Chemie - Int. Ed.*, 2019, **58**, 1030–1034.
- 106 T. Y. Yang, H. Y. Kang, U. Sim, Y. J. Lee, J. H. Lee, B. Koo, K. T. Nam and Y. C. Joo, *Phys. Chem. Chem. Phys.*, 2013, **15**, 2117–2124.
- 107 M. L. Crespillo, J. T. Graham, F. Agulló-López, Y. Zhang and W. J. Weber, *J. Phys. D: Appl. Phys.*, 2017, **50**, 155303.
- 108 M. L. Crespillo, J. T. Graham, F. Agulló-López, Y. Zhang and W. J. Weber, *J. Phys. Chem. C*, 2017, **121**, 19758–19766.
- 109 M. L. Crespillo, J. T. Graham, F. Agulló-López, Y. Zhang and W. J. Weber, *Appl. Mater. Today*, 2018, **12**, 131–137.
- 110 X. Chen, L. Liu and F. Huang, *Chem. Soc. Rev.*, 2015, **44**, 1861–1885.
- 111 R. Van De Krol, *Photoelectrochemical Hydrogen Production*, 2012, vol. 102.
- 112 X. Zhao, J. Hu, X. Yao, S. Chen and Z. Chen, *ACS Appl. Energy Mater.*, 2018, **1**, 3410–3419.
- 113 J. Hu, X. Zhao, W. Chen, H. Su and Z. Chen, *J. Phys. Chem. C*, 2017, **121**, 18702–18709.
- 114 K. T. Butler, B. J. Dringoli, L. Zhou, P. M. Rao, A. Walsh and L. V. Titova, *J. Mater. Chem. A*, 2016, **4**, 18516–18523.
- 115 N. A. Jayah, H. Yahaya, M. R. Mahmood, T. Terasako, K. Yasui and A. M. Hashim, *Nanoscale Res. Lett.*, 2015, **10**, 1–10.
- 116 I. Grigioni, K. G. Stamplecoskie, E. Selli and P. V. Kamat, *J. Phys. Chem. C*, 2015, **119**, 20792–20800.
- 117 N. Aiga, Q. Jia, K. Watanabe, A. Kudo, T. Sugimoto and Y. Matsumoto, *J. Phys. Chem. C*, 2013, **117**, 9881–9886.
- 118 J. K. Cooper, S. E. Reyes-Lillo, L. H. Hess, C.-M. Jiang, J. B. Neaton and I. D. Sharp, *J. Phys. Chem. C*, 2018, **122**, 20642–20652.
- 119 J. Ravensbergen, F. F. Abdi, J. H. van Santen, R. N. Frese, B. Dam, R. van de Krol and J. T. M. Kennis, *J. Phys. Chem. C*, 2014, **118**, 27793–27800.
- 120 D. Hayes, R. G. Hadt, J. D. Emery, A. A. Cordones, A. B. F. Martinson, M. L. Shelby, K. A. Fransted, P. D. Dahlberg, J. Hong, X. Zhang, Q. Kong, R. W. Schoenlein and L. X. Chen, *Energy Environ. Sci.*, 2016, **9**, 3754–3769.
- 121 Z. Huang, Y. Lin, X. Xiang, W. Rodríguez-Córdoba, K. J. McDonald, K. S. Hagen, K.-S. Choi, B. S. Brunschwig, D. G. Musaev, C. L. Hill, D. Wang and T. Lian, *Energy Environ. Sci.*, 2012, **5**, 8923.
- 122 B. Klahr and T. Hamann, *J. Phys. Chem. C*, 2014, **118**, 10393–10399.

- 123 O. Zandi and T. W. Hamann, *Phys. Chem. Chem. Phys.*, 2015, **17**, 22485–22503.
- 124 K. M. H. Young, B. M. Klahr, O. Zandi and T. W. Hamann, *Catal. Sci. Technol.*, 2013, **3**, 1660–1671.
- 125 M. Valant and D. Suvorov, *J. Am. Ceram. Soc.*, 2004, **83**, 2721–2729.
- 126 B. J. Trześniewski, I. A. Digdaya, T. Nagaki, S. Ravishankar, I. Herraiz-Cardona, D. A. Vermaas, A. Longo, S. Gimenez and W. A. Smith, *Energy Environ. Sci.*, 2017, **10**, 1517–1529.
- 127 T. R. Hopper, A. Gorodetsky, J. M. Frost, C. Müller, R. Lovrincic and A. A. Bakulin, *ACS Energy Lett.*, 2018, **3**, 2199–2205.
- 128 P. Guyot-Sionnest, M. Shim, C. Matranga and M. Hines, *Phys. Rev. B*, 1999, **60**, R2181–R2184.
- 129 J. Eichhorn, C. Kastl, J. K. Cooper, D. Ziegler, A. M. Schwartzberg, I. D. Sharp and F. M. Toma, *Nat. Commun.*, 2018, **9**, 4–11.
- 130 L. Zhang, X. Ye, M. Boloor, A. Poletayev, N. A. Melosh and W. C. Chueh, *Energy Environ. Sci.*, 2016, **9**, 2044–2052.
- 131 M. Barroso, C. a Mesa, S. R. Pendlebury, A. J. Cowan, T. Hisatomi and K. Sivula, *Pnas*, 2012, **109**, 15640.
- 132 F. W. Vance, R. D. Williams and J. T. Hupp, *Int. Rev. Phys. Chem.*, 1998, **17**, 307–329.
- 133 H. Shen and M. Dutta, , DOI:10.1063/1.360131.
- 134 J. Tang, J. R. Durrant and D. R. Klug, *J. Am. Chem. Soc.*, 2008, **130**, 13885–13891.
- 135 S. R. Pendlebury, M. Barroso, A. J. Cowan, K. Sivula, J. Tang, M. Grätzel, D. Klug and J. R. Durrant, *Chem. Commun. (Camb.)*, 2011, **47**, 716–8.
- 136 M. Haumann, P. Liebisch, C. Müller, M. Barra, M. Grabolle and H. Dau, *Science*, 2005, **310**, 1019–1021.
- 137 P. E. M. Siegbahn, *Comput. Inorg. Bioinorg. Chem.*, 2009, 229–239.
- 138 C. C. L. McCrory, S. Jung, J. C. Peters and T. F. Jaramillo, *J. Am. Chem. Soc.*, 2013, **135**, 16977–16987.
- 139 A. Kafizas, X. Xing, S. Selim, C. A. Mesa, Y. Ma, C. Burgess, M. A. McLachlan and J. R. Durrant, *Catal. Today*, 2019, **321–322**, 59–66.
- 140 A. Paracchino, V. Laporte, K. Sivula, M. Grätzel and E. Thimsen, *Nat. Mater.*, 2011, **10**, 456–461.
- 141 A. Kafizas, X. Wang, S. R. Pendlebury, P. Barnes, M. Ling, C. Sotelo-Vazquez, R. Quesada-Cabrera, C. Li, I. P. Parkin and J. R. Durrant, *J. Phys. Chem. A*, 2016, **120**, 715–723.
- 142 I. Grigioni, M. Abdellah, A. Corti, M. V. Dozzi, L. Hammarström and E. Selli, *J. Am. Chem. Soc.*, 2018, **140**, 14042–14045.
- 143 Z. Chen, T. F. Jaramillo, T. G. Deutsch, A. Kleiman-Shwarsstein, A. J. Forman, N. Gaillard, R. Garland, K. Takanabe, C. Heske, M. Sunkara, E. W. McFarland, K. Domen, E. L. Miller, J. a. Turner

- and H. N. Dinh, *J. Mater. Res.*, 2010, **25**, 3–16.
- 144 I. Grigioni, K. G. Stamplecoskie, D. H. Jara, M. V. Dozzi, A. Oriana, G. Cerullo, P. V. Kamat and E. Selli, *ACS Energy Lett.*, 2017, **2**, 1362–1367.
- 145 L. Steier, I. Herraiz-Cardona, S. Gimenez, F. Fabregat-Santiago, J. Bisquert, S. D. Tilley and M. Grätzel, *Adv. Funct. Mater.*, 2014, **24**, 7681–7688.
- 146 F. M. Pesci, A. J. Cowan, B. D. Alexander, J. R. Durrant and D. R. Klug, *J. Phys. Chem. Lett.*, 2011, **2**, 1900–1903.
- 147 S. Corby, E. Pastor, Y. Dong, X. Zheng, L. Francàs, M. Sachs, S. Selim, A. Kafizas, A. A. Bakulin and J. R. Durrant, *J. Phys. Chem. Lett.*, 2019, **10**, 5395–5401.
- 148 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737–740.
- 149 M. Cornuz, M. Grätzel and K. Sivula, *Chem. Vap. Depos.*, 2010, **16**, 291–295.
- 150 I. Cesar, A. Kay, J. A. G. Martinez and M. Grätzel, *J. Am. Chem. Soc.*, 2006, **128**, 4582–4583.
- 151 J. A. Seabold and K. S. Choi, *J. Am. Chem. Soc.*, 2012, **134**, 2186–2192.
- 152 A. J. Cowan, W. Leng, P. R. F. Barnes, D. R. Klug and J. R. Durrant, *Phys. Chem. Chem. Phys.*, , DOI:10.1039/c3cp50318f.
- 153 M. W. Kanan and D. G. Nocera, *Science*, 2008, **321**, 1072–1075.
- 154 L. Trotochaud, S. L. Young, J. K. Ranney and S. W. Boettcher, *J. Am. Chem. Soc.*, 2014, **136**, 6744–6753.
- 155 J. Michael, E. L. Demeter, S. M. Illes, Q. Fan, J. R. Boes and J. R. Kitchin, *J. Phys. Chem. C*, 2015, **119**, 11475–11481.
- 156 X. Li, F. C. Walsh and D. Pletcher, *Phys. Chem. Chem. Phys.*, 2011, **13**, 1162–1167.
- 157 M. Gong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei and H. Dai, *J. Am. Chem. Soc.*, 2013, **135**, 8452–8455.
- 158 X. Lu and C. Zhao, *Nat. Commun.*, , DOI:10.1038/ncomms7616.
- 159 D. A. Corrigan, *J. Electrochem. Soc.*, 1987, **134**, 377–384.
- 160 A. M. Smith, L. Trotochaud, M. S. Burke and S. W. Boettcher, *Chem. Commun.*, 2015, **51**, 5261–5263.
- 161 M. W. Louie and A. T. Bell, *J. Am. Chem. Soc.*, 2013, **135**, 12329–12337.
- 162 M. Barroso, A. J. Cowan, S. R. Pendlebury, M. Grätzel, D. R. Klug and J. R. Durrant, *J. Am. Chem. Soc.*, 2011, **133**, 14868–71.
- 163 C. Du, X. Yang, M. T. Mayer, H. Hoyt, J. Xie, G. McMahon, G. Bischofing and D. Wang, *Angew. Chemie - Int. Ed.*, 2013, **52**, 12692–12695.
- 164 M. Gorlin, J. F. De Araujo, H. Schmies, D. Bernsmeier, S. Dresch, M. Gliech, Z. Jusys, P. Chernev, R. Kraehnert, H. Dau and P. Strasser, *J. Am. Chem. Soc.*, 2017, **139**, 2070–2082.

- 165 Z. K. Goldsmith, A. K. Harshan, J. B. Gerken, M. Vörös, G. Galli, S. S. Stahl and S. Hammes-Schiffer, *Proc. Natl. Acad. Sci. U. S. A.*, 2017, **114**, 3050–3055.
- 166 M. Görlin, M. Gliech, J. F. De Araújo, S. Dresch, A. Bergmann and P. Strasser, *Catal. Today*, 2016, **262**, 65–73.
- 167 O. Diaz-Morales, D. Ferrus-Suspedra and M. T. M. Koper, *Chem. Sci.*, 2016, **7**, 2639–2645.
- 168 S. Klaus, Y. Cai, M. W. Louie, L. Trotochaud and A. T. Bell, *J. Phys. Chem. C*, 2015, **119**, 7243–7254.
- 169 S. Selim, E. Pastor, M. García-Tecedor, M. R. Morris, L. Francàs, M. Sachs, B. Moss, S. Corby, C. A. Mesa, S. Gimenez, A. Kafizas, A. A. Bakulin and J. R. Durrant, *J. Am. Chem. Soc.*, , DOI:10.1021/jacs.9b09056.
- 170 B. Moss, F. S. Hegner, S. Corby, S. Selim, L. Francàs, N. López, S. Giménez, J.-R. Galán-Mascarós and J. R. Durrant, *ACS Energy Lett.*, 2018, 337–342.
- 171 Y. Ma, F. Le Formal, A. Kafizas, S. R. Pendlebury and J. R. Durrant, *J. Mater. Chem. A*, 2015, **3**, 20649–20657.
- 172 C. Y. Cummings, F. Marken, L. M. Peter, A. A. Tahir and K. G. U. Wijayantha, *Chem. Commun.*, 2012, **48**, 2027–2029.

Appendix |

A.1 Impedance Measurements

Electrochemical impedance spectroscopy (EIS) allows the determination of interfacial processes such as redox reactions, charge transfer processes as well as capacitance and resistances encountered at photoelectrodes, by modelling photoelectrode systems as model circuits. All EIS data presented in this thesis were kindly collected and analysed by Dr Miguel Garcia-Tecedor, Universitat Jaume I.

The impedance spectroscopy (IS) measurements were carried out in a potentiostat/galvanostat Autolab (model PGSTAT-30). Measurements were performed in a three-electrode configuration, where a platinum wire was used as counter electrode, the sample under study was used as the working electrode, and an Ag/AgCl (3 M KCl) electrode was used as the reference electrode. An aqueous phosphate buffer solution at pH 7 (0.1 M NaH₂PO₄/Na₂HPO₄) was used as electrolyte. The electrochemical measurements were referred to the reversible hydrogen electrode (RHE) through the Nernst equation (equation 1), where $V_{Ag/AgCl}^0$ (3 M KCl) is 0.210 V.

Mott-Schottky analysis are widely used to extract useful parameters of semiconductors, such as the charge carrier/donor density (N_D) and flat band potential (E_{FB}). The capacitance generated across the space-charge layer as a result of applying a potential to the semiconductor is related to the Mott-Schottky equation:

$$\left(\frac{1}{C_{sc}}\right)^2 = \frac{2}{e\epsilon_r\epsilon_0 N_D} \left(V - E_{FB} - \frac{K_B T}{e}\right) \quad (\text{Equation A1})$$

Where C_{sc} is the space charge layer capacitance, ϵ_r is the dielectric constant of the material, ϵ_0 is the vacuum permittivity, e is the charge of an electron, K_B is the Boltzmann constant, T is the temperature and V is the applied potential.

The Mott-Schottky plot of typical BiVO₄ photoanodes employed in this study is presented below in Figure A1.

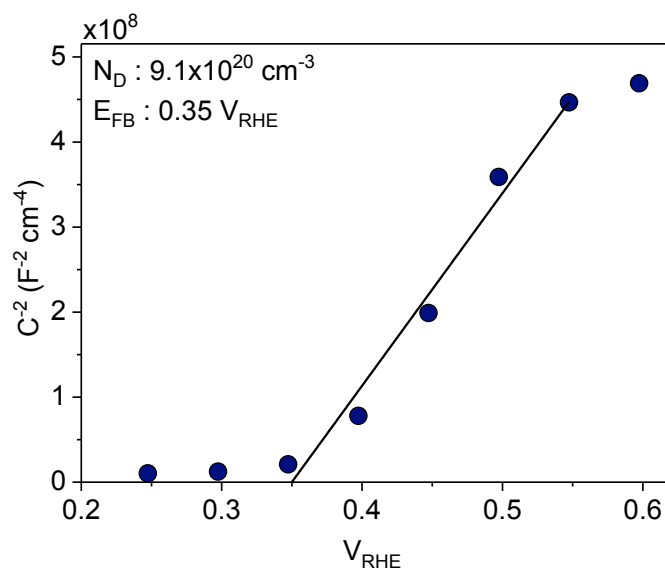


Figure A1| The Mott-Schottky plot of the BiVO_4 photoanode in 0.1 M potassium phosphate buffer, from which the donor density (N_D) and the flat-band potential (E_{FB}) were determined. The E_{FB} value determined for the photoanodes studied herein is more positive than previously reported for BiVO_4 (typically 0.1 – 0.3 V_{RHE}),^{40,56} and the Mott-Schottky characteristic for the photoanodes studied herein is linear over a narrow range, giving rise to some uncertainty in the reported values. All measurements were taken in 0.1 M phosphate buffer.

A.2 UV Pump – IR push – visible probe spectra and kinetics – additional data

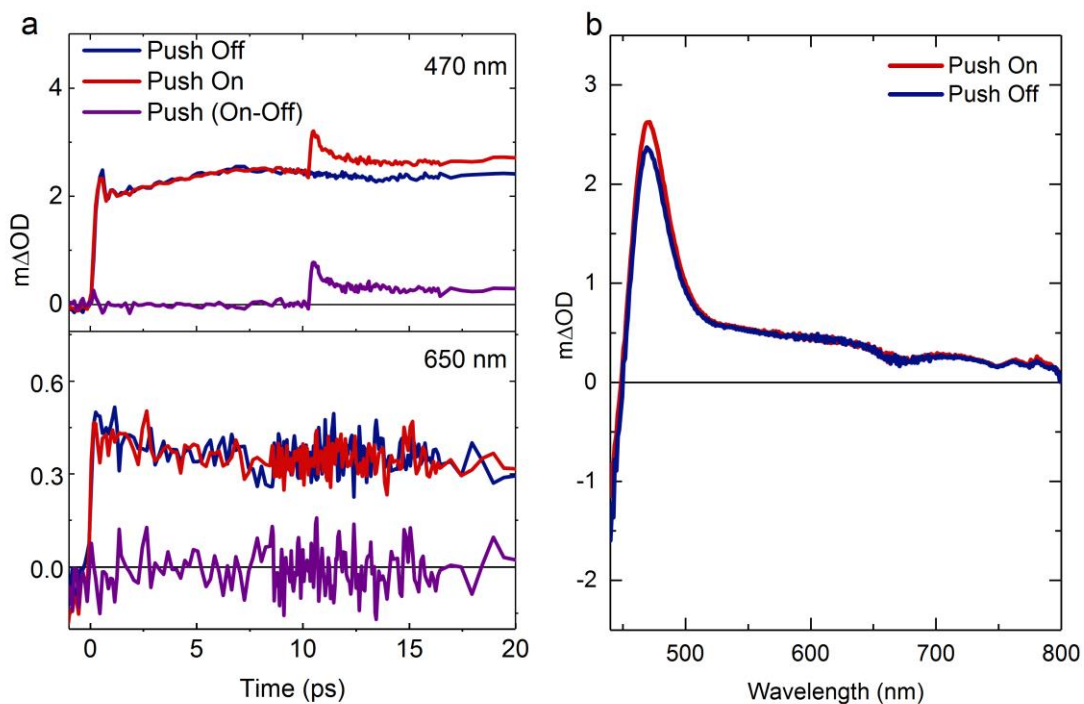


Figure A2 | 3-pulse *pump-push-probe* measurements in air showing the effect of electron excitation from V_{OV}^{4+} to the conduction band, with $\lambda_{ex}(push)$: 2060 nm. **a, *Push* on and *push* off kinetics at 470 nm and 650 nm showing enhancement only at 470 nm band with the *push* excitation. **b**, *Push* On - Off spectra at a *push* – *probe* time delay of 15 picoseconds. The *pump* wavelength for all measurements were set to $\lambda_{ex}(pump)$: 400 nm. *Pump* and *push* excitation densities were $200 \mu J cm^{-2}$ and $3 mJ cm^{-2}$, respectively.**

A.3 UV-Vis absorption spectra of WO₃/BiVO₄ films

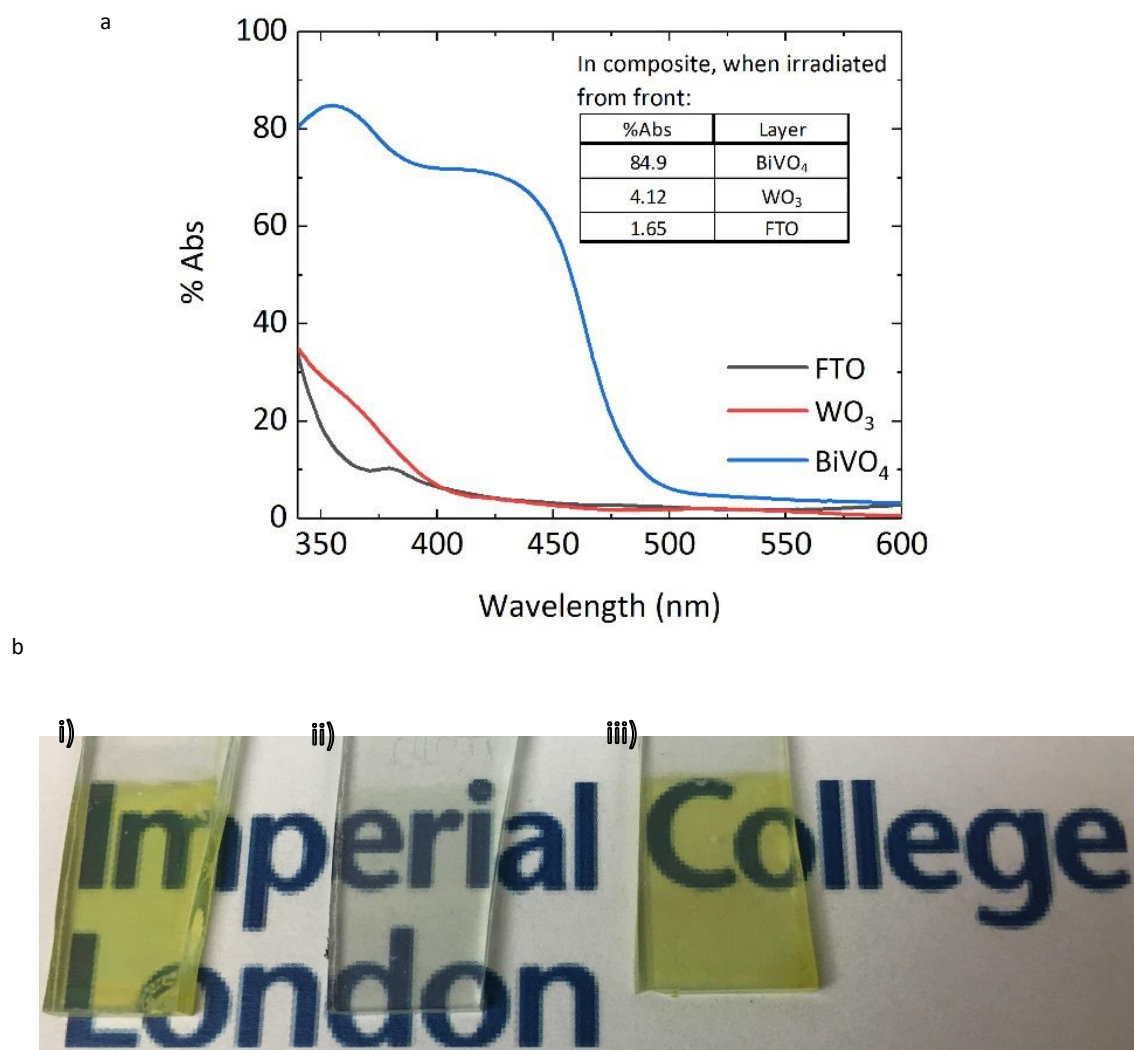
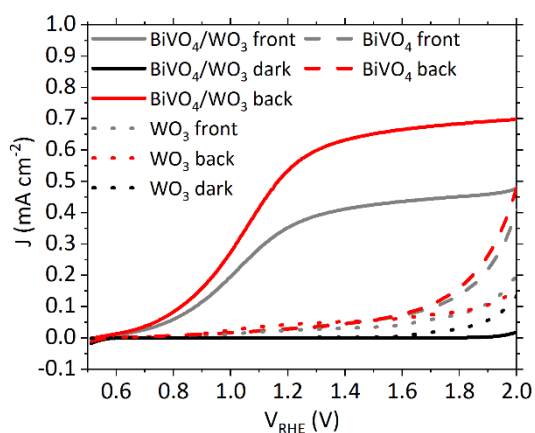


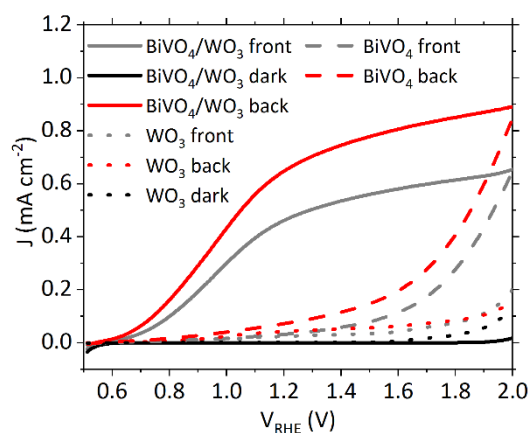
Figure A3 | UV-Vis spectra of WO₃/BiVO₄ photoanode films. The spectra were obtained using a Shimadzu UV-2700 equipped with an integrated sphere. (a) Absorptance of films taking into account of transmittance, diffuse reflectance and specular reflectance. (b) images of the films: (i) BiVO₄, (ii) WO₃ and (iii) WO₃/BiVO₄

A.4 Photoelectrochemical response of BiVO₄ and WO₃/BiVO₄ photoanodes of varying thickness

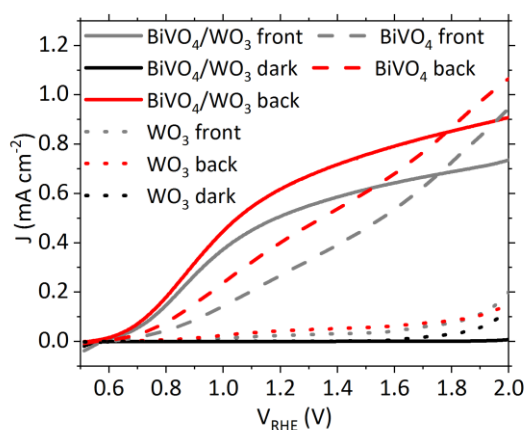
a



b



c



d

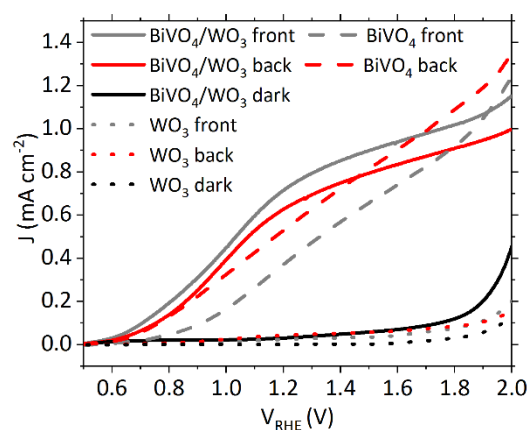


Figure A4 | JV curves of WO₃/BiVO₄ (solid line) with varying thicknesses of BiVO₄ (dashed lines) for thicknesses: (a) 75 nm, (b) 125 nm, (c) 175 nm and (d) 350 nm. The measurements were carried out in pH 7, 0.1 M phosphate buffer, under simulated 1 sun illumination (Xe lamp). The photoelectrochemical response of the WO₃ film is included for reference (dotted line).

A.5 Simulated 1 sun illumination

The photon flux of the simulated 1 sun illumination source is shown below.

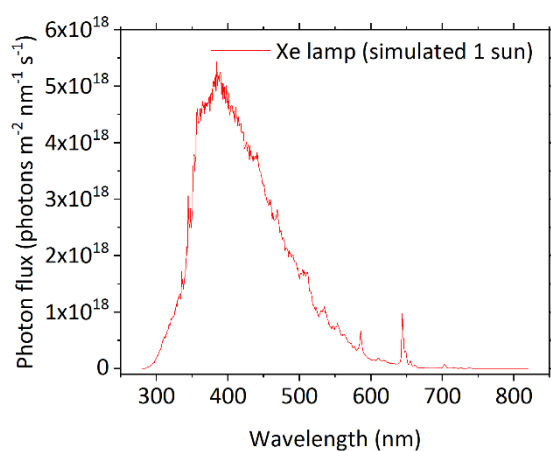
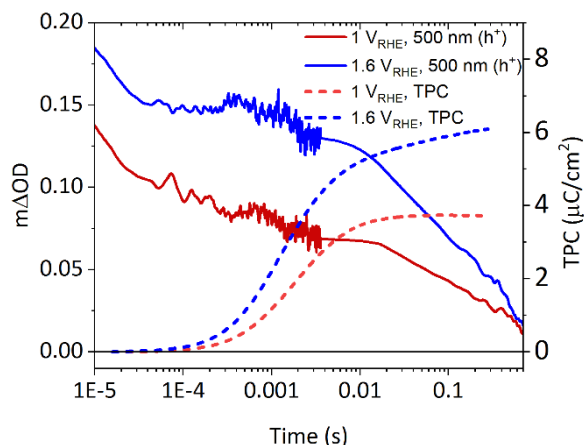


Figure A5| Spectral output of the Xe lamp at 100 mW/cm² with a KG3 filter (simulated 1 sun irradiance).

A.6 Kinetics of photogenerated holes in BiVO₄ and WO₃/BiVO₄ photoanodes in presence of hole scavenger

a



b

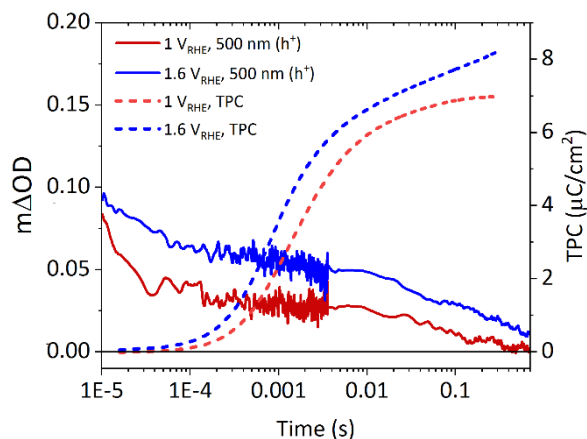


Figure A6| Comparison of TA kinetics of holes accumulated in BiVO₄ (solid) against the integrated transient photocurrent, monitoring charge extraction from the WO₃/BiVO₄ heterojunction photoanode (dash), under applied potential of 1 V_{RHE} (red) and 1.6 V_{RHE} (blue) for (a) water oxidation and (b) sulphite oxidation. Water oxidation exhibits greater bias dependence in hole dynamics and greater hole accumulation, due to the slower kinetics of water oxidation, also reflected in the charge extracted from the film. Whereas for sulphite oxidation, the bias dependence is less pronounced, also shown in the charge extraction, due to sulphite oxidation being more facile in comparison to water oxidation. Less holes accumulate at the surface due to a faster reaction of holes to oxidise sulphite. The films were illuminated from the front (BiVO₄ side), excited at 355 nm, pump fluence: 500 μJ/cm², at 500 nm probing holes in BiVO₄, with and without hole scavenger. Hole scavenger used: 0.1 M Na₂SO₃.

A.7 Comparison of electron dynamics and charge extraction kinetics of BiVO₄, WO₃ and WO₃/BiVO₄ photoanodes

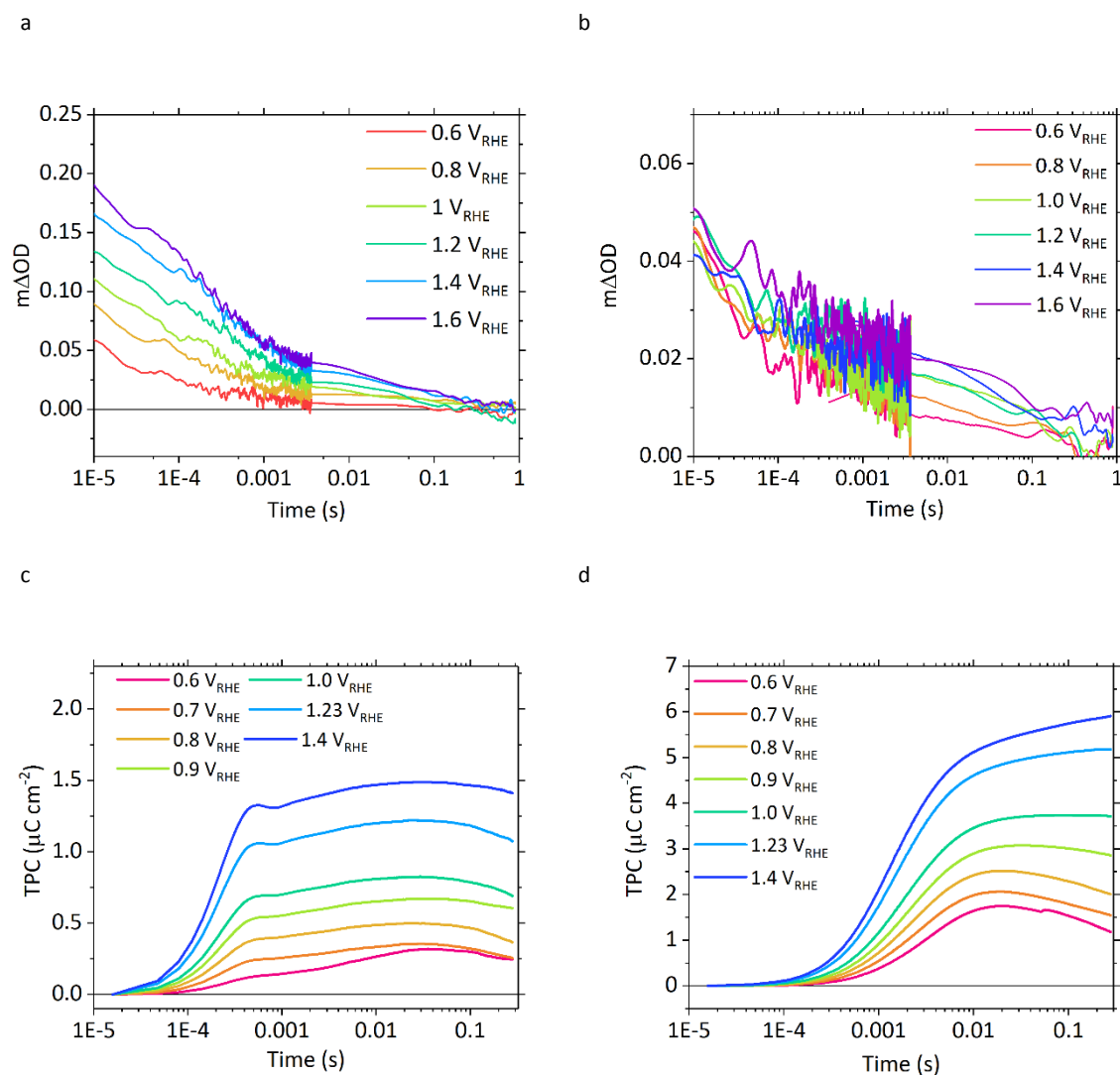
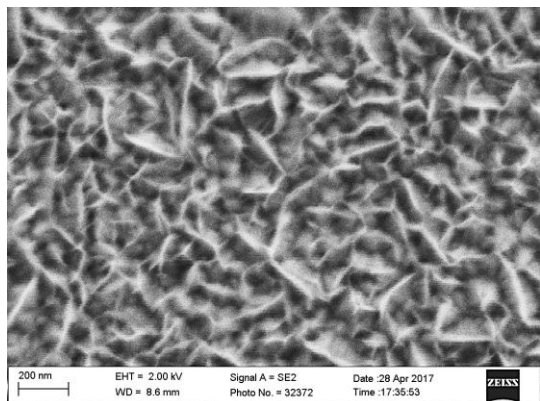


Figure A7| TA kinetics and TPC of BiVO₄ and WO₃/BiVO₄ under front illumination, excited at 355 nm, with varying applied anodic bias in 0.1 M phosphate buffer; pump fluence: 500 μJ/cm². TA kinetic trace at 800 nm of (a) WO₃/BiVO₄, probing electrons in WO₃, and (b) BiVO₄ (absorption tail of broad h⁺ absorption). TPC of (c) BiVO₄ and (d) WO₃/BiVO₄.

A.8 NiOOH electrocatalyst deactivation

The following data shows the deactivation of NiOOH when used under pH 7.

a



b

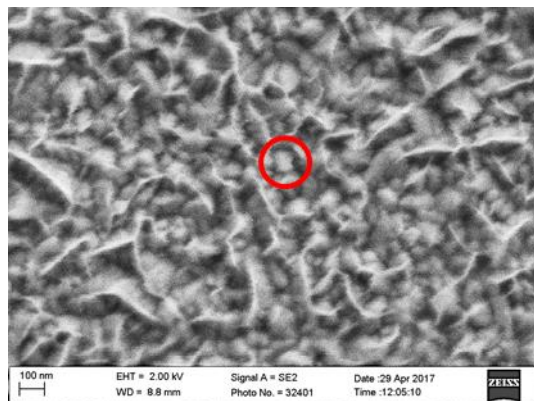
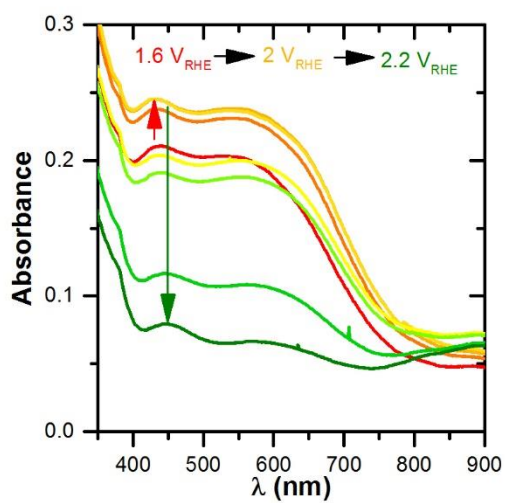


Figure A8 | SEM images of a NiOOH (a) before and (b) after a bulk electrolysis of 2 h applying $2 V_{\text{RHE}}$. The red circle indicates bare FTO observed after the experiment.

a



b

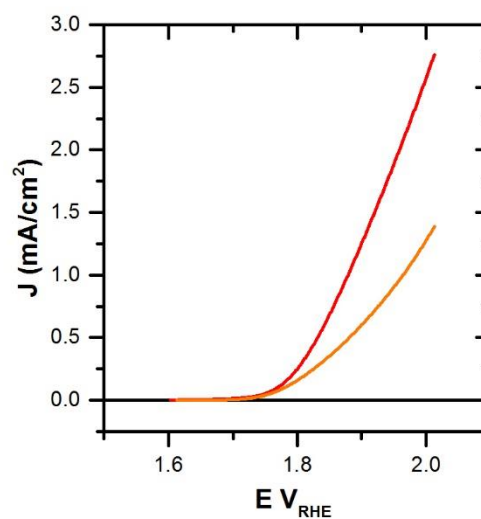


Figure A9 | Degradation process occurring at high applied potentials $> 2 V_{\text{RHE}}$ (a) UV-Vis spectra from $1.6 V_{\text{RHE}}$ (red) to $2 V_{\text{RHE}}$ (yellow-orange) and to $2.2 V_{\text{RHE}}$ (green). (b) LSV before (red) and after (orange) the experiments shown in part (a).

A.8 Sample stability checks during *in situ* measurements

To ensure the observed trends in sample behaviour didn't change during an experiment, measures were taken to check the sample characteristics before and after *in situ* measurements. When data were collected, the order of data acquisition were randomised, e.g. when obtaining TA spectra on the μs – s timescale, the kinetic traces at different wavelengths were obtained in a randomised order. When possible, photoelectrochemical and electrochemical characteristics before and after experiments were also compared using LSV curves. A few examples are shown below.

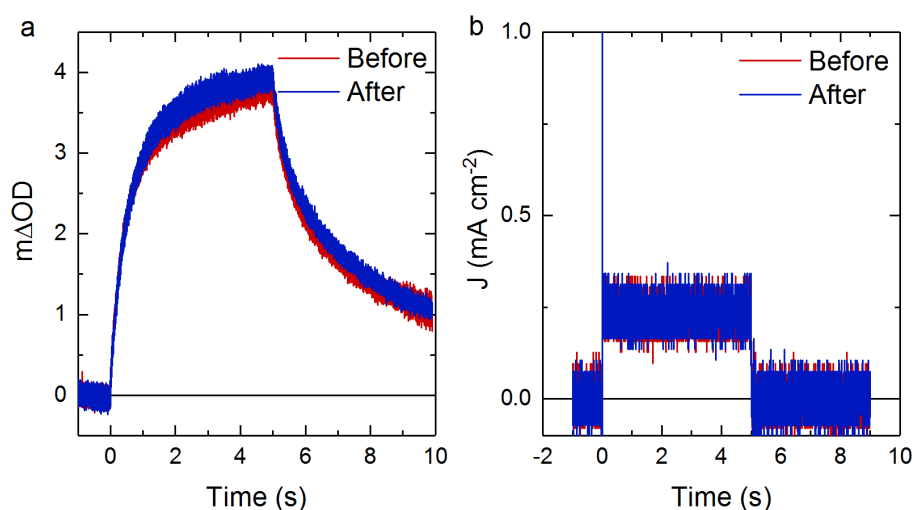


Figure A10 | SEC-PIAS signal traces of $\text{BiVO}_4/\text{FeOOH}$ sample obtained at the start of experiment (red trace) compared with that obtained at the end (blue trace) for the (a) optical signal at 550 nm and the (b) TPC signal. Data were collected with 365 nm LED illumination (1.28 mW/cm^2) at $1.4 V_{\text{RHE}}$ in 0.1 M phosphate buffer.

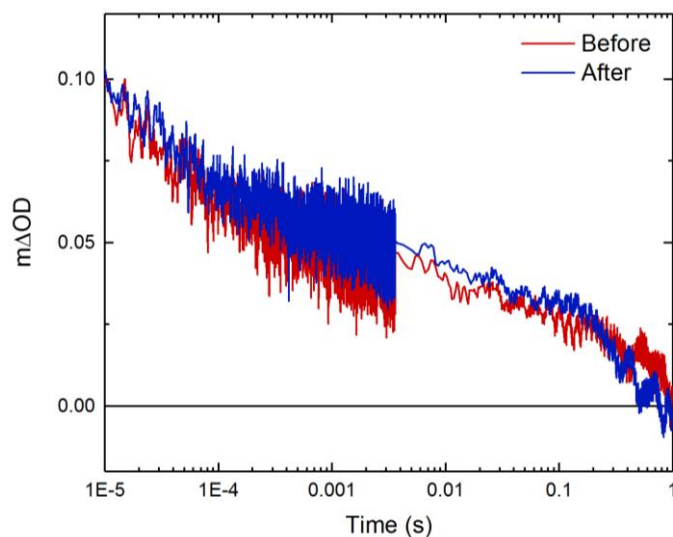


Figure A11 | TA kinetic traces of BiVO_4 sample monitored at 550 nm, at the start of experiment (red trace) compared with that obtained at the end (blue trace). Data were collected with 355 nm excitation ($500 \mu\text{J/cm}^2$) at $1.23 V_{\text{RHE}}$ in 0.1 M phosphate buffer.

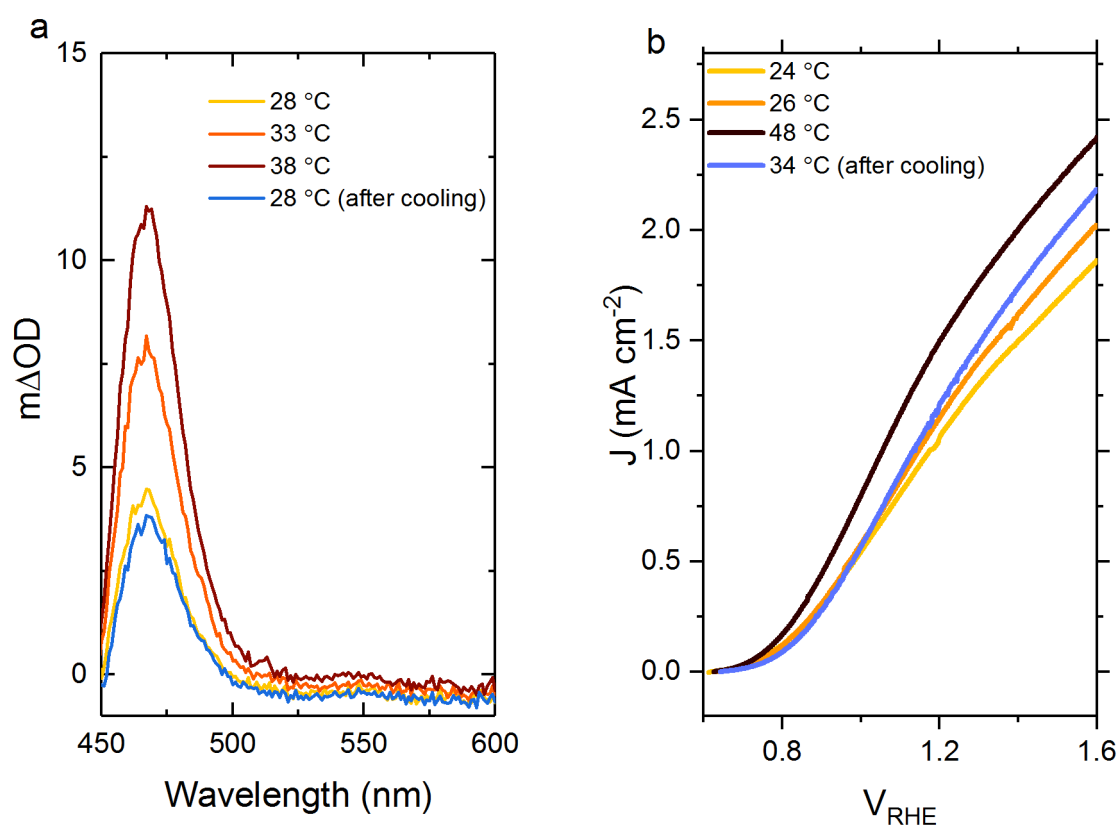


Figure A12 | Comparison of sample characteristics before and after temperature dependence measurements for BiVO₄ samples. (a) Thermally modulated difference spectra under open circuit conditions, where the blue trace shows the spectra obtained after cooling the sample. (b) Temperature dependence of PEC performance under simulated 1 sun illumination (Xe lamp), where the blue trace shows the PEC performance after cooling the sample. All measurements were obtained in 0.1 M phosphate buffer.