

Transient optical studies of metal oxides for water oxidation

Thesis submitted for the degree of Doctor of Philosophy

Department of Chemistry
Imperial College London

by

SACHA CORBY

Supervisor

Prof. James R. Durrant

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Except where specific reference is made, the material presented in this thesis is solely the result of my own work over the period of October 2016 to November 2019. Any experiments performed by collaborators have been clearly credited. This thesis does not exceed 100 000 words in length.

S. C.

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*The secret of change is to focus all of your energy
not on fighting the old,
but on building the new.*
— Socrates

*Little by little,
one moves forward.*
— J.R.R. Tolkien

To those challenging convention . . .

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London, November 2019

S. C.

Abstract

As the next energy crisis looms threateningly before us and we teeter on the edge of the irreparable and undeniably catastrophic loss of global ecosystems as a result of man-made climate change, the quest for alternative fuels is of paramount importance. Solar water splitting is an active area of research which seeks to produce renewable hydrogen fuel from two abundant resources: water and sunlight. However, it is the formation molecular oxygen, the necessary by-product of water splitting, that presents the major chemical challenge, both in terms of kinetics and thermodynamics. As such, high-performing, stable and Earth-abundant materials for water oxidation are highly sought after. The focus of this thesis is the understanding of two such materials.

While Chapter 1 gives a more detailed overview of the current environmental situation, the challenges in global energy and fuel supply, and the field of artificial photosynthesis, Chapter 2 introduces transition metal oxides, the workhorses of the water oxidation reaction. The frequently studied oxides are discussed and particular focus is given to current kinetic understanding and performance limitations. The methods applied in this thesis are then detailed in Chapter 3.

This body of research concerns the spectroscopic analysis of two metal oxide systems for water oxidation: tungsten trioxide (WO_3) and mixed nickel-iron oxides, which become oxyhydroxides during catalysis ($\text{Ni}_x\text{Fe}_y\text{OOH}$). WO_3 , a visible and ultraviolet light absorber, has been studied as a photoanode for photoelectrochemical water oxidation from the first conceptualisation of this reaction in the 1970s. Despite many years of intensive research, much regarding the mechanism and factors limiting the performance of this robust and relatively abundant oxide remain unclear and are frequently debated. Chapter 4 sets the stage for WO_3 within the growing field of water oxidation, with direct comparison to other metal oxides. The kinetics of water oxidation and electron extraction are examined, revealing some unexpected trends. The timescale of water oxidation is found to be remarkably fast, $t_{50\%} < 1$ ms, while electron extraction is limited by trap-mediated transport.

In Chapter 5, I delve deeper into this complex material to understand the role of the most common intrinsic defects to transition metal oxides: oxygen vacancies. This chapter begins by probing the initial charge separation of photogenerated carriers on ultrafast timescales,

Acknowledgements

through which I uncover that electrons trap into defect states on pre-picosecond timescales. I then go on to examine the effects of altering band-bending before investigating samples with different oxygen content to deduce the importance of the resultant defect states generated. The space-charge layer was found to boost the attainable concentration of surface holes from ultrafast timescales, while an intermediate concentration of oxygen vacancies was deemed vital to adequately separate photogenerated charges. I conclude by highlighting the wider significance that defect control has across all timescales monitored, from picoseconds to seconds, and emphasise this as a means to the betterment of existing photoanodes for water oxidation.

In the final results chapter, Chapter 6, I examine a different approach to water oxidation. This chapter explores Ni/Fe oxyhydroxides; dark catalytic materials that can be used as co-catalysts in conjunction with a photoanode (such as WO_3) or employed independently for dark electrolysis using renewably-generated electricity. This chapter presents spectroelectrochemical analyses and examines the rate law for water oxidation on these materials. In particular, the relationship between nickel and iron (the latter an often unintended dopant of the former) is examined, with the aim of unearthing the origin of the synergistic benefit observed when both metals are present. I find that the reactive intermediates accumulated under catalytic conditions are nickel centred at low iron concentrations, but become iron-centred at greater Fe:Ni ratios. However, the rate order with respect to these species is four in each case, suggesting a similar catalytic mechanism between all samples examined.

In Chapter 7, I conclude by summarising this body of work and discuss the impact it may have on the next steps in water oxidation research. Finally, I give my insights into the role that transitional metal oxides may have in the future of solar energy conversion.

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"Separating bulk and surface processes in NiO_x electrocatalysts for water oxidation", S. Corby, M. Garcia-Tecedor, S. Tengeler, C. Steinert, B. Moss, H. Heiba, A. Wilson, C.A. Mesa, B. Kaiser, W. Jaegermann, L. Francàs, S. Giménez, J.R. Durrant, submitted

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"Understanding the effect of Pd co-catalysts on the photoelectrochemical performance of WO₃ photoanodes", A. Wilson, S. Corby, L. Francàs, A. Kafizas, J.R. Durrant, in preparation

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Chapter 1



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1 Introduction

1.1 Mankind and the environment

1.1.1 The beginning

The most memorable tales and prolific parables follow the same general form: a beginning, an introduction to the lead players, the interesting characters and the laws of the land; a middle, in which the protagonist faces deep challenges and hits the lowest point or nadir; and finally a conclusion, which in any Hollywood blockbuster translates to regained glory and ‘happily ever after’, though in some more interesting allegories can offer an alternative, bitter end. The great story of mankind and the environment is, of course, still playing out and, like any gripping novel, the conclusion is yet unknown. From the beginning of written history, the relationship humanity has had with mother nature has been one of great complexity. The provider of food to nourish and sustain, but also with the power to deprive through drought, flood and famine, all beings are subject to nature’s will. However, as the human population has expanded and left the cradle of Africa, so too have ambitions grown to harvest more from the Earth. Ever unsatisfied with the status quo, mankind wants not just to survive and reproduce, but to thrive, to expand and to control. As a species, this has taken us further than any individual could have imagined. From humble dwellings to towering, climate-controlled edifices, from the birth of commercial agriculture to genetically modified corn fields the size of small nations, the last 200 years have brought unprecedented changes to our global landscape alongside a quadrupling of our population.¹ While from an evolutionary standpoint this is the very definition of a successful species, our story began as a two-way relationship, and the other side of our metaphorical coin tells of a high cost to this success. As we shall see in the next section, if our obsession with growth and increased comfort and convenience is left unchecked, the destruction caused will be

irreparable and, in time, will likely be our own demise. The clock is ticking but the conclusion is yet to be carved in stone. Through measured actions, global awareness and a complete shift in our energy generation and usage, we may be able to pull ourselves up from the low point in our story with the environment and provide the fairytale ending we owe to generations to come. Or maybe we won't.

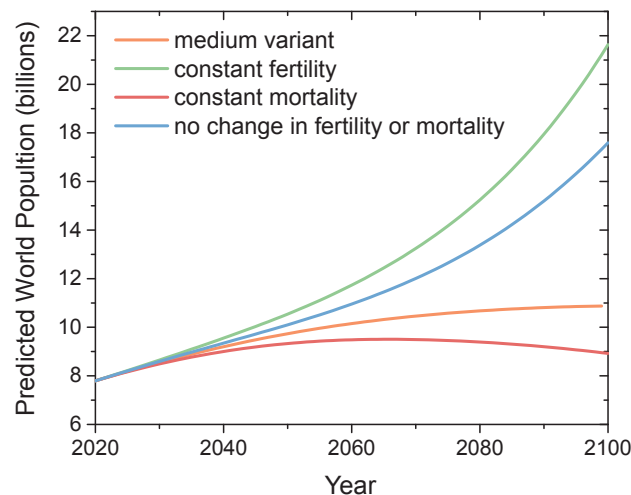


Figure 1.1 – The predicted world population up to the year 2100 for different possible fertility and mortality regimes. The medium variant (orange) is statistically most probable. Data taken from United Nations, Department of Economic and Social Affairs, Population Division (2019). World Population Prospects 2019, Online Edition.²

1.1.2 Economic gain and environmental loss

Today, as this thesis was written, the current global population stands at 7.7 billion individuals.² Current forecasts proffered by the likes of the United Nations predict this number to increase to almost 10 billion by 2050 (Figure 1.1), presumably necessitating a corresponding growth in our collective energy footprint.^{2,4} Energy, however, is not a term that all are comfortable conversing in – an annual global consumption of just over 400 exajoules (> 110,000 TWh) sounds like a pretty big number, but to most, without wider context to appreciate the magnitude of this value, that is all it is, a number.⁵ So for emphasis, let us consider a simple comparison: the longest duration non-stop flight currently in operation flies from Singapore to Newark, New Jersey (> 15000 km, ~18 hours) and requires on average 44000 gallons of kerosene fuel or 142 million joules of energy.^{6,7} Our annual global energy consumption is therefore the equivalent of making this flight ~300 million million times a year, and doing so every year, year after year.

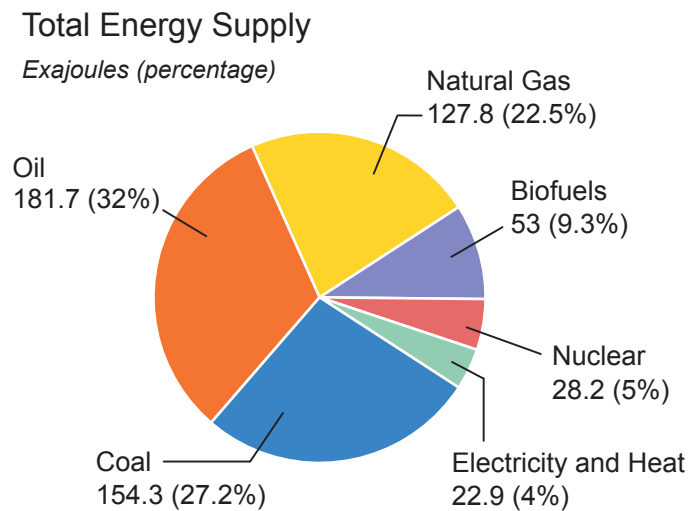


Figure 1.2 – Global energy supply by source in 2016, with 82% coming from finite fossil sources. Electricity and heat refers to both renewable and non-renewable electricity generation. Adapted from United Nations, Department of Economic and Social Affairs, Statistics Division (2019). Energy Statistic Pocketbook, 2019, Online Edition.³

Or alternatively, the energy cost is equivalent to every single person on this planet making that same journey ~100 times every single year. We are talking in really big numbers, with price tags to match. This energy is, of course, a global sum and is not evenly distributed across the planet and its inhabitants. Neither are the natural resources from which the majority of this energy is obtained. Coal, oil and natural gas – the infamous trio collectively known as fossil fuels – make up 82% of the world's energy supply and are found deep underground across the continents in vastly varying quantities (Figure 1.2).³ This makes energy a frequent source of political debate and thus, too, an economic issue. Collectively, the stock market value of the fossil fuel industry is a staggering ~\$4.7 trillion USD (a very big number indeed, 6% of the global GDP),⁸ and this eye-watering sum has kept Big Oil at the forefront of political decisions for decades, with widespread environmental consequences. As developing countries have sought the lifestyles of wealthier nations, so too has global fossil fuel consumption increased, rising by almost 20% in just 9 years from 2005 to 2014.⁹ In 2018 alone, global coal consumption increased by 0.7%, oil consumption by 1.3% and gas consumption by a whopping 4.6%, with little signs of usage abating.¹⁰ Globalisation and increased international trading have further fed the drive for greater profit margins, pushing companies to exploit ever more remote and fragile ecosystems in the hunt to extract more black, liquid gold.^{11,12} The intense and often politically grounded debate regarding fractional distillation or 'fracking' and other controversial means of fossil fuel extraction are beyond the scope of this thesis. What is undoubtedly clear, however, is that fossil

fuel companies have dominated the energy sector for decades, profiting off the land and filling the pockets of some powerful allies who will be reluctant to support any change.¹³

And change we must, for two very obvious reasons. The first reason, though still argued against by those with financial interest at stake, is the more readily acknowledged: fossil fuel resources are limited (Figure 1.3). The predictions vary widely in the number of years of carbon burning we have remaining, but even the most optimistic predictions suggest that we'll be scraping the bottom of the barrel by 2120.^{13,14} As such, it is imperative that we develop alternative means of powering transport and heating homes if we are to sustain our current lifestyles.

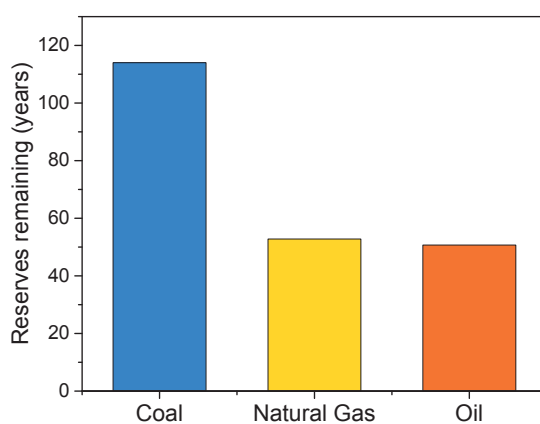


Figure 1.3 – The reserves of each fossil fuel source given in years, calculated from reserves-to-production (R/P) ratio which measures the number of years of fuel supplies left based on current annual consumption rates. Note that this can change with time through the discovery of new fuel reserves, and increases in annual consumption. Adapted from the BP Statistical Review of World Energy 2016.¹⁴

The other justification for curbing our relentless fossil fuel consumption is multifaceted but these facets can largely be grouped under the umbrella term *climate change*, or this term's predecessor, *global warming*. The scale of effect that a shift in global climate will incur is still being brought to light by scientists across the world, 97% of whom are in agreement that mankind has had a more-than-significant contributing role.¹⁵ However, from more extreme weather events to losses in biodiversity, some of the consequences of our damaged relationship with our environment are already frighteningly clear. To some, it seems too far-fetched, egotistical even, to imagine that humanity could have such an impact on planet Earth, which has been in existence billions of years before us. The science, however, is irrefutable to the point that it is frequently taught to school children: our atmosphere acts like a greenhouse, letting in the necessary light and heat from the sun for life to flourish but protecting from the harshest UV-light and solar flares.

Atmospheric pollutants, or 'greenhouse gasses' such as CO₂, released from the combustion of carbon fuels, become trapped in the stratosphere and prevent the solar rays reflected off the planet's surface from escaping into space. The result is excess trapping of thermal energy and a consequential rise of average global temperatures. Compared to temperatures at the dawn of the industrial age, average global temperatures have risen by more than one degree Celsius (Figure 1.4). This change may seem small at first, but our ecosystems are in such fine balance that even a minute shift can have significant consequences. Figure 1.4 shows that the increase in global mean surface temperature over the last 100 years is correlated with an increase in global mean sea levels as a result of a drastic loss of sea ice, particularly in the polar regions. Antarctica's land mass is decreasing at a rate of ~220 billion metric tonnes per year, dumping thousands of litres of fresh water into the world's oceans, reducing their salinity.¹⁶ The acidity of the oceans has also increased by 30% over this time period as more CO₂ is absorbed, affecting all manner of marine life.^{17, 18}

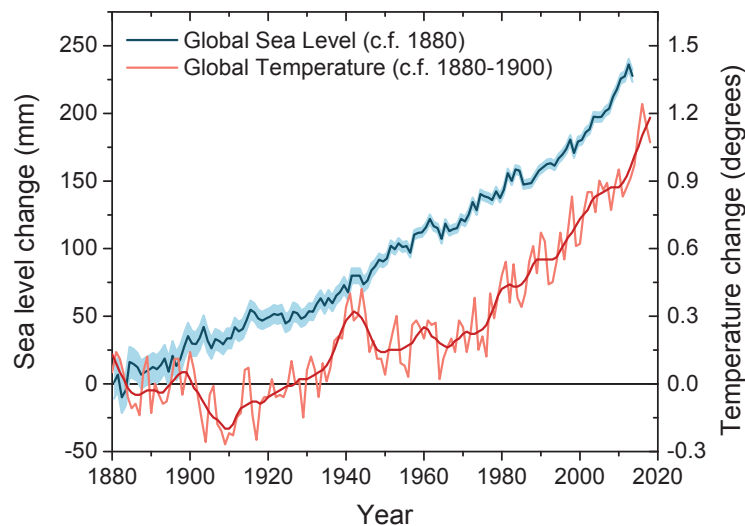


Figure 1.4 – The change in global mean sea level compared to the mean in 1880 (*blue*), and the change in global mean surface temperature compared to the average temperature between 1880-1900 (*red*). The light blue data gives uncertainty region. Dark red line is lowest smooth (5). Adapted from Goddard Institute for Space Studies, NASA, Global Mean Sea Level Trend from Integrated Multi-Mission Ocean Altimeters TOPEX/Poseidon, Jason-1, OSTM/Jason-2, Version 4.2, PO.DAAC, CA, USA.¹⁹

The International Panel on Climate Change (IPCC) is a committee of over 1300 scientific experts that was set up to analyse the extent of climate change and provide advice to policy makers on how to mitigate these effects. The IPCC have reported that the last 40 years have produced

as much as half of the accumulative anthropogenic CO₂ emitted since 1750, a direct result of increased population and global energy consumption.²⁰ And just as population and energy consumption are predicted to continue increasing over this century, so too are emissions and global temperature set to rise further. Figure 1.5 shows the climbing global CO₂ emissions produced each year since 1990 alongside future projections. Without energy policies in place, the IPCC predicts emissions to soar towards 100-200 Gt of annual CO₂ by 2100, accompanied by temperature increases of up to 4.5°C over pre-industrial levels.²¹ This would induce such dramatic changes to our planet that it is not possible to predict the full impact. Even if temperatures are limited to a 2°C increase, the IPCC Special Report states that all marine coral will be wiped-out (affecting ~0.5 billion people who dependent on them),²² multiple regions of the oceans will become dead-zones that cannot support aquatic life, habitable environments for many species of insects and vertebrate will shrink, and food security and water resources will be of increasing concern, thrusting millions into extreme poverty.²³ The loss to the Earth's biota as a result of human-induced climate change has already been so severe that we are widely considered to be entering a 6th mass extinction event, greater than its five predecessors, including that which eradicated the dinosaurs.^{24–26}

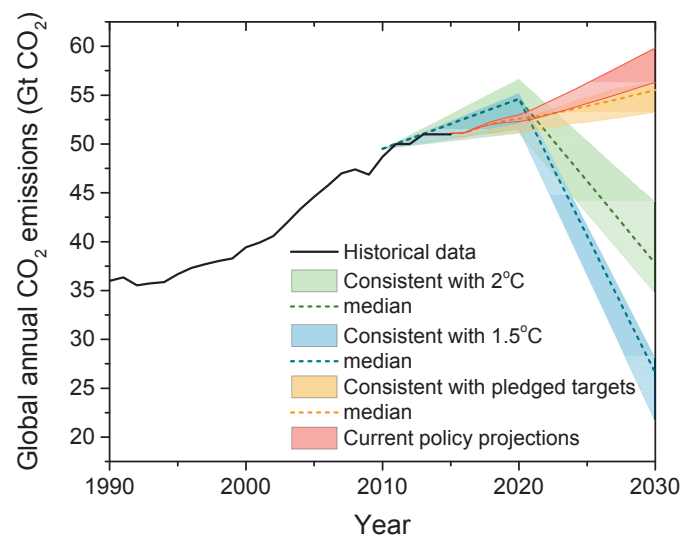


Figure 1.5 – Annual CO₂ emissions in gigatonnes (1 billion tonnes) and the current projections for future emissions. The current projections remain higher than those pledged (median given to account for different pledges) and significantly greater than the target emissions required to limit global warming to 2°C (Cancun agreement) and 1.5°C (Paris agreement). Adapted from Climate Analytics and New Climate Institute, 2019.²¹

The effects of a couple of degrees increase in temperature are so devastating that even leading politicians have been forced to take notice. In 2015, a monumental step for climate activists around the world was achieved when the Paris Agreement was reached, with 195 nation states (including all EU nations) signing a pledge to keep the global average temperature this century under a 2°C increase over pre-industrial levels.²⁷ The secondary aim of the agreement is to limit the temperature increase to 1.5°C, which, through a myriad of numbers, figures and comparisons, the IPCC Special Report has outlined as essential in order to mitigate the worst of the damage.

However, while the agreement is promising, actions speak louder than words and current data trends do not tell favourably of progress. As shown in Figure 1.5, the annual CO₂ projections based on currently pledged targets leave us far short of the 1.5°C warming goal. In fact, if climate change is to be limited to a 1.5°C increase over pre-industrial levels, net CO₂ emissions must drop to zero by 2050. As such, we cannot rely on the finite fossil fuels remaining until a solution is found. An entire shift in energy production and consumption is required, and quickly.

1.2 Fuel for the future

With the severity of our predicament elucidated, the quest for greener alternatives to fossil fuels is of paramount importance. In order to mitigate the effects outlined above, alternative fuel sources must be abundant and non-polluting. Several main candidates have risen above the rest; geothermal, wave and tidal, biomass, wind and solar. It is probable that our future energy landscape will involve a combination of these renewable sources. In particular, our current global renewable landscape, although still small compared to the fossil fuel giants, is dominated by hydropower (Figure 1.6, *left*). This stems, at least in part, from the maturity of this technology which has been used since the 1920s. Yet, despite providing a cleaner alternative to carbon energy sources, hydropower is not particularly environmental friendly. In fact, there are a number of studies that highlight the negative impact that hydropower dams can have on the surrounding environment, from the flooding and subsequent displacement or loss of wildlife, to the high energy cost of building and maintaining the necessary infrastructure.^{28,29}

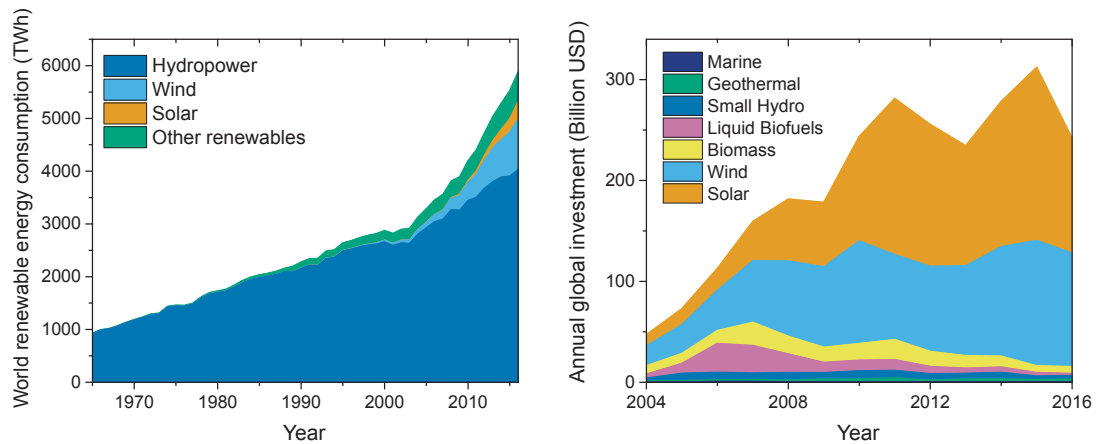


Figure 1.6 – *left*: A breakdown of the main renewable energy sources based on their annual worldwide consumption. Hydrothermal (*blue*) dominates over other energy sources while solar energy (orange) barely achieved global scale impact until 2010. *right*: Annual global investments into various renewable energies. Solar and wind energy currently receive by far the greatest financial investment. Adapted from the BP Statistical Review of World Energy 2019 and IRENA International Renewable Energy Agency.^{30,31}

In comparison to hydropower, solar energy has only reached a scale of global significance relatively recently (Figure 1.6, *left*), however, the contributions of this young field to global energy consumption are growing more rapidly than for any other renewable source. And, with enough solar energy irradiating Earth every two hours to power our planet for an entire year, it is easy to see the attraction.³² Figure 1.6 (*right*) compares recent annual global investment for each of the major renewable energy technologies (excluding large hydropower schemes). In light of its huge potential, solar energy has received the largest financial investment over the last decade.^{30,31} Interestingly, we can see in Figure 1.7 that this investment has largely spurred the increase in both the accumulative module capacity of solar harvesting materials (a measure of both the quantity and performance of solar technology) and the contribution that solar has had to world energy consumption.³¹ This is both hopeful, in that increased investment has fuelled real progress, and a little disappointing, as it affirms that scientific progress and thus change is, as ever, dictated by where the money flows. It does, however, clearly demonstrate that solar energy will have an increasingly significant role in tomorrow's energy provision.

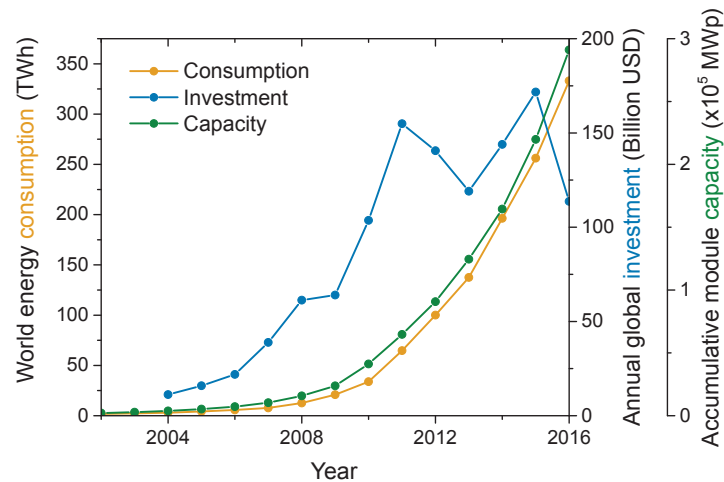


Figure 1.7 – Annual global investment in solar energy (in billions of USD, *blue*) compared to the installed solar photovoltaic (PV) capacity (MW, *green*) and the total annual consumption solar photovoltaic energy (TWh, *orange*). Adapted from the BP Statistical Review of World Energy 2019 and IRENA International Renewable Energy Agency.^{30,31}

1.2.1 Day and night

There are several ways by which one can harness the power of the sun. The most well-known and well-studied of these is the field of photovoltaics (PV), which utilises the photovoltaic effect first observed by Becquerel in the 17th century.³³ The first photovoltaics, or solar cells, for generating electricity consisted of single semiconducting materials and gave rather poor efficiencies (< 1%), but today, through the use of multi-junction silicon cells, efficiencies as high as 30-40% are readily attainable, approaching the theoretical limits for this material.³⁴ Furthermore, the cost of these silicon PV modules has dropped dramatically since their first manufacture in the 1970s, plummeting from ~100 \$/W down to between 0.20 – 0.40 \$/W in 2018, and thus allowing widespread installation, even in remote, off-grid locations.^{35,36} Significant progress has also been made on flexible alternatives to silicon cells, such as organic photovoltaics (OPV) and perovskites, which have reached efficiencies of 17.3% and 25.2%, respectively.^{34,37} These solution-processable alternatives have yet to reach wide-scale commercial production owing to as-yet-unresolved stability issues, but are predicted to have niche applications where light-weight technologies or transparent surfaces are required. Other means of extracting solar energy utilise the heat irradiated. These include small-scale solar thermal systems, usually used to heat water for residential purposes, and large-scale plants, employing multiple mirrors to concentrate sunlight and direct it towards a turbine to generate electricity.^{38,39}

Both PV and solar thermal conversion systems (as well as many other renewable technologies) are limited by the same fundamental restriction in their power generation: the intermittency of the energy source. The diurnal cycle of Earth as it orbits the sun naturally inhibits solar energy generation for several hours each day – the same hours of darkness in which electricity usage peaks. This mismatch in the periods of peak energy generation and consumption results in energy loss during the day, as excess electricity cannot be absorbed by the grid, and insufficient supplies at night. Incidences of poor irradiance in bad weather and stronger seasonal variation in the global north and south can also add to this supply and demand issue.

An obvious solution to this problem is to find a means of storing the excess energy generated in periods of high photon flux so that this may be used as and when needed. Research into batteries to try to meet this challenge is growing, and with large success, but is predicted to face size and weight limitations for certain applications such as powering ships and aircraft.⁴⁰ Alternative storage solutions are likely to be essential if renewable sources are to power the future.

1.2.2 A source of inspiration

Fortunately for us, mankind was not the first to develop an energy storage system for sunlight. Green plants obtain the energy they need to thrive from sunlight, using this to drive chemical reactions in the process known as photosynthesis. Photosynthesis converts water and CO₂ into O₂ and simple carbohydrates such as glucose, the latter which acts as both a food source for plant growth and a building block for formation of more complex carbohydrates. A thermodynamically up-hill reaction, photosynthesis is only possible with the input of solar energy. In other words, nature has developed a means of storing solar energy within chemical bonds.

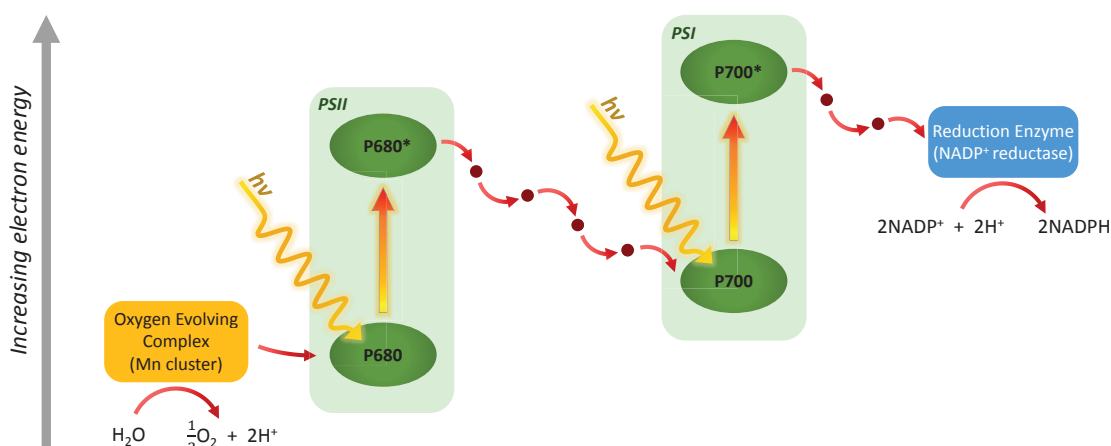


Figure 1.8 – Schematic representation of natural photosynthesis in green plants and algae. The two light-absorbing systems, PSII and PSI, are separated by a redox shuttle (red arrows).

Inspired by nature's ingenuity, the field of artificial photosynthesis was born, with scientists seeking to generate so-called solar fuels by storing solar energy in chemical bonds. In line with this goal, there is an immense body of academic work examining the exact mechanism by which natural photosynthesis is achieved – work that the length restrictions of this thesis do not permit me to discuss in detail. A basic depiction of the photochemical steps involved is given in Figure 1.8, the Z-scheme of photosynthesis. In short, there are several key components that need be replicated if one is to mimic nature: a chromophore or light harvester; a redox shuttle to separate the photogenerated charges; a reactive site for reductive chemistry; and a reactive site for oxidative chemistry.

In natural photosynthesis, light absorption is separated into two parts – photosystem one (PSI) and photosystem two (PSII) – named, rather counter-intuitively, in order of their discovery and not their sequential activity. Chlorophyll antennae in PSII absorb visible light ($\lambda_{\text{max}} = 680 \text{ nm}$), exciting one electron for each photon absorbed and thereby generating a population of electrons with greater energy. To prevent the relaxation of this excited population back to the ground state with the re-emission of a photon, the electrons are spatially separated from the ground state through a series of electron transporting complexes (shown in red in Figure 1.8). This cascading reaction sequence brings the electrons to PSI, permitting further light absorption ($\lambda_{\text{max}} = 700 \text{ nm}$) and a similar separation of photogenerated charge. In this manner, electrons of sufficient energy to reduce CO_2 to carbohydrates (via the Calvin cycle or other biochemistry) are produced. Meanwhile, the resting state of PSII is recovered by removing electrons from water, thereby oxidising H_2O to O_2 , the protons from which can be used in the carbon fixation chemistry.^{41–43}

Photosynthesis is a beautiful example of the intricate and sophisticated mechanisms present in the natural world. Indeed, this process is so complex that to attempt to replicate it seems almost ludicrous. Not only has nature had a ~3 billion year head-start to develop this system (a rather long time compared to our ~70,000 year existence),⁴⁴ but photosynthetic organisms are, of course, living, and capable of self-repair. This last point is particularly important as natural photosynthesis is actually very inefficient. Proteins in PSII suffer constant damage from photo-degradation and, depending on the species examined and the irradiated light intensity, need to rebuilt and repair themselves as frequently as every 20 minutes.^{45,46} Furthermore, the efficiency of converting light energy into biomass through natural photosynthesis is reported to be 3-6% on average, with some plant species only achieving efficiencies of 0.1%.⁴⁷ It is evident, therefore, that if mankind is to rely on solar energy storage to fuel the future, it cannot be based on a system of mass conversion of sunlight to traditional biofuels, particularly when considering the competition this would create between energy and food sources. Rather than mimic natural photosynthesis in all its detail, the Z-scheme depicted in Figure 1.8 should serve as inspiration, a concept to be adapted and altered, shaped and moulded, to provide for the ever growing needs of humanity.

PV technologies, as discussed in Section 1.2.1, provide a light harvesting platform that could form the basis of an artificial photosynthesis process, absorbing photons and separating charges as seen in PSII. However, the conversion of charge into chemical fuel is an ongoing challenge, complicated by the blurred definitions of what a useful fuel or product is. Considering the urgency with which we must reduce our greenhouse gas emissions to combat climate change, it arguably follows that we should further imitate nature in targetting CO₂ as the starting material for fuel synthesis, thereby forming a carbon fuel. An example of a Z-scheme for artificial photosynthesis from CO₂ and water is given in Figure 1.9.

The reduction of CO₂ can lead to a number of different products, however, depending on the reaction conditions employed, such as the pH, temperature, flow rate, electron flux and catalyst material. A-LEAF is an EU-funded consortium of 13 research groups from across Europe aiming to build an 'artificial leaf' to reduce CO₂ to formate.⁴⁸ This product was chosen for both its volatility (liquid at room temperature and thus easier to separate from unreacted gasses) and its comparative ease of synthesis compared to longer chain hydrocarbons (current carbon fuels). Likewise, the Joint Centre for Artificial Photosynthesis (JCAP) is an older (and larger) American cousin to the European project, having received \$75 million from the US Department of Energy in its second round of funding to 'convert carbon dioxide into renewable transportation fuels,' though the target fuel has yet to be specified.⁴⁹

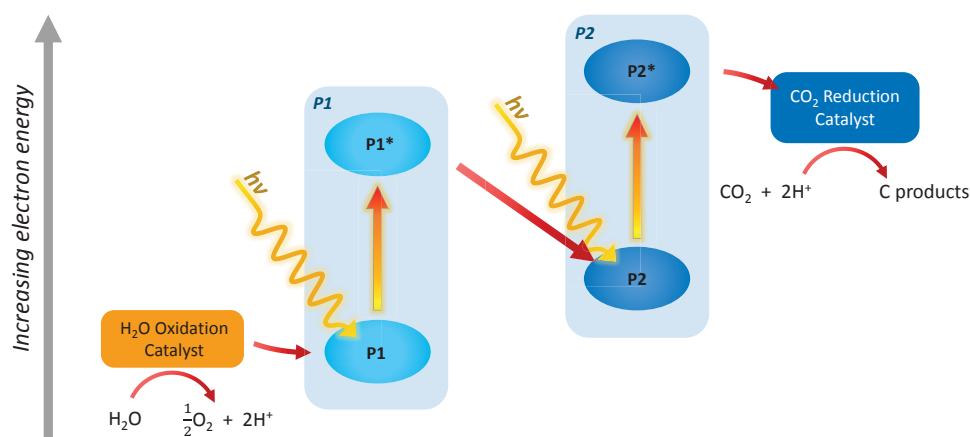


Figure 1.9 – Schematic representation of the process of artificial photosynthesis to synthesise carbon-based fuels from CO₂ and H₂O. P1 and P2 are photoabsorbers configured in a Z-scheme or type II heterojunction. However, artificial photosynthesis could also be possible with one photoabsorber with ground and excited states of adequate energy.

From the severity of our current predicament outlined in Section 1.1.2, it is clear that for both A-LEAF and JCAP to be successful in their missions, the fuel synthesised must be of immediate practical applicability as a real alternative to fossil fuels – both in terms of energy capacity and adoption into existing energy infrastructure. Naturally, this necessitates that CO₂ conversion efficiencies must far exceed those observed in natural photosynthesis. However, while the field of artificial photosynthesis has grown significantly over the last 20 years, bringing with it improved designs, concepts and efficiencies, we are still far off the mark needed if we are to maintain global average temperatures less than 1.5°C above pre-industrial levels. The best solar energy-to-fuel conversion systems working to reduce CO₂ to carbon fuel report efficiencies of between ~0.2 – 13% depending on the product and reactor^{50,51} – an admirable scientific effort, but not enough to challenge our global energy system in time to mitigate climate disaster.

There is, however, another option. An alternative, simpler, non-carbon fuel which can be synthesised far more readily and put into effect without detracting from continued research into true artificial photosynthesis. Better still, this fuel has an incredibly high energy density and, because it is carbon-free, its combustion is completely non-polluting. Furthermore, there is already the infrastructure in place along with expanding investment to bring this energy source to a globally relevant scale. This fuel, the simplest in all the cosmos, is hydrogen.

1.3 Solar water splitting

The term ‘hydrogen economy’ is one frequently used by businesses, governments, scientists and policy makers alike to describe the use of hydrogen as a ‘green’ energy storage medium. And this economy is already, at least in part, a reality. Electric vehicles that make use of fuel-cells (reacting O_2 and pressurised H_2 to give electricity) have been commercially available since the early 2000s.⁵² Some modes of public transport such as buses are also now H_2 -powered, with >10 million km driven across Europe by fuel-cell buses thus far.⁵³ A new fleet of H_2 -powered buses has even been purchased to hit the congested streets of London in 2020 in an attempt to ease local atmospheric pollution.⁵⁴ But, while these examples suggest a promising awakening of public consciousness to the threat our current fossil fuel consumption entails, none of these H_2 -powered vehicles can truly be considered ‘green’. This is because the H_2 used in these cases is not from a ‘green’ source. As the lightest atomic element, very little hydrogen is found naturally on Earth and so >95% of H_2 used in all industrial processes comes from the steam-reforming of methane, a process which releases copious CO_2 into the atmosphere. In other words, hydrogen fuel, while clean at the point of use, is almost as dirty as the fossil fuel it aims to replace.

Methane, however, is not the only source of hydrogen. Water is a comparatively abundant, non-polluting source from which hydrogen fuel may be generated. Electrolysis is the process of applying sufficient potential to water to reduce protons to molecular hydrogen and oxidise hydroxyl groups to molecular oxygen, the reverse process of that occurring in a fuel-cell. If the electrolysis of water could be powered by sunlight, then solar energy could be stored as a fuel (hydrogen) which could then be used in existing technologies such as fuel-cells to power everyday life. This is the concept of solar water splitting, the main focus of this thesis.

1.3.1 Two methods, one goal

There are two main methods by which the scientific community is attempting to generate renewable, green hydrogen (Figure 1.10). Unfortunately, both practices have yet to reach market and the second in particular is still at the lab-scale research stage. The first relies on existing technologies, thereby offering the potential for more immediate results, whereas the second option draws further on inspiration from natural photosynthesis, which may provide cost benefits in the long term. Ideally, both technologies will be implemented in the near future to encourage alternative energy consumption.

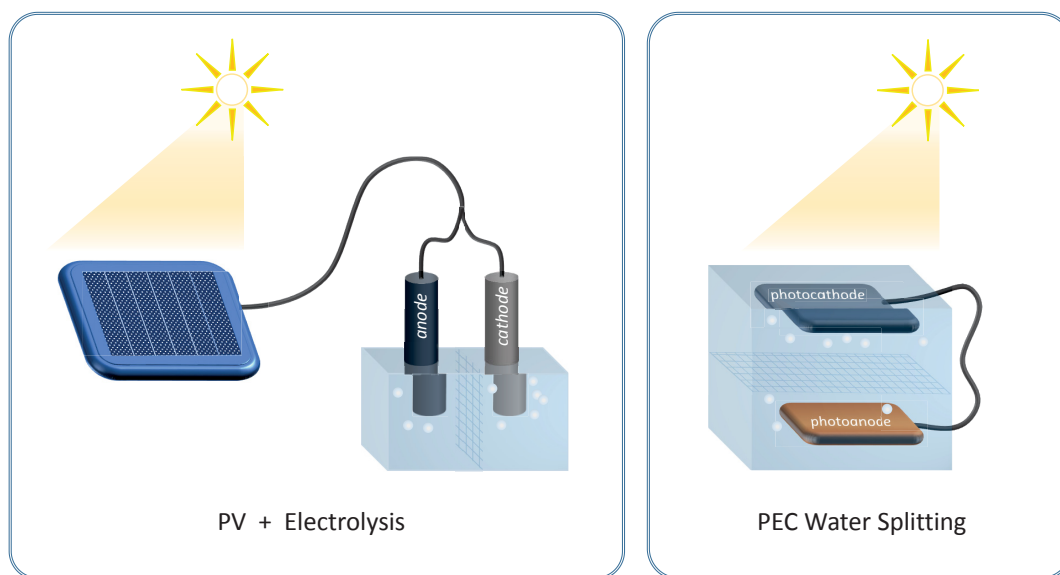


Figure 1.10 – A simplified schematic representation of a combined PV-electrolysis setup (*left*) and a setup for photoelectrochemical (PEC) water splitting (*right*). A proton conducting membrane is shown in both cases as an example of a possible gas separation method.

PV-electrolysis

By coupling high-performing photovoltaics with electrolyser materials, PV-electrolysis is perhaps the most obvious means of achieving solar water splitting. This method affords the separation of the light harvesting process from fuel generation, as solar electricity generated by PVs could be transported many miles to an electrolysis facility. As such, this method may be best suited to large scale fuel plants, particularly because electrolyser materials are often precious metals such as platinum, inferring high costs.

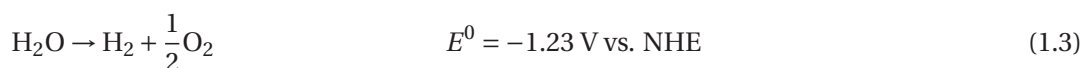
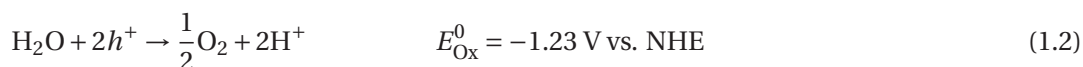
Photoelectrochemical water splitting

Photoelectrochemical (PEC) water splitting seeks to combine light absorption and catalysis into one integrated device. This is, in essence, much more similar to the water oxidation reaction in natural photosynthesis, with direct charge transfer between PSII and the manganese cluster that evolves oxygen from water (Figure 1.8). In natural photosynthesis, the protons generated in this process are shuttled to aid CO₂ reduction chemistry, but in an artificial water splitting device would be reduced to molecular hydrogen.

In principle, a PEC water splitting device could consist of just one material submersed in water that is capable of absorbing solar radiation and performing the oxidation and reduction reactions required to generate O₂ and H₂, respectively. In practice, however, there are few known materials that meet these requirements and those that do have restrictions on their maximum achievable efficiencies. As such, two different materials are often employed in tandem, one performing the oxidation chemistry and the other the proton reduction. Before we can examine such integrated devices in detail, we must understand the physical and chemical limitations of solar water splitting.

1.3.2 The bottleneck

The two reactions involved in (photo)electrochemical water splitting are given in Equations 1.1 and 1.2 below, which, when combined, give Equation 1.3. The reduction potentials for each are also given, referenced against the normal hydrogen electrode (NHE) at pH 0:



These equations represent the reactions occurring under acidic conditions, though similar equations can be drawn under alkaline conditions. Overall water splitting thus theoretically requires an energy equivalent to 1.23 V. In reality, as discussed in more detail in Chapter 2, a significantly higher voltage than this must be applied to overcome additional losses associated with these reactions. This additional voltage, known as an overpotential (η), is larger for the water oxidation reaction (Equation 1.2) than proton reduction (Equation 1.1), in part owing to the chemical requirement for four oxidative equivalents, or holes (h^+), to come together to form one molecule of O₂ and the sluggish kinetics that result.

Taking these overpotentials into account, efficient water splitting requires an applied potential in the range of 1.7 – 2.4 V, depending on the materials used. In PV-electrolysis, this voltage can be achieved by increasing the number of junctions in multi-junction solar cells, usually at the cost of the attainable current. The development of photovoltaics for this purpose, with high power conversion efficiencies and minimal losses, is an entire field of its own and is not discussed further in this thesis. In PEC water splitting, the materials employed are almost exclusively semiconductors, as these materials can be excellent light absorbers with tunable properties. The necessary voltage for water splitting can be achieved in this case by a suitably large band-gap between the highest occupied electronic states of the semiconductor (which form the valence band – VB) and the lowest unoccupied electronic states of higher energy (the conduction band – CB).

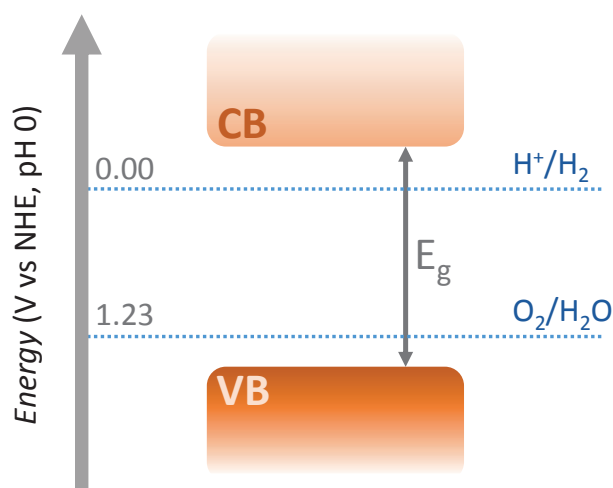


Figure 1.11 – A simplified schematic representing the conduction band-edge (CB) and valence band-edge (VB) for a semiconductor of adequate band-gap (E_g) to meet the thermodynamic requirements of PEC water splitting. The CB-edge must be of greater energy than the proton reduction potential and the VB-edge must be of lesser energy than the O_2 reduction potential, as shown.

Just as an excited population is obtained by light absorption in PSII (Figure 1.8), so can the same occur in a semiconductor, exciting electrons from the occupied valence band to the empty conduction band. In order for the excited electrons to have enough energy to reduce protons to H_2 , and for the holes (the absence of electrons) in the valence band to be able to accept electrons from water and thereby evolve O_2 , the bands must straddle the reduction and oxidation potentials given in Equations 1.1 and 1.2. This is demonstrated in Figure 1.11.

While there are a few semiconductors with adequately aligned band-edges, maintaining a band-gap large enough to afford the required photovoltage reduces the proportion of solar irradiation that may be absorbed by the semiconductor. Titanium dioxide (TiO_2) was the material first employed for PEC water splitting in the pioneering work of Fujishima and Honda in 1972.⁵⁵ However, TiO_2 has a band-gap of 3.2 eV, which equates to an absorption edge of 420 nm. Figure 1.12 shows the absorption spectrum of TiO_2 (*blue*) projected on top of the solar irradiation spectrum that reaches the Earth's surface (AM 1.5G, *yellow*). The overlap between the two spectra gives an idea of how much of the solar spectrum can be utilised. By assuming that all irradiation in this region is used with 100% efficiency, one can calculate the maximum solar-to-hydrogen efficiency that can ever be obtained for any material, which for TiO_2 , despite its well aligned band-edges, is only $\sim 4\%$.

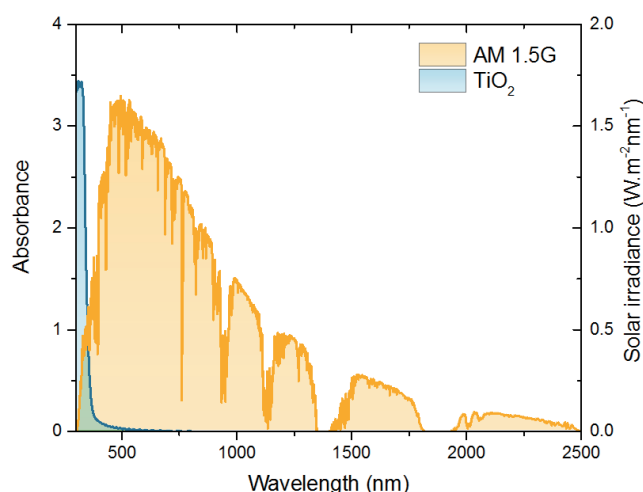


Figure 1.12 – A typical absorbance profile for a TiO_2 film (*blue*) is plotted against the solar irradiation spectrum at the Earth's surface (AM 1.5G, *yellow*). The overlap between the two spectra is very small (*green*), revealing the limited capacity of TiO_2 for absorbing sunlight. This is a problem for all wide band-gap semiconductors for solar water splitting.

It is for this reason that researchers are pursuing Z-schemes for solar water splitting, as shown in Figure 1.8 for natural photosynthesis and in Figure 1.9 for artificial photosynthesis. Such designs afford the decoupling of the two reactions involved by connecting an anode and cathode together in tandem. Either or preferentially both of these electrodes can be light absorbing, and by selecting semiconductors with complementary band-gaps, a larger proportion of the solar spectrum can be utilised.

Metal oxides are the most frequently employed semiconductor materials for solar water splitting, used as photoanodes, photocathodes, and catalyst layers to aid the chemical reactions at the electrode surfaces. As mentioned above, the 4-hole water oxidation reaction is considered to be the kinetic bottleneck to PEC water splitting, and it is in this area in particular that metal oxides have had a dominating role. In order to make hydrogen the global fuel of tomorrow, it is essential that the efficiencies of the water oxidation reaction are improved. To achieve this, a fundamental understanding of the successes and limitations of the champion materials is necessary. In particular, the charge carrier dynamics and loss pathways in metal oxides need to be understood and the results fed into the development of the next generation of solar fuel devices. As we shall see in the next chapter, there already exists a large body of research dedicated to this task. The aim of this thesis is to further contribute towards our enhanced collective understanding on the road to a more stable energy future.

Chapter 2



Image from unsplash.com with permission

2 Metal oxide photoanodes: kinetics from charge generation to catalysis

Metal oxides are the most commonly used materials for solar water splitting, with numerous examples in the literature of their success as both photoanodes and electrocatalysts for water oxidation. In this chapter, the state-of-the-art and frequently employed oxides are introduced and our current understanding of their performance limitations are discussed. The timescales of trapping and recombination in different oxides are examined, as well as the kinetics of water oxidation catalysis. The disparity between the timescales of recombination and catalysis underpins many of the challenges facing these materials, and as such forms the basis of this chapter. Specific detail is given to tungsten oxide (WO_3) and mixed nickel/iron oxyhydroxides (Ni/FeOOH), the materials on which the results of this thesis focus. I conclude this chapter by outlining some of the questions remaining regarding these metal oxides for water oxidation.

2.1 Metal oxides in water oxidation

As mentioned at the end of the last chapter, metal oxides have dominated laboratory research on solar water oxidation since the first conceptualisation of the process using TiO_2 in the 1970s. There are several good reasons for the persistent use of this class of material. Firstly, metal oxides are relatively Earth-abundant (admittedly to varying extent, and discounting noble metal oxides). The first-row transition metals iron and nickel are amongst the most prevalent elements on the planet, and their semiconducting oxides, such as Fe_2O_3 (a component of rust), are the predominant form in which they are found.⁵⁶ This natural abundance feeds directly into the second benefit of these oxides – cost. Low material cost and high availability are crucial for the development of a new renewable energy technology if it is to meet the size of the demand outlined in Chapter 1. Aside from these economically inclined considerations, the prevailing use of metal oxides for solar water oxidation predominantly stems from their high stability under the strong oxidising condition imposed, coupled with their relative ease of synthesis.^{57–60} From atomic layer deposition (ALD) of aluminium oxide to the templated growth of titania, there are multiple synthetic methods currently employed to give a myriad of divergently-structured oxides, each of which can be altered in composition to contain various dopants, defects, or mixed stoichiometries.⁶¹ As such, metal oxides are a playground of possibility and it can be far from obvious which oxides will be best suited to a given application.

Broadly speaking, there are two possible applications of metal oxides in solar water oxidation: as a semiconductor photoanode or as a catalyst, the latter of which includes co-catalysts atop photoanodes and dark electrocatalysts (see Figure 1.10). Owing to the additional requirements on photoanodes to absorb solar irradiation and separate photo-induced charges as well as perform water oxidation catalysis, we shall consider this photoanode application first.

2.1.1 Semiconductors and junctions

Bands and band-gaps

A semiconductor, as the name suggests, is a material with a degree of conductivity greater than that of an insulator but less conductive than a metal. The property of semi-conductivity arises from the relatively small size of the band-gap between the occupied electronic states that form the valence band (VB), and the un-occupied states of the conduction band (CB). The absence of a break in the electronic states of metals allows for free conduction, whereas the large gap present in insulators inhibits thermal or optical excitation to a conductive state under ambient conditions. In semiconductors, the band-gap is still small enough that electrons may be readily excited into

the upper band (hence the name ‘conduction band’). The bands consist of discrete molecular orbitals for each of the many bonding and anti-bonding interactions present, but these discrete levels are so close to one another in energy that they can be considered a single band (Figure 2.1, *upper left*). The centre of these bands are therefore a function of the energy of the constituent atomic orbitals, and the band-widths give the degree of electron delocalisation in the solid. The band positions are determined by the strength of the bonding (and therefore also anti-bonding) interactions between the constituent atoms. This is readily understood for diatomic interactions when forming molecular orbitals as shown in Figure 2.1 (*upper right*), where ΔE translates to the energy gap between the centre of the resultant bands and the gap between the edges of the bands is the band-gap (E_g). The size of the band-gap in a solid is therefore determined by the band-widths, i.e. the degree of overlap of the constituent orbitals. In a three-dimensional solid, bonding can occur in multiple directions resulting in a highly complex electronic band structure, usually depicted along symmetry lines in reciprocal space (k-space) as shown, for example, in Figure 2.1 (*lower left*). While the information contained within such a diagram is undoubtedly highly useful, this degree of detail is usually not considered when examining an oxide for a single light absorption/oxidation step. Instead, a diagram such as that shown in the lower right panel of Figure 2.1 can be drawn which depicts the lowest band-gap for the material of interest. This lowest energy transition is known as *direct* if there is no change in the wave-vector k between VB and CB, as the transition is allowed according to the laws of quantum mechanics, or *indirect* if there is a change in k during excitation, thus denoting a forbidden transition. As a forbidden transition is less probable, indirect band-gap semiconductors often need to be thicker to absorb as much incoming irradiation as direct band-gap analogues.

For an ideal semiconductor, the Fermi level (E_F) is placed directly in the middle of the band-gap and represents the chemical potential at which the theoretical likelihood of finding an electron is 1/2 (Figure 2.1, *lower right*). This stems from the Fermi-Dirac distribution function describing the thermal excitation of a small number of electrons from the valence to conduction band. In a real solid, however, the Fermi level is seldom found half-way between the two bands. In practice, all metal oxides contain impurity atoms, or deviations from stoichiometry, which shift the chemical potential away from this intrinsic equilibrium position. Even a very small number of impurities can be enough to completely mask the number of thermally generated carriers and alter the semiconducting properties of the material. As such, semiconductors are usually defined by these impurities, referred to as dopants when introduced intentionally. Doping an intrinsic semiconductor with metal atoms of lower atomic number than the host metal results in an electron deficiency and thus a lower Fermi level, closer to the valence band. The electron deficiency can also be considered as an excess of positively charged holes which are then the

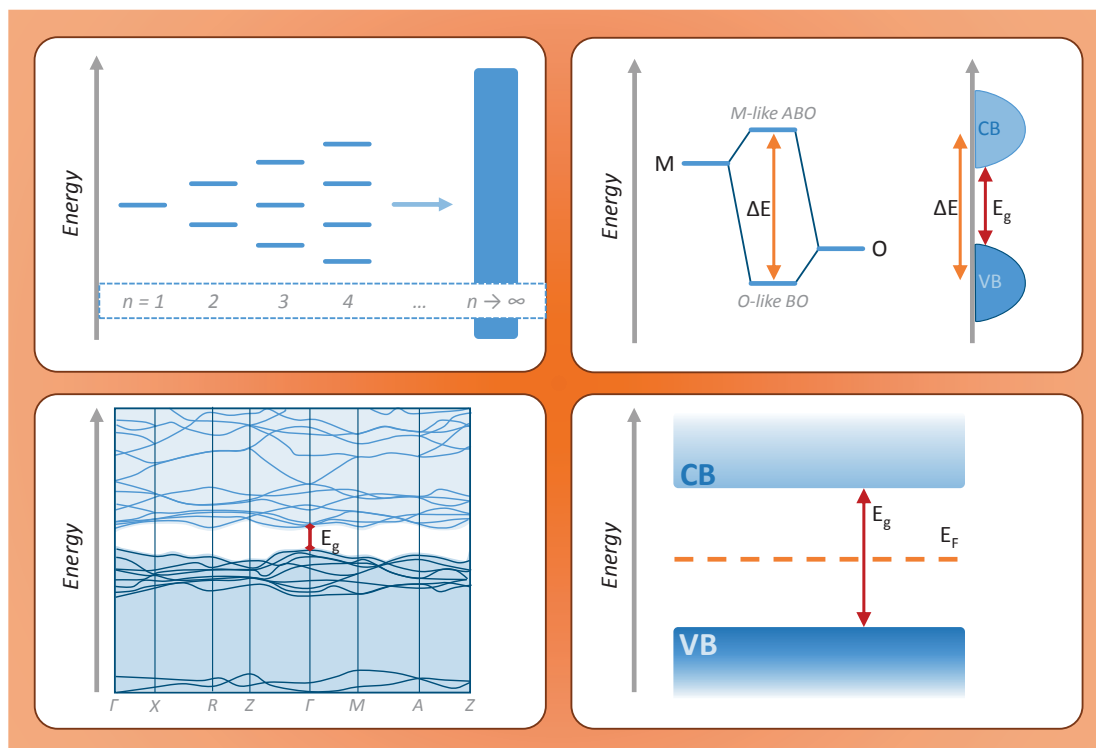


Figure 2.1 – *upper left*: The construction of a band from multiple orbitals (n) of equal or similar energy. *upper right*: Consideration of molecular orbital theory in the character of bands. As the metals will invariably be more electropositive than the oxygen atoms, the valence band is often oxygen-like in nature, consisting of O 2p orbitals or related hybridised orbitals, whereas the conduction band is usually metal-like. *lower left*: An example of the band structure of a metal oxide (in this case based on rutile TiO_2 ⁶²) along different axes in reciprocal space. The direct band-gap is highlighted. *lower right*: A simplified diagram used when considering only the smallest band-gap of a semiconductor. The Fermi level (E_F) is located in the middle of the band-gap in an intrinsic (undoped) semiconductor.

majority charge carrier in the resultant material, referred to as a *p-type* semiconductor. When dopants of greater atomic number are added to the semiconductor, the Fermi level is lifted closer to the conduction band and the material is said to be *n-type*, with electrons as the majority charge carrier and holes as the minority carrier. The most common dopants to metal oxides are oxygen vacancies – sub-stoichiometric oxygen concentrations resulting in excess electrons (n-type doping) – as discussed in more detail in Section 2.2.1.

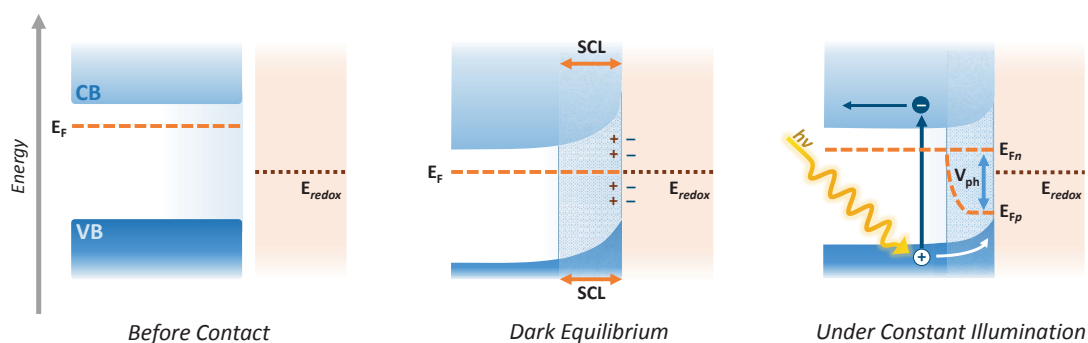


Figure 2.2 – *left*: The position of the bands and Fermi level (E_F) before equilibration with the electrolyte (E_{redox}) for a typical n-type semiconductor. *centre*: After equilibrating in the dark. The Fermi level of the semiconductor aligns with E_{redox} , forming upwards band-bending in the semiconductor with a space-charge layer (SCL). *right*: Positions of the bands at equilibrium under constant illumination. A photovoltage (V_{ph}) is created by the splitting of the quasi Fermi levels for electrons and holes. Holes are drawn towards the surface where they may perform oxidative chemistry.

Almost all semiconductors used as photoanodes for water oxidation, or any light-driven oxidation reaction, are n-type. This is due to the phenomena that occur when a semiconductor is introduced to a suitable electrolyte medium, demonstrated with the schemes in Figure 2.2. Contact of the semiconductor with the electrolyte results in the formation of a semiconductor-liquid junction (SCLJ) and an equilibration of the electrode Fermi level with the chemical potential of the dominant redox couple in the electrolyte. As n-type semiconductors commonly have Fermi levels higher in energy than the redox couple to which they are coming into contact with, this equilibration is usually achieved by a flow of electrons from the semiconductor to the electrolyte. This loss of the majority carriers in the semiconductor leads to the formation of a depletion region – a layer at the surface of the photoanode that is depleted of electrons and thus slightly positively charged. The charge is balanced by an equal negative charge in the electrolyte at the electrode surface, the Helmholtz layer, which forms part of the electrical double-layer that defines the structure of the electrolyte near the interface (Helmholtz and Gouy-Chapman-Stern layers). Importantly for photoanode functionality, the formation of the depletion region – also known as the space-charge layer (SCL) – creates a field within the semiconductor as a result of the difference in charge between this surface region and the bulk material, bending the conduction and valence bands. The upward band-bending observed in most n-type semiconductors encourages the desired directionality of excited carrier movement, with electrons drawn into the bulk and holes promoted to the surface where they may react (see central schematic, Figure 2.2).

Aside from the dielectric constant of the semiconductor (invariable) and any external bias applied (variable), the width of the SCL (W_{SC}) is primarily determined by the doping density of the semiconductor (N_D). In essence, there is an inverse proportionality between the two terms; the lower the donor density of the film, the further into the bulk electrons must be depleted in order for equilibrium with the electrolyte to be achieved, and thus the wider the SCL. And vice versa; a larger doping density gives a narrower SCL. The potential drop between the electrode surface and bulk will be the same in both cases, as will the total integrated field generated, but the field will be far weaker at any one point for a system with a wider depletion region. The effect of space-charge layer width on photoanode performance is an activate area of solar fuel research and is further examined in Chapter 5.

The final schematic given in Figure 2.2 shows the semiconductor–liquid junction at equilibrium under constant illumination. When light of energy equal to or greater than the band-gap is irradiated on the semiconductor, electrons are excited into the conduction band, generating minority holes in the valence band. This distinct generation of charge splits the Fermi level into quasi-Fermi levels that represent the energy of the electron (E_{Fn}) and hole (E_{Fp}) populations. The energy difference between these newly generated quasi-Fermi levels is referred to herein as the photovoltage (V_{ph}) (the use and definition of this term is frequently under debate in the literature). If the photovoltage were equal to the 1.23 V + overpotential (η) required for water splitting, then the semiconductor could theoretically perform complete water splitting under irradiation, assuming correct energy alignment of the VB and CB, as was shown in Figure 1.11.

Performance metrics

More often than not, the semiconductors examined for the solar water oxidation reaction do not have a sufficiently energetic conduction band edge to also perform the proton reduction reaction, with narrower band-gaps preferred to optimise light absorption. As mentioned in the previous chapter (Section 1.3), tandem systems coupling a photoanode and photocathode provide a means of reducing the requirements on a single semiconductor by dividing the two half-reactions between two electrodes. Ultimately, pairing semiconductors of complementary band-gaps is desirable, with both electrodes presenting similar efficiencies and rates of catalysis such that charge neutrality may be maintained at all times. In reality, the yields and kinetics of water oxidation catalysis are currently lagging behind those for hydrogen evolution.⁶³ Thus, to optimise potential semiconductors for the sluggish water oxidation reaction, photoanodes are frequently examined without a coupled photocathode, using instead a standard three-electrode cell with a counter electrode such as platinum. A potential can be applied between the photoanode (the

working electrode of the cell) and the counter electrode, as shown in Figure 2.3, to complete the circuit. Further details on the experimental set-up of the three-electrode cell are given in Chapter 3, Section 3.2.4.

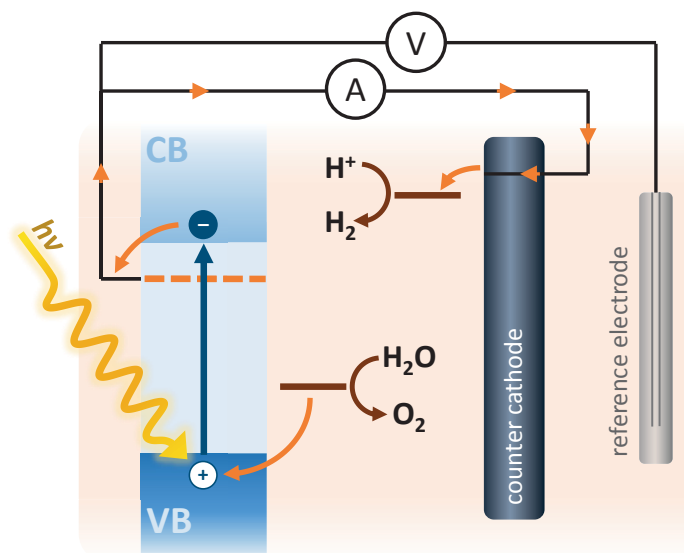


Figure 2.3 – Schematic of a three-electrode cell in which the working electrode is the metal oxide photoanode of interest. The proton reduction reaction occurs at the counter electrode (usually platinum) and the potential applied to the working electrode is referenced against a separate reference electrode (often Ag/AgCl couple). The cell has a window to allow illumination of the photoanode. The direction of electron flow is given by the orange arrows. Current flow and voltage is measured or controlled via the potentiostat (A = ammeter, V = voltmeter).

Using this set-up, the performance of different metal oxides can be compared. In each case, the reaction at the cathode is set to be non-limiting and can thus be largely ignored. The main method by which candidate photoanodes are initially assessed is by their current output as a function of applied voltage, i.e. a J-V curve (see Figure 2.4). If we first consider an ideal n-type electrode equilibrated in the dark, the application of a cathodic potential will work against the in-built field of the space-charge layer to reduce the surface band-bending. The voltage needed to completely flatten the bands, bringing the field to zero, is referred to as the flat-band potential (V_{FB}). For a photoanode to oxidise water in the dark, a voltage equal to 1.23 V (the thermodynamic requirement for water splitting excluding overpotentials) need be applied as well as any additional potential required to bring the Fermi level down to the valence band such that there are oxidised states to accept electrons. Under illumination, the voltage demand is reduced by the photo-generation of holes in the valence band, i.e. the creation of a photovoltage, which

also works to partially flatten the bands (see Figure 2.2, *right*). Therefore under illumination, the minimum voltage required for an ideal photoanode (no overpotentials for either half-reaction) is just enough to ensure band-bending to give carrier directionality – just positive of the flat-band potential. The additional energy requirement to raise electrons from the conduction band edge of the anode to the proton reduction potential at the counter electrode is accounted for by the potentiostat but will not be observed in the J-V curve for the photoanode, which is referenced against the reference electrode (Figure 2.3).

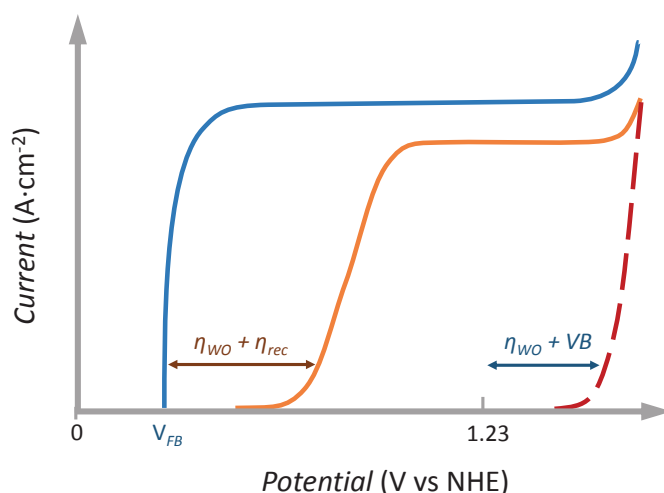


Figure 2.4 – Representative J-V curves for ideal (*blue*) and real world (*orange*) metal oxide photoanodes for water oxidation. The dashed line (*red*) gives the current produced by the real catalyst in the dark. The onset of dark catalysis is delayed by the overpotential for water oxidation and the VB position. The total overpotential for photocurrent onset is the sum of the minimum recombination turn-off potential and the water oxidation overpotential.

The ideal J-V curve under illumination should therefore resemble that shown in blue in Figure 2.4. The onset in photocurrent will be relatively sharp as it is determined by thermodynamics and plateaus with increasing voltage as the maximum current is dictated by the number of carriers generated (the number of photons absorbed). In reality, there are significant kinetic overpotentials to be considered for the water oxidation reaction (η_{WO}) which manifest as a shift in the voltage at which photocurrent onset is observed (Figure 2.4, orange). Furthermore, as discussed in more detail in Section 2.2, charge separation yields are often poor under small fields, necessitating larger applied potentials to really drive current (η_{rec}). Thus, by determining how late the onset is in comparison to the flat-band potential, one can define a total overpotential for water oxidation on the metal oxide examined. Naturally, an earlier onset (smaller η) is desired as this reduces the external energy input required for the process, thereby improving efficiency. The rise in photocurrent in real systems is also not as sharp as the ideal scenario due to competing

recombination processes, which also affect the maximum attainable photocurrent in the plateau region. As such, the J-V curve is a useful metric for initial assessment of any potential metal oxide photoanode, but ultimately, this simple line is defined by multiple underlying competing processes with different kinetics. Therefore, if we want to understand more about a candidate material and its limitations, we need to probe the charge carrier dynamics directly.

2.2 Charge carrier dynamics

As mentioned at the start of this chapter, there are many different processes that need to come together for water oxidation to occur effectively. For the most part, these can be considered sequentially: light absorption, followed by charge separation, carrier migration, surface accumulation and finally catalysis. However, there are also processes by which charge is lost through recombination and these loss events can occur at different times between charge generation and catalysis. This is complicated further by acknowledging the non-linear movement of carriers, the potential for charge trapping on either intentionally placed dopant sites or unintentional defects, and the complex nature of the interface with the electrolyte. Moreover, there are many orders of magnitude difference in the timescales of charge generation and that of catalysis, thus necessitating that carriers survive all recombination processes in-between (Figure 2.5).⁶⁴ As such, I shall try where possible to be chronological and begin at the beginning.

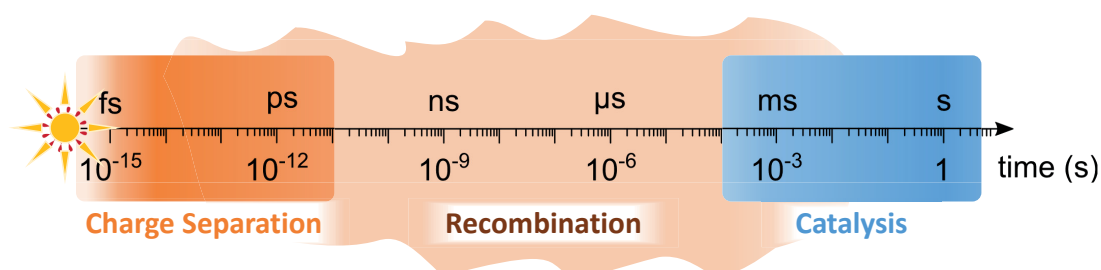


Figure 2.5 – Timeline of charge carrier dynamics from femtoseconds to seconds, with approximate timescale ranges for charge separation (*orange*) at one extreme and catalysis (*blue*) at the other. Recombination (*beige*) can occur over almost the entire timeline, leading to performance losses.

2.2.1 Charge generation and bulk recombination

The absorption of light of suitable energy by a metal oxide semiconductor results in excitation of an electron from valence band to conduction band for each photon absorbed, leaving a positively charged hole in the valence band (see Figure 2.3). If light with even greater energy

than the band-gap is absorbed, the carriers generated relax or *cool* to the band edges, usually sub-picosecond.^{65,66} In semiconductor physics, these charges together are referred to as a bound electron-hole pair, and the number of these pairs generated (i.e. the number of photons absorbed) constitutes the upper limit in current generation and product formation. Owing to the high dielectric constants for metal oxides, the electron and hole, though initially considered a pair, are seldom excitonic in nature, meaning that they may readily separate and move independently of one another. The movement of excited electrons and holes through the photoanode is largely governed by one of two processes: *drift* or *diffusion*. Drift is the directional charge movement under an applied field and thus is the dominant motion of charges within the SCL. Electrons photogenerated within this depleted region are drawn towards the bulk of the material and the back contact to be extracted, whereas holes are promoted towards the surface to react with the electrolyte. This directional movement aids spatial charge separation and is discussed in more detail in the following section. Diffusion of charge carriers occurs when there is no field present, which constitutes the bulk of the photoanode. Depending on the thickness of the material (or constituent particle size, if mesoporous) and the width of the SCL (determined by the doping density), the bulk may or may not represent a significant proportion of the electrode. Charge carriers generated in the bulk, and thus moving by diffusion, are far more likely to annihilate one another by recombining with a carrier of the opposite charge. This recombination is referred to as *geminate* if the electron and hole originated from the same excitation episode, i.e. the same electron-hole pair, and *non-geminate* if they were generated by absorption of different photons. Geminate recombination is therefore more probable in the first few picoseconds following excitation before charges have had a chance to move apart, and is predicted to be more limiting in materials with lower dielectric constants and thus is less relevant to metal oxides.

Independent of whether bulk charge carriers recombine via geminate or non-geminate recombination, the largest loss of photogenerated carrier concentration tends to occur in the bulk over the first couple of nanoseconds after excitation.^{67,68} The kinetics of these loss processes can be monitored using techniques such as transient absorption spectroscopy – a pump-probe technique, in which carriers are optically excited (pumped) and the induced change in absorbance (probe) is monitored with time. Depending on the temporal resolution of the instrumentation used, carrier kinetics can be monitored from attoseconds to tens of seconds, permitting viewing of such rapid recombination processes (see Chapter 3 for more details). Poor charge separation, alongside slow kinetics of catalysis (see Section 2.2.3), is considered to be the limiting factor in photoanode performance for most commonly examined transition metal oxides such as titania (TiO_2), hematite ($\alpha\text{-Fe}_2\text{O}_3$) and bismuth vanadate (BiVO_4)^{69–73} For example, hematite presents many of the desired qualities of a photoanode for PEC water oxidation – it is Earth-abundant,

stable under oxidation, and has a band-gap of 2.1 eV, thereby giving a predicted maximum solar to hydrogen (STH) efficiency of 15.4%.⁷⁴ However, the maximum attained STH is typically much less than half this value (often around 1–2%).⁷⁵ Absorbed photon-to-current efficiency (APCE) measurements provide a measure of how many of the charges generated in a photoanode survive recombination episodes to give current, also referred to as the internal quantum efficiency (IQE). The highest IQE percentages reported for doped hematite are only 40–50% under 400 nm irradiation, suggesting that more than half of electrons and holes are lost to recombination.⁷⁶ Slightly larger values have been reported for tungsten oxide (WO₃), the material of focus in Chapters 4 and 5, although the maximum does not exceed 80%.^{75,77}

To improve these efficiencies, the charge separation efficiency intrinsic to each material needs to be improved. There are several means by which the scientific community is attempting to achieve this. One of the simplest methods is to reduce the quantity of bulk material to minimise carrier movement by diffusion, although care must be taken to retain enough material for adequate photon absorption. The most elegant way to maximise light absorption and minimise bulk transport is by nanostructuring the oxide material to increase the surface to bulk ratio. Over the last 20 years, various morphologies and synthetic methods have been introduced and some degree of nanostructuring is common to all current state-of-the-art photoanodes. The extent to which nanostructuring is required depends upon the carrier diffusion lengths in the material. In hematite, the minority carrier (hole) diffusion length is only 2–4 nm, implying that holes may only travel 2–4 nm from their site of generation in the absence of a field before they are annihilated.^{73,78} As such, holes in hematite should ideally be generated no further than 4 nm from the SCL if they are to perform useful chemistry.

Aside from altering the quantity of bulk material, there are other methods proposed to increase the lifetime of charge carriers that target the SCL at the surface. Increasing applied bias may broaden the SCL and thus allow photogenerated charges to experience directional fields, thereby aiding charge separation. The formation of solid-state junctions such as type II heterojunctions or overlayers have also been shown to increase charge carrier lifetimes.⁷⁹ These surface modifications are discussed in more detail in Section 2.2.2.

The final major method by which one can attempt to limit bulk recombination losses is to step away from the intrinsic material and alter extrinsic dopant concentrations.

Doping

Doping of a metal oxide can lead to a broad array of characteristics depending on both the host material and dopant. As discussed with regards to Figure 2.1, the valence band of a metal oxide tends to be based on oxygen (2p) orbitals, whereas the conduction band has greater character of the more electropositive metal (though hybridisation can occur in both bands). This electronic nature defines the transport of charge carriers through the material, which is termed small polaron hopping.^{80,81} A polaron is formed by the temporary localisation of a charge and resultant distortion of the relaxed surrounding lattice. The size of the polaron is related to the degree of delocalisation of the charge, thus a small electron-polaron is a temporary localisation of an electron over one or two metal centres. In WO_3 , electron-polarons form following light absorption, which result in the localised reduction of some W^{6+} centres to W^{5+} centres. As the electrons travel (either by drift or diffusion), the reduced centres hop to neighbouring sites. As such, charge carrier mobility in most metal oxides is low, and, since conductivity is a product of mobility and carrier density, poor mobility increases the likelihood of fast recombination events, resulting in the short carrier diffusion lengths mentioned.

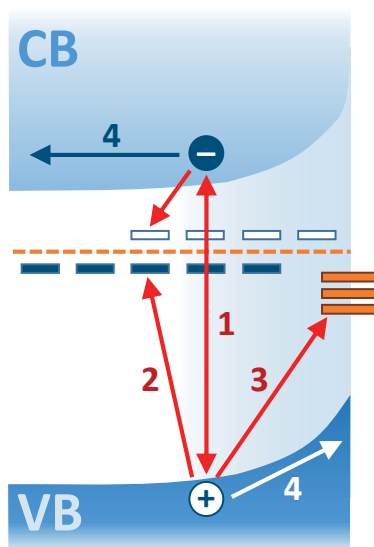


Figure 2.6 – A simplified band diagram indicating the main recombination processes (*red arrows*) that may occur, including those through trap states (*boxes*). Route 1 indicates band-to-band recombination (geminate or non-geminate), route 2 indicates trapping into defect states introduced through doping. White boxes are ionised defect states which may trap electrons, and blue states are non-ionised (filled) states which may trap holes. Route 3 indicates hole trapping into surface states (*orange*) formed by termination of the semiconductor lattice at the SCLJ. Route 4 indicates the desired movement of charge carriers.

One objective of chemically doping with a foreign atom is to increase the electronic doping density (the number of majority carriers) to counteract low carrier mobilities and increase conductivity. However, the addition of dopants usually entails introducing chemical defects to the host material, which frequently give rise to energetic states within the band-gap (Figure 2.6). These states are often referred to as traps because photo-generated charges may relax to these states and potentially recombine or simply reduce the attainable photovoltage and reductive/oxidative power of the electrons/holes, respectively. As such there are many studies examining the role of bulk defects in fast recombination processes, with much uncertainty remaining. For example, in α -Fe₂O₃ photoanodes, doping with Ti is widely considered to improve conductivity,^{82,83} but there are also studies that suggest that the electronic states formed may act as shallow traps which mediate recombination.⁷⁶ Similarly, there have been multiple publications examining elemental doping of BiVO₄, with different degrees of effect observed and even larger variations in the assigned rationale.^{84–86} This is further complicated by semantics, as the terms ‘trapping’ and ‘recombination’ are sometimes taken to be synonymous and at other times are not. Nitrogen is a common dopant added to TiO₂ samples, with reports that the states formed result in a lower effective band-gap and thus improved visible light absorption.^{87–89} A recent time-resolved optical study on this material proposed that improved performances were the result of increased charge trapping, rather than a reduction in trapping.⁹⁰ As such, it is clear that further studies of this kind are required to elucidate the full impact of doping.

Doping need not always take the form of addition. The most common dopants and defects to metal oxide photoanodes are metal or oxygen vacancies, which give rise to altered stoichiometries and associated trap states. In particular, oxygen vacancies are intrinsic to the most frequently studied oxides, but their role in charge separation is poorly understood.⁷³ Chapter 5 is dedicated to further elucidating the impact of oxygen vacancies on trapping and recombination in WO₃ as a model material for water oxidation.

2.2.2 Kinetics at junctions

As mentioned in the previous section, forming a junction is one means of potentially increasing charge carrier lifetimes. These can largely be split between two classes: the semiconductor-liquid junction (SCLJ) introduced in Section 2.1.1 and junctions between semiconductors and other solids (SCSJ).

The semiconductor–liquid junction

Introduction of an n-type semiconductor into an aqueous medium results in the formation of a space-charge layer (SCL), as was discussed in Section 2.1.1. Photogenerated charges formed within (and those that manage to diffuse to) this region are subject to the SCL field, which runs perpendicular to the electrode surface. This field preferentially drives holes towards the electrolyte, thereby aiding their spatial separation from electrons. Recombination is still possible within this depleted region, however, if the field does not adequately inhibit the coulombic attraction between photogenerated electrons and the population of accumulated holes at the interface. To further enhance charge separation, greater external bias may be applied to increase band-bending, preventing electron flow towards the surface, as well as increasing the proportion of charges generated within the widened SCL. The success of this approach has been demonstrated in hematite, for example, for which the application of just 0.4 V versus the reversible hydrogen electrode (RHE) was found to increase the half-lifetime of charge carriers by a factor of 1000.⁹¹ Similar results detailing improved carrier lifetimes with applied bias can also be found on other metal oxides, such as BiVO₄ and TiO₂,^{64,92–95} and added to with new analyses of WO₃ in Chapter 4. Of course, the application of an external bias is not desirable in a final PEC cell as this detracts from the total energy efficiency of the conversion process, but it does serve to demonstrate the importance of the depletion region on carrier dynamics. A potential alternative method of altering the SCL width, without succumbing to the energy losses associated with an additional input bias, is to further adjust doping densities. As addressed in Section 2.1.1, the degree of n-type doping dictates the width of the SCL. This approach is examined in Chapter 5 by varying the intrinsic oxygen vacancy concentration in WO₃.

Another important consideration in analysing charge carrier dynamics at the SCLJ is the nature of the semiconductor surface. Termination of the bulk lattice will result in a different chemical structure at the electrolyte interface, thereby presenting opportunity for the formation of trap states at dangling bonds. These traps are frequently referred to simply as surface states (see Figure 2.6) and their role in water oxidation is heavily debated. In part, this debate stems from uncertainty of the energy of these surface states with respect to the band-edges and, more importantly, the redox potential for water oxidation. Some claim that water oxidation may proceed through these states, but this will only be possible if they lie higher in energy (closer to the VB) than the water oxidation potential.^{96,97} A larger number of publications suggest that it is necessary to passivate these surface states, removing the possibility of holes trapping to an energetic level from which they can no longer perform useful chemistry.^{98–101} Whether passivation is simply achieved by hydroxylation of the surface by the electrolyte is not well

reported or understood. Regardless of whether active passivation is required or not, the addition of overlayers and formation of solid-state junctions has shown promising results on charge carrier lifetimes, as discussed below.

Semiconductor–solid-state junctions

There are several solid-state junctions that may be used to improve photoanode performance for water oxidation. One such example is the use of overlayers: thin layers of oxides or metals added to passivate surface states or improve stability and through which holes may reach the electrolyte.^{101–103} Another common type of SCSJ is referred to as a heterojunction, in which two metal oxides with different band-gaps form one photoanode. The idea is that photogenerated charges in one oxide are transferred to the other, creating improved spatial separation of electrons and holes and thereby prolonging carrier lifetimes. The concept is analogous to that observed in the redox cascade in natural photosynthesis (see Figure 1.8). Heterojunctions can be further sub-categorised into type I, II, or III, depending on how the band-edges of the two oxides involved relate to one another. Type II heterojunctions are the most common for water oxidation, in which the band-edges are staggered such that the conduction and valence band-edges of one oxide are higher in energy than the respective band-edges of the other (see Figure 2.7, *left*). This set-up encourages holes to flow to one oxide, and electrons to flow to the other, thereby reducing the likelihood for recombination.⁶⁴ Which of the oxides forms the primary light absorber will depend on the materials used (their band-gaps) and their thicknesses, as well as the order in which they are deposited and oriented relative to the irradiating light source. Both overlayers and heterojunctions also have the potential to induce band-bending at the SCSJ, which, depending on the relative Fermi levels of the materials involved, may work to further aid or hinder the separation of photogenerated charge.

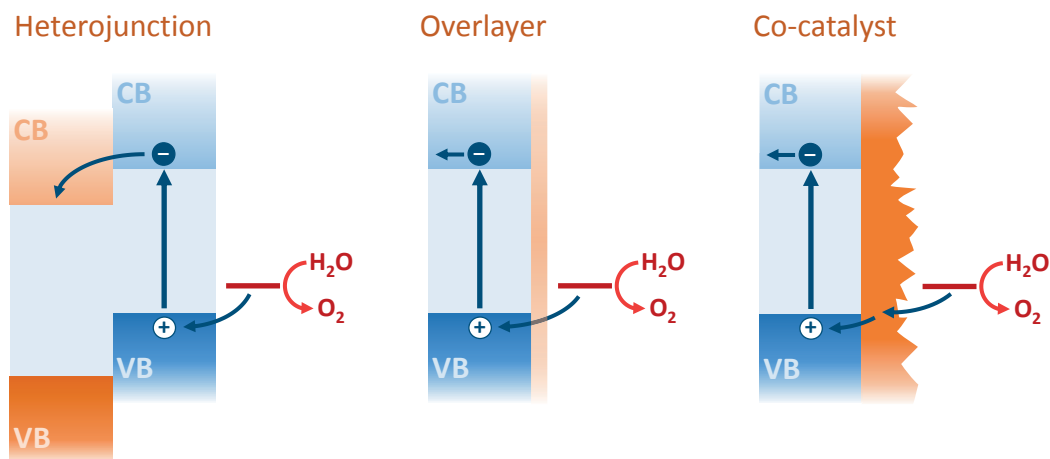


Figure 2.7 – Schematic illustrating the three main types of semiconductor-solid-state junctions found in water oxidation catalysis using metal oxides. *left*: A type II heterojunction in which the upper material is absorbing the light. *centre*: A photoanode with an overlayer to passivate the surface. *right*: A photoanode with a co-catalyst deposited on top.

Arguably the most regularly employed SCSJ in water oxidation is that between a metal oxide photoanode and an added co-catalyst (see Figure 2.7, *right*). According to IUPAC's Gold Book, a catalyst is any substance that increases the rate of a reaction without altering the overall energy change involved in said reaction.¹⁰⁴ This is, of course, well understood, but it is not always trivial to determine whether the rate of water oxidation has been enhanced by the addition of a catalyst material, or whether improved performance originates from a supposed catalyst preferentially acting in the role of an overlayer or heterojunction. As such, determining the kinetics of catalysis using time-resolved techniques is of importance to better our understanding of such materials.

2.2.3 The kinetics of catalysis

At the furthest end of the kinetic timeline given in Figure 2.5, we reach the timescales of water oxidation catalysis. The slow reaction rates frequently reported for oxygen evolution on metal oxides give rise to two significant issues. The first, as we have already encountered, is that recombination processes tend to occur at much faster timescales, depleting holes before they have the chance to react with the electrolyte. As discussed in Sections 2.2.1 and 2.2.2, material improvements such as control of doping or addition of junctions may be used to retard recombination processes and increase charge carrier lifetimes. If slowing recombination is not adequate, the alternative approach is to speed up catalysis. This can be achieved by adding a more reactive co-catalyst, as discussed in more detail in this section. The second issue incurred by slow water oxidation

kinetics is the potential for reactive holes to perform alternative chemistry at the surface. If another reaction is kinetically and/or thermodynamically more feasible, it is probable for this oxidation to use up the available holes before oxygen may be evolved. The Faradaic efficiency of a material is a measure of how much of the photocurrent obtained arises from the desired reaction – in this case water oxidation to molecular oxygen. In most photoanodes, this value approaches unity, although WO_3 is often reported to have a Faradaic efficiency lower than the other common oxides. The addition of a catalyst therefore has the potential to offer a second benefit, improving the Faradaic efficiency for water oxidation as well as enhancing the rate of catalysis. Depositing co-catalysts, however, can add to material and manufacture costs, particularly in the case of precious metal catalysts such as platinum, palladium, or iridium oxide. Thus, the kinetics of the bare photoanode should be examined and optimised first before any catalyst addition is considered.

Catalysis on photoanodes

There are multiple ways by which the kinetics of catalysis on a semiconductor may be calculated. Two, in particular, dominate the work in this thesis, as well as much of the work found in literature produced by the Durrant group on this topic. That is not to say that these two techniques are necessarily superior to others, merely that each offers a different perspective, relying on different assumptions, and better suited to different materials. The two techniques elaborated on herein are namely transient optical spectroscopy (often abbreviated to TAS, where 'A' is for absorption) and variants of spectroelectrochemistry (SEC). Both families of techniques are optical and their details are given in Chapter 3.

As mentioned briefly in Section 2.2.1, TAS can be used to monitor carrier kinetics over a wide range of timescales. The earlier time ranges are more applicable to the recombination processes discussed above and are used to great effect in Chapter 5. Optical spectroscopy at slower times, however, can detail the rates at which remaining carriers are consumed in reactions at the electrode surface. Fortunately, photoexcited electrons and holes tend to give absorbance features at optical wavelengths that can be readily probed. In TiO_2 , it has been shown that holes may be probed with blue light (400-550 nm) and electrons with red light (~ 800 nm),^{105–108} with similar characteristic wavelengths found in $\alpha\text{-Fe}_2\text{O}_3$, BiVO_4 and WO_3 .^{109–112} Using these wavelengths to probe the kinetics of the photogenerated carriers, Tang et al. reported that holes at the surface of TiO_2 require between 0.3–1 second on average to react with water and evolve oxygen.¹¹³ Furthermore, they demonstrate that recombination may be reduced by use of an electron scavenger, thereby increasing the yield of active holes. Cowan et al. also found that both increased bias and

reduced laser intensity can work to limit bimolecular recombination in TiO_2 and thus increase hole lifetimes (which reacted with 100% Faradaic efficiency).⁹³ A later study by the same authors compared water oxidation rates of nanocrystalline TiO_2 with $\alpha\text{-Fe}_2\text{O}_3$, revealing an even greater demand on hole lifetime in the latter (~ 3 s required for O_2 evolution) as a result of a thermal barrier to hole transfer.¹¹⁴ TAS experiments conducted on BiVO_4 also reveal rate-limiting water oxidation kinetics on the timescale of seconds.^{92, 115} WO_3 remained the only commonly studied metal oxide photoanode for which water oxidation kinetics had yet to be determined prior to the work herein.¹¹⁶

It is not only bulk recombination processes, or recombination at surface states that may pose a threat to the reaction of holes with the electrolyte. The sluggish nature of the water oxidation kinetics reported on these materials results in the accumulation of large numbers of holes at the SCLJ. This build up of positive charge can pull electrons in the opposite direction of desired current flow, leading to the annihilation of accumulated charge in a process termed *back electron-hole recombination*. As electrons are drawn away from the back-contact, this process results in negative currents in transient photocurrent data, which may then be used as an electronic signature. Overcoming this additional loss pathway necessitates the application of greater bias to further enhance the space-charge layer and the charge-separating field. In $\alpha\text{-Fe}_2\text{O}_3$ photoanodes, back electron-hole recombination has been observed on catalytic timescales when anodic bias is less than 1.3 V versus the reversible hydrogen electrode (V_{RHE}), although this value is likely to be sample dependent.¹¹⁷ Similar potential requirements have also been reported in BiVO_4 ($1.4 V_{\text{RHE}}$) and TiO_2 .^{115, 118} Once again, WO_3 was the only frequently used transition metal oxide for which the turn-off potential of back electron-hole recombination was unknown prior to this thesis work.¹¹⁶

The second family of techniques relevant to the catalytic studies in this thesis are based on spectroelectrochemistry (SEC) and offer a very different approach to the study of catalysis by exploiting the steady-state. Pure SEC in itself doesn't offer any kinetic information, measuring only the change in absorbance as a function of applied potential. However, the Durrant group have developed this further, adding a temporal element and merging with the concepts of TAS to fabricate a new technique: stepped light absorption spectroscopy (SLAS), also known as PIAS (photo-induced absorption spectroscopy). Like TAS, this technique is also pump-probe, but the pump duration is long enough to allow pseudo-steady-state catalysis to be achieved. The pump is stepped to different light intensities such that the kinetics of accumulating holes may be determined as a function of their population. The pseudo-steady-state current is collected simultaneously, and interpreted with the optical data to give a full rate law analysis according to

the following equation¹¹²:

$$\frac{dp_s}{dt} = J_{\text{holes}} - k_{\text{WO}} \cdot p_s^\beta \quad (2.1)$$

where p_s is the concentration of surface holes, J_{holes} is the flux of holes to the surface (photocurrent), k_{WO} is the rate constant for water oxidation, and β is the order of reaction with respect to the concentration of surface holes. This equation assumes that back electron-hole recombination at the surface is negligible due to application of sufficient bias (the threshold for which can be calculated using TAS and transient current data, as discussed above).

Under the pseudo-steady-state conditions of SLAS, the rate of change of surface hole concentration with time will be zero and thus the photocurrent will be equal to the rate of consumption of holes, i.e. the rate of water oxidation. In this manner, the rate constant may be determined as well as the order of reaction with respect to the species that are observed in the optical signal.^{112, 118, 119} A recent publication by the Durrant group draws parallels between rate-law studies of the common metal oxide photoanodes, which appear to give similar reaction orders with respect to accumulated holes, suggesting similar water oxidation mechanisms.¹²⁰

The limitation for both TAS and SLAS is that samples must have a band-gap energy equivalent to a wavelength that can be readily pumped (ideally UVC, visible or NIR) as well as give rise to species that can be optically probed. For this reason, there have been no rate-law studies to date on dark catalyst materials.

Catalysis on catalysts

At the very beginning of this chapter in Section 2.1, I mentioned that there were two main roles that metal oxides tend to fill in water oxidation catalysis. The first, more frequented role, which has been discussed in detail thus far, is that of the photoanode – responsible for light absorption, charge separation, and often (though not necessarily) catalysis. The second role adopted by these robust materials is that of a dark catalyst, *i.e.* an active catalytic material that does not participate in light harvesting. This catalyst may function independently as an electrocatalyst for PV-electrolysis devices, or be deposited on top of a photoanode to act as a co-catalyst. Previously, these roles have been dominated by precious metal catalysts such as iridium oxide, palladium and platinum which give high catalytic efficiencies. However, the low natural abundance of such metals, along with their cost, makes them unattractive for the development of large scale water splitting devices.^{40, 121} Metal oxides may therefore present reasonable alternatives, though much is still unclear regarding their reaction mechanisms.

In particular, the functionality of a co-catalyst may be readily misinterpreted or mixed with that of an overlayer. As mentioned in Section 2.2.2, according to IUPAC definitions, a material should work to increase the rate of a reaction by lowering the activation energy in order to be termed a catalyst,¹⁰⁴ and yet it is not clear that many so-called co-catalysts function in this manner. For example, cobalt phosphate (CoPi) has been thoroughly studied as a co-catalyst for water oxidation atop BiVO_4 , WO_3 and $\alpha\text{-Fe}_2\text{O}_3$ electrodes, generating notable improvements in performance over the bare electrodes.^{85, 122, 123} However, as studies produced by the Durrant group have highlighted, the rate of water oxidation on CoPi surfaces is not significantly greater than on the bare underlying photoanodes.^{115, 124, 125} The improved performance is therefore assigned to enhanced charge separation and a reduction in back electron-hole recombination, rather than a true catalytic effect.

Currently, the most active metal oxide-based electrocatalysts for water oxidation, particularly at alkaline pH, are the family of mixed nickel and iron oxyhydroxides (Ni/FeOOH).^{126, 127} However, while the number of publications dedicated to enhanced performances using these catalysts has grown substantially over the last few years, there exists little kinetic data from which one may determine how truly ‘catalytic’ these oxyhydroxides are.

To add further complication, catalysts may also be doped with different foreign atoms, just as photoanodes often are. It is widely reported that the additional of iron, cobalt and/or zinc dopants to nickel oxyhydroxide electrocatalysts leads to lower overpotentials for water oxidation.^{128–131} Tafel analyses by the likes of Mark Koper’s group have shown there to be a pH dependence to the rate of catalysis on pure NiOOH and have concluded there to be an important deprotonation step of a Ni-dimer in the water oxidation mechanism.¹³² However, the mechanism on Fe-doped NiOOH is argued by Friebe et al. to proceed otherwise, invoking isolated corner Fe sites and thereby suggesting different reactive intermediates.¹³³ A consensus has yet to be reached regarding which metal centres are active during catalysis on high-performing mixed oxyhydroxides, necessitating further mechanistic studies to understand the roles of each metal in the oxygen evolution reaction.

2.3 Questions to answer

From bulk recombination on the fs–ps timescale to back electron-hole recombination on the order of ms–s, it is apparent that there are many loss processes to which photogenerated charge carriers may fall fate. As such, it is equally evident that the study of charge carrier dynamics is essential if we are to isolate the dominant loss pathways in promising materials and thereby better determine where improvements need to be made in the next generation of water splitting devices. With this in mind, several questions have risen to the forefront, which I have aimed to answer in this thesis, seeking to bridge multiple small gaps in our ever-expanding understanding of metal oxides for water oxidation.

WO₃

The first series of questions are related to metal oxide photoanodes – how does the space-charge layer affect charge separation? What is the role of applied bias in early timescale processes? How is recombination affected by electrolyte? How does changing the doping density of an oxide alter charge carrier transport? To answer these questions, I chose to examine nanostructured WO₃ as a model photoanode material. This interesting oxide has been studied for its electrochromic properties since the mid-twentieth century and was quickly put to work in photoelectrochemical water splitting shortly after the first study with TiO₂ in the 1970s. However, kinetic studies on WO₃ have been very limited. With a narrower band gap than TiO₂, WO₃ can absorb a larger proportion of the solar spectrum, while maintaining a deep valence band energy to provide a large thermodynamic driving force for water oxidation.^{134, 135} WO₃ is significantly more Earth-abundant than BiVO₄ and demonstrates good photocurrent onset for oxygen evolution.^{134, 136} Unlike BiVO₄ and α -Fe₂O₃, WO₃ is stable at acidic pH, which may be critical for preferential pairing with acid-stable photocathodes.^{134, 137, 138}

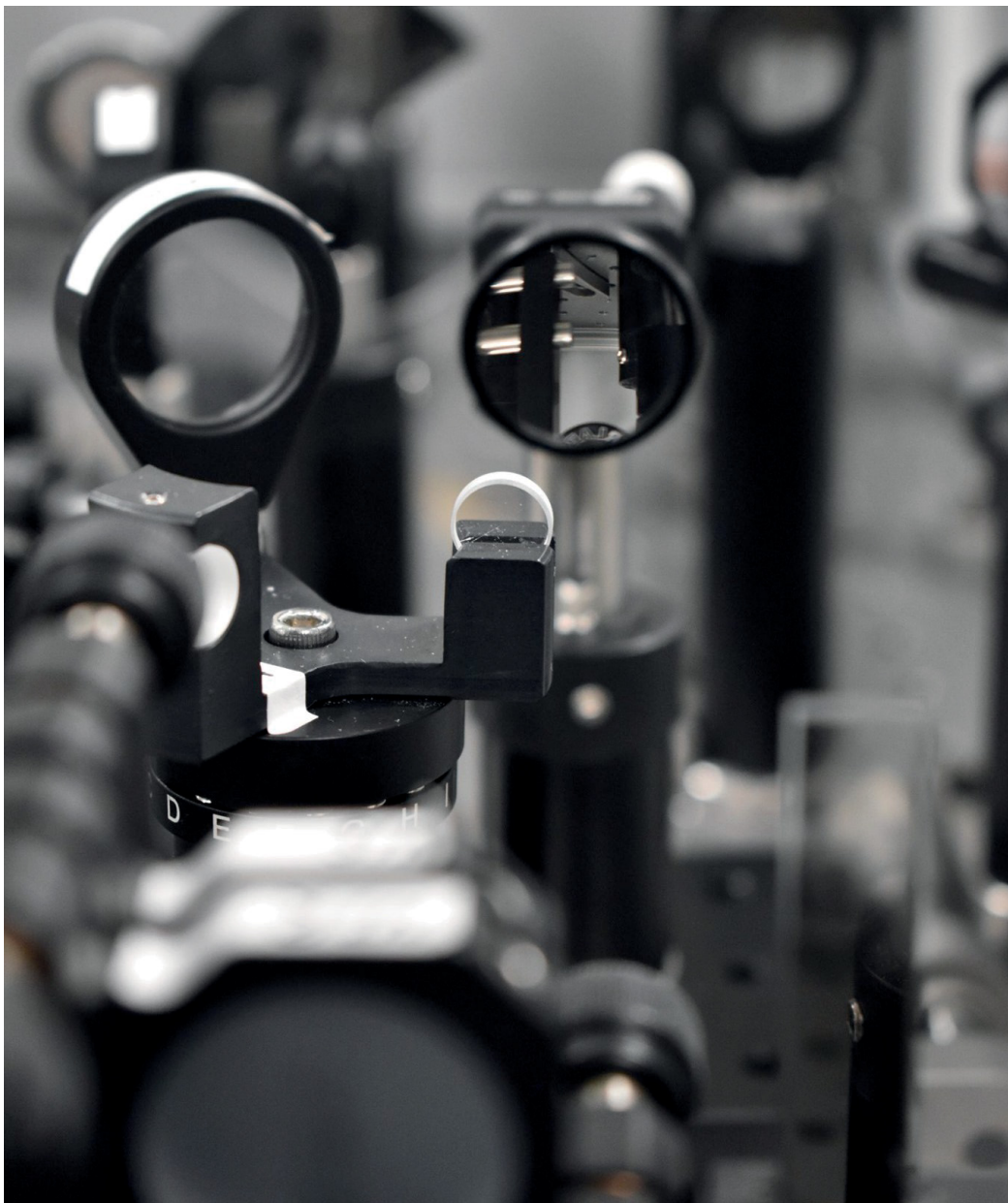
Potentially most critical in the selection of this material for kinetic studies in this thesis is the high tolerance that WO₃ has for large quantities of defects. The intrinsic doping density of WO₃ results from sub-stoichiometric oxygen concentrations (oxygen vacancies) in the lattice. A very broad range of doping densities has been reported, thereby revealing a potential for the oxygen content to be systematically varied and the role of these dopants to be analysed.^{134, 139, 140} Chapters 4 and 5 focus on this poorly understood oxide, the kinetics of water oxidation, and the role that oxygen vacancies have in charge separation and recombination processes.

Ni/FeOOH

The remaining questions addressed in this thesis specifically refer to Ni/FeOOH electrocatalysts, as much is still uncertain regarding the mechanisms of these high-performing catalysts – why are both metals required? Which metal centre accumulates catalytic charge? Do these materials function as real catalysts, how fast do they perform water oxidation? Is all of the material catalytically active? Chapter 6 presents results examining each of these questions.

Of particular note, Chapter 6 also presents the first rate-law analyses of dark-catalytic electrodes for water oxidation. As is detailed in Chapter 3, Section 3.3.3, an adapted version of SLAS was applied in which the optical pump was exchanged for a voltage input. Referred to herein as stepped-voltage absorbance spectroscopy (SVAS), this technique may be applicable to a wider range of materials, affording a better understanding of both photoanodes and potential co-catalysts for water oxidation catalysis.

Chapter 3



Photograph by author

3 Experimental methods

In this chapter details of the materials used in this work and their syntheses are given, as well as descriptions of the techniques applied to their analysis. These techniques include transient diffuse reflectance spectroscopy, spectroelectrochemistry and stepped-voltage absorption spectroscopy (SVAS).

3.1 Material synthesis

3.1.1 WO₃

All of the tungsten trioxide samples used in this thesis were deposited on FTO-coated glass substrate by aerosol-assisted chemical vapour deposition (AA-CVD). The procedure was altered to give films with different morphologies.

Briefly, CVD is a widely used synthetic technique for the deposition of thin films and can be easily upscaled for industrial purposes. The various letters prefixing the CVD acronym refer to the different methods used to introduce precursors into the reaction chamber. Aerosol-assisted CVD (AA-CVD) utilises an ultrasonic hydrolyser to vaporise the precursors, which are then transported into the reaction chamber by an inert carrier gas, in this case nitrogen. The substrate, thoroughly cleaned by consecutive sonication in soapy water, ethanol and acetone, lies on top of a carbon heating block in the chamber with the conductive side exposed. A small strip of the substrate is covered at the end furthest from the gas inlet to allow for a contact region for each sample. The precursor material nucleates onto the substrate and reacts to form the targeted material. Unused or bi-product material is disposed of through the exhaust by the carrier gas. The general AA-CVD deposition process is summarised in Figure 3.1.

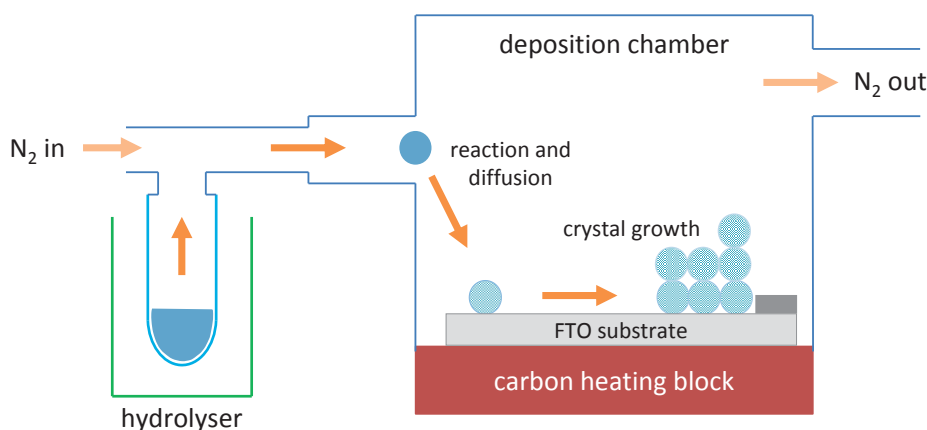


Figure 3.1 – A schematic demonstrating the aerosol-assisted chemical vapour deposition setup used in this work. Adapted from Choy.¹⁴¹ The specific conditions used for each sample type are presented in Table 3.1.

To grow the WO₃ used in this work, a precursor solution of W(CO)₆ (0.6 g, 98%) in methanol (50 ml) and acetone (100 ml) (Sigma-Aldrich, reaction grade) was used, as previously reported by Palgrave et al.¹⁴² Films with different morphologies, here named ‘flat’, ‘short needles’ and ‘long

needles', were synthesised by varying the carrier flow rate and the deposition temperature. All nanostructured films – upon which a substantial proportion of the data in this thesis was collected – comprised of a 'flat' seed layer deposition, followed immediately by a 'needle' deposition at the required temperature. The reaction conditions used for each morphology are given in Table 3.1. These were largely taken from work by Kafizas et al.¹⁴³

The deposited films were allowed to cool to below 100°C before removal from the reactor. Each was deep blue in colour, with opacity increasing with sample thickness. This blue colour, as discussed heavily in Chapters 4 and 5, arises from oxygen deficiency in the films and was observed in every synthesis, although the degree of colouration (and thus defect concentration) varied slightly between samples. The majority of the WO₃ films used in this work were annealed at 500°C in air for 2 hours before use to replenish oxygen content. Changes to annealing conditions are otherwise specified for each case (e.g. Chapter 5, Section 5.2.5).

Sample	Precursor (ml)	Deposition (°C)	N ₂ flow (sccm)
flat	2.5	325	300
short needles	5.0	375	180
long needles	10.0	375	180

Table 3.1 – AA-CVD conditions for deposition of WO₃ morphologies.

3.1.2 Ni/FeOOH

The data discussed in Chapter 6 comes from experiments on samples synthesised by collaborators outside of Imperial College London. As such, sample syntheses are summarised briefly and grouped according to the institution from which they came. Physical characterisation of these samples was largely performed by collaborators at their respective institutions, with any additional characterisation given in Chapter 6 and Appendix A.4.

Ni(Fe)OOH — UW Madison

NiOOH (as well as FeOOH and FeOOHNiOOH) was synthesised by the group of Professor Choi at the University of Wisconsin, Madison, (UW Madison) and based on an electrodeposition procedure they published in Science.¹⁴⁴ An aqueous solution (40 ml) of 100 mM NiSO₄·6H₂O (Sigma Aldrich, 98%) was prepared and purged with N₂ for 30 minutes before deposition. The pH was adjusted to 6.8–7.0 using a 0.070 M NaOH (Sigma Aldrich, 97%) aqueous solution prior to raising the temperature. In a three-electrode cell with Pt counter electrode and Ag/AgCl (4 M KCl) reference electrode, 1.2 V_{Ag/AgCl} was applied to the FTO working electrode at 70°C, passing

150 mC/cm² of charge while stirring gently. Ni(Fe)OOH, indicating NiOOH with a small quantity of incorporated iron (<10%), was formed unintentionally during deposition from Fe impurities in the electrolyte. The concentration of Fe initially incorporated was low but increased with use during electrochemistry experiments, as detailed in Chapter 6. The as-deposited Ni(Fe)OOH was black but it gradually became transparent due to the conversion of Ni(Fe)OOH to Ni(OH)₂.

NiOOH — UW Madison

To investigate NiOOH without any Fe impurities, samples were prepared in the same manner as Ni(Fe)OOH but with two modifications. First, a higher purity NiSO₄·6H₂O (Sigma Aldrich, 99.998%) was used to make a plating solution. (Low purity Ni sources can contain Fe as an impurity.) Second, the pH of the plating solution was not further adjusted because NaOH added to adjust the pH can also contain Fe impurities. The pH of the as-prepared 100 mM NiSO₄·6H₂O aqueous solution was 6.1. The absence of Fe in the NiOOH film prepared from this plating solution was confirmed by ICP-OES. All the subsequent electrochemical analyses of the Fe-free NiOOH samples were performed in purified electrolyte, in accordance with a procedure reported by Trotochaud et al.,¹⁴⁵ to maintain the pure NiOOH.

FeOOH — UW Madison

FeOOH was formed under very similar deposition conditions to NiOOH. The same potential and temperature were used, though less charge needed to be passed to obtain the same thickness (23 mC/cm² for ~80 nm thick films). A solution of 10 mM FeSO₄·7H₂O (Sigma-Aldrich, 99%) was used for the deposition (pH ~4.8).

FeOOHNiOOH — UW Madison

FeOOHNiOOH was grown by sequential deposition of FeOOH onto FTO followed by deposition of NiOOH, as described in the two steps above (23 mC/cm² was passed to deposit FeOOH and 150 mC/cm² was passed to deposit NiOOH). As the FeOOH is more porous in nature than NiOOH, the latter deposits within, as well as over, the FeOOH layer, resulting in a large surface area between the two materials and a total film thickness that is less than the sum of the two individual layers (120 nm in total). The ratio of Fe:Ni was calculated from inductively-coupled plasma analysis and found to be 79:21. Further details on these three samples are given in Chapter 6.

NiO_x — TUD

Thin films of NiO_x on FTO were provided by members of Professor Jägermann's group at the Technical University of Darmstadt (TUD). Films of 5, 10, 20 and 100 nm thickness were deposited via magnetron sputtering at room temperature and with a power setting of 15 W. The deposition was performed in a 0.03 mbar argon/oxygen atmosphere (19.6 sccm Ar and 0.4 sccm O₂) employing a 99.99% pure Ni target obtained from Kurt J. Lesker. The deposition time was altered to produce different film thicknesses. The deposition has been published in other works by the same group.^{146,147} Once the catalyst was oxidised in electrolyte under water oxidation conditions, it formed Ni(Fe)OOH.

NiO_x — ICIQ

Samples of NiO_x on FTO were also provided by Dr Bucci from the group of Professor Lloret at ICIQ. These films were synthesised by solution combustion in a one-pot reaction involving Ni(NO₃)₂(H₂O)₆ (350 g in 10 mL water) and ethylene glycol (67 uL, reaction grade) to give a metal concentration of 0.12 M. The combustion mixture was stirred for 1 h before transferring inside a muffle furnace. Two temperature gradients were applied: an initial fast ramp of 10°C/min from room temperature to 100°C, followed by a 2°C/min ramp, until a final temperature of 350°C was reached. The reactor remained at this temperature for 1 hour before cooling and removing.

3.2 Physical characterisation

A variety of physical techniques were used to characterise the material properties of the samples used, both in terms of chemical nature and of water splitting performance.

3.2.1 Scanning electron microscopy

A JEOL-6301F field emission microscope was used for scanning electron microscopy (SEM) to examine the surface morphology of the WO₃ samples. Imaging of Ni/FeOOH samples were performed externally by collaborators.

3.2.2 X-ray diffraction

X-ray diffraction (XRD) data were collected with the help of Dr Andreas Kafizas using a Bruker-Axs D8 diffractometer equipped with parallel beam optics and a PSD LinxEye silicon strip detector.

The incident irradiation beam (Cu K α 1, $\lambda = 1.54056 \text{ \AA}$, and Cu K α 2, $\lambda = 1.54439 \text{ \AA}$ in 2:1 ratio) was held at 1 degree and diffraction patterns were collected between $20 \leq 2\theta \leq 66$, with a step size of 0.05. Each pattern was fitted using GSAS-EXPGUI software.¹⁴⁸

3.2.3 X-ray photoelectron spectroscopy

X-ray photo-electron spectroscopy (XPS) was carried out using a Thermo K-Alpha spectrometer with monochromated Al K α radiation. Survey scans were collected over the 0 – 1400 eV binding energy range with 1 eV resolution and a pass energy of 200 eV. Higher resolution scans (0.1 eV) encompassing the principal peaks of C (1s), O (1s), W (4f) and W (4p), and W (4f) were also collected at a pass energy of 50 eV. Peaks were modelled using CasaXPS. [Casa Software Ltd.] Peak positions were calibrated to adventitious carbon (284.8 eV), and peak areas were adjusted using the appropriate sensitivity factors to determine the population fraction of each state.¹⁴⁹

3.2.4 Photoelectrochemical characterisation

All photoelectrochemical experiments were conducted using a three-electrode setup, with either 0.1 M H₂SO₄ (pH 1) electrolyte for WO₃ studies or 0.1 M NaOH (pH 13) for NiO_x studies, unless otherwise specified. The sample of interest formed the working electrode, platinum gauze was used as the counter electrode and an Ag/AgCl/saturated KCl (Metrohm) or Ag/AgCl/3 M KCl (Basi) electrode was used as the reference electrode ($E^o = +0.197$ volts versus the normal hydrogen electrode (V_{NHE})). All potentials are referenced against the reversible hydrogen electrode (RHE) by use of Equation 3.1.

$$E_{\text{RHE}}(V) = E_{\text{Ag/AgCl}}^o + E'_{\text{Ag/AgCl}} + 0.059 \cdot \text{pH} \quad (3.1)$$

A home-made PTFE ‘cappuccino’ cell was used with two quartz windows to allow light transmission. The front window is 0.503 cm^2 and most experiments involved front-side illumination (EE; electrode-electrolyte). As the electrodes were held at approximately fixed distances from one another by the geometry of the cell and electrolytes of sufficient conductivity were used, drops in iR were minimised. Herein, iR losses were considered negligible, unless otherwise stated, as scan rates never exceeded 50 mV/s and current densities greater than 10 mA/cm^2 were not recorded. The cell was connected to either a PalmSens (PalmSens3) or Autolab (PGSTAT101) potentiostat to monitor current as a function of applied bias. The irradiation source in linear sweep voltammetry (LSV) and cyclic voltammetry (CV) experiments was a 75 W xenon arc lamp (Hamamatsu), modulated with a KG3 filter and neutral density filters to provide $\sim 100 \text{ mW/cm}^2$

and a closer approximation to '1 Sun' irradiation conditions (solar AM 1.5G). Using a silicon diode as a control reference (known to give 0.914 mA photocurrent under 1 Sun), the position of the cell could be adjusted to give the correct intensity. Absorbed photo-to-current efficiencies (APCE) could be calculated by dividing the IPCE by the UV/Vis absorption spectrum of the sample.

Incident photon-to-current efficiency measurements

Incident photon-to-current efficiency (IPCE), also referred to as the external quantum efficiency (EQE), is the ratio of photocurrent produced under illumination to the number of photons irradiated onto the sample. This is calculated as a function of incident wavelength, as shown in Equation 3.2, and thus presents a good gauge of performance under steady-state conditions.

$$\%IPCE(\lambda) = \frac{\text{electrons } (cm^{-2}s^{-1})}{\text{photons } (cm^{-2}s^{-1})} = \frac{|j_{ph}(mA/cm^2)| \times 1240}{P_{mono}(mW/cm^2) \times \lambda(nm)} \times 100 \quad (3.2)$$

The same three-electrode-cell setup described above was used for IPCE experiments and a potential of 1.23 V_{RHE} applied by the same potentiostat. The light source was a monochromated beam from the 75 W xenon arc lamp, and the intensity was measured using another silicon diode at 25 nm intervals between 250 – 550 nm, unless otherwise specified, allowing the number of photons to be calculated.

Faradaic efficiency measurements

Faradaic efficiency experiments were performed with a three-electrode setup, analogous to the photoelectrochemical measurements but in a gas-tight H-cell with a fine frit to allow ion exchange. A Clark electrode (OXNP Unisense Oxygen Sensor) was used to quantify the oxygen evolution under applied potential and 365 nm LED light irradiation. The LED intensity was modulated between 15 and 25 mW/cm² to give approximately 1 mA of photocurrent for each of the samples. The electrode was calibrated with fixed quantities of air following each measurement. With the knowledge that four oxidative equivalents (holes) are required to oxidise water, the theoretical oxygen yield was calculated from the photocurrent obtained during the experiment and compared to the actual quantity observed to determine the Faradaic efficiency.

3.3 Optical and electrical spectroscopy

A significant proportion of this thesis is built upon spectroscopic data, particularly experiments using transient absorption spectroscopy (TAS).

3.3.1 Transient absorption spectroscopy

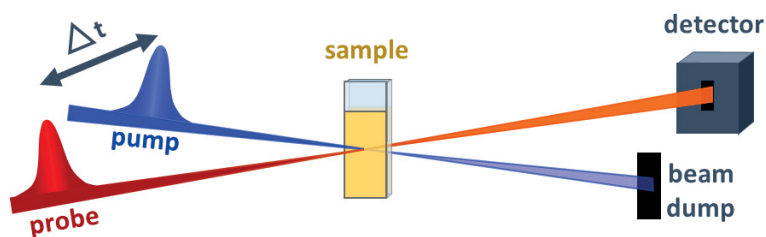


Figure 3.2 – A basic visualisation of transient absorption spectroscopy, indicating the pump and probe light sources and the time delay between them, Δt .

Transient absorption spectroscopy (TAS) is a pump-probe technique that was first developed by Lord Porter in the 1950s as a means of examining the short-lived excited species that formed under illumination in biological systems. This technique, then named flash-photolysis, has since been adopted by multiple research groups across the world to monitor the temporal evolution of photogenerated charges in numerous materials. A TAS experiment involves optically exciting the target sample with a short laser pulse (*pump*), usually at an energy sufficient to excite electrons across the band-gap of the material. The photogenerated population is then interrogated by a second light source (*probe*) – either laser or continuous wave lamp depending on the setup – and the difference in light detected is recorded as a change in optical density of the sample ($\Delta O.D.$) at a certain time delay from the original excitation (Δt). The concept is shown in Figure 3.2.

The only restrictive requirement of TAS is that the interaction of light and matter need result in a change that can be measured optically, i.e. transient species must absorb light and do so differently to the resting state of the sample. Fortunately, the absorption profiles of the photogenerated charges in most transition metal oxide systems empirically fall between the high ultraviolet (UVC) and near infrared (NIR) spectral regions, which may be readily probed. In practice, the initial generation of excited charges may present greater restrictions if a pump beam of adequate wavelength for band-gap excitation is not available. This is true of many electrocatalyst materials, such as the Ni/FeOOH samples studied in this work, which are not photoactive. Hence, TAS was only used to examine WO_3 and the other photoanodes in this thesis.

sured simultaneously via the oscilloscope during the measurement to provide information on the electron extraction (see Section TPC). Each optical and photocurrent decay presented in Chapter 4 is the average of 50-100 laser pulses. Figure 3.3 gives a schematic representation of the setup.

Calculating $\Delta O.D.$ and %Abs

In transient absorption spectroscopy, the change in optical density ($\Delta O.D.$) is computed from the change in light intensity of the probe that is detected by the photodiode after interaction with the sample. The optical density is given by the Beer-Lambert law as demonstrated in the following equation:

$$O.D._{(\lambda,t)} = -\log(T_{(\lambda,t)}) = -\log\left(\frac{I_{(\lambda,t)}}{I_{(\lambda,i)}}\right) = \epsilon_{(\lambda)} \cdot c_{(t)} \cdot l \quad (3.3)$$

where $T_{(\lambda)}$ represents the transmittance at a given wavelength (λ), $I_{(\lambda,i)}$ is the incident light intensity, $I_{(\lambda,t)}$ is the transmitted light intensity, $\epsilon_{(\lambda)}$ is the molar extinction coefficient of the absorbing species, c_t is the concentration of that species at a given time (t) and l is the optical path length. A change in the optical density is calculated as a difference between the $O.D.$ measured under pump illumination and at rest ($O.D._0$):

$$\Delta O.D._{(\lambda,t)} = O.D._{(\lambda,t)} - O.D._0_{(\lambda,t_0)} \quad (3.4)$$

$$\Delta O.D._{(\lambda,t)} = -\log\left(\frac{I_{(\lambda,t)}}{I_{(\lambda,i)}}\right) + \log\left(\frac{I_{(\lambda,t_0)}}{I_{(\lambda,i)}}\right) = -\log\left(\frac{I_{(\lambda,t)}}{I_{(\lambda,t_0)}}\right) \quad (3.5)$$

Equation 3.5 gives the term for the new probe intensity detected, $I_{(\lambda,t)}$, as a summation of the initial intensity pre-pump ($I_{(\lambda,t_0)}$) and some change in intensity as a result of the pump ($\Delta I_{(\lambda,t)}$) thus allowing $\Delta O.D.$ to be expressed as follows:

$$\Delta O.D._{(\lambda,t)} = -\log\left(\frac{I_{(\lambda,t)} + \Delta I_{(\lambda,t)}}{I_{(\lambda,t_0)}}\right) = \log\left(1 + \frac{\Delta I_{(\lambda,t)}}{I_{(\lambda,t_0)}}\right) \quad (3.6)$$

The change in intensity of the light detected by the photodiode ($\Delta I_{(\lambda,t)}$) produces a proportional change in voltage output recorded ($\Delta V_{(\lambda,t)}$), hence the $\Delta O.D.$ can be given in such terms as shown in Equation 3.7.

$$\Delta O.D._{(\lambda,t)} = -\log\left(1 + \frac{\Delta V_{(\lambda,t)}}{V_0}\right) \approx \frac{-1}{\ln(10)} \cdot \frac{\Delta V_{(\lambda,t)}}{V_0} = \frac{-1}{2.303} \cdot \frac{\Delta V_{(\lambda,t)}}{V_0} \quad (3.7)$$

In transient diffuse reflectance spectroscopy, the change in reflected light intensity is detected by the photodiode ($\Delta R_{(\lambda,t)}$) rather than the change in transmitted light. As such, the photodiode function is similar and the change in voltage is recorded, but this quantity cannot be referred to as $\Delta O.D.$. Instead, the term ‘percentage absorptance’ is defined as follows:

$$\%Abs = 1 - R_{(\lambda,t)} = \frac{\Delta R_{(\lambda,t)}}{R_{(\lambda,t_0)}} \quad (3.8)$$

The resultant optical signal, regardless of whether it is a TAS experiment ($\Delta O.D.$) or a TDRS experiment ($\%Abs$), can be composed of different contributing elements. A positive signal is observed when a new absorption feature is generated by excitation (i.e. the excited state has an associated absorbance at the probed wavelength). Alternatively, a negative signal, also referred to as a bleach, is observed when excitation inhibits a ground-state absorption or generates stimulated emission. A transient optical spectrum may be a combination of a number of these contributing signals.

Transient photocurrent

In this thesis, the term transient photocurrent (TPC) refers to any short-lived current generated during a spectroscopic measurement involving a ‘pump-probe’ technique. In TAS experiments under applied potential, transient current resulting from the ‘pump’ excitation is monitored by the oscilloscope alongside the optical signal. This data is often presented in integrated form to give the change in charge with time. Though there is no optical excitation involved, stepped-voltage absorption spectroscopy (SVAS) is also considered to be a pump-probe technique (see Section 3.3.3). As such, the transient current generated during these measurements is also referred to herein as TPC to avoid unnecessary new acronyms. If preferred, TPC may here be considered an abbreviation for transient pumped current, though this term is not used in wider literature. As with TAS experiments, the TPC in SVAS is acquired simultaneously with the optical signal and the change in both data sets is monitored as the ‘pump’ is varied.

Ultrafast transient absorption spectroscopy

An alternative variant of TAS is required to examine charge carrier dynamics at earlier times (pre- μs). This ultrafast-TAS (uf-TAS) setup uses a second laser beam as a probe which is also pulsed to allow better temporal resolution (see Figure 3.4). A regeneratively amplified Ti:sapphire laser system (Solstice, Spectra-Physics) and Helios spectrometers (Ultrafast Systems) were used, which generate 800 nm laser pulses (pulse width: 92 fs, repetition rate: 1 kHz). To generate the pump, a

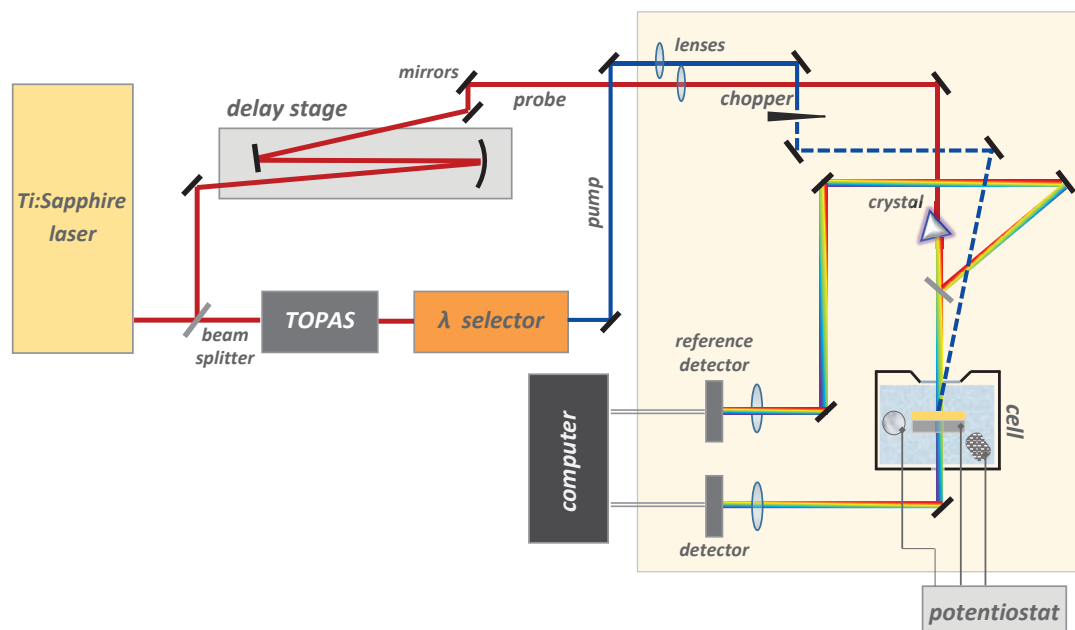


Figure 3.4 – A schematic representation of the ultrafast transient absorption spectroscopy setup used to monitor charge carriers on the sub-picosecond to nanosecond timescale. Both pump and probe beams come from a pulsed laser, but the former is then also chopped to give 'on' and 'off' spectra. The white light continuum (WLC) is generated by the crystal.

fraction of the 800 nm beam was directed through a sequence of optical parametric amplifiers (TOPAS Prime, Spectra-Physics) and a frequency mixer (NIR/UV-Vis, Light Conversion) to tune the excitation wavelength to 355 nm. 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 ever-so-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 was delayed with respect to the pump beam using a motorised delay stage to alter the path length of the probe beam before generation of the WLC. To reduce noise, the WLC was split into two beams, one of which is passed through the sample, and the other used as a reference. Both beams were 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 was then adjusted to match the rise of the signal at each wavelength. $\Delta O.D.$ data from 0.2 ps to 6 ns were determined with this setup. The data presented in Chapter 5 were averaged over a spectral range of *ca.* 10 nm.

3.3.2 Spectroelectrochemistry

As dark electrocatalyst materials are ill suited to TAS experiments, other techniques were used to study these materials. One such technique is spectroelectrochemistry (SEC), which monitors the steady-state change in sample absorption as a function of applied potential. SEC was performed using the same standard three-electrode setup and cappuccino cell described in Section 3.2.4. A background UV-Vis spectrum (Cary60, Agilent Technologies) of the electrolyte was taken at the beginning of each experiment. The sample was then immersed, connected to an Autolab (PGSTAT101) potentiostat and an absorbance spectrum measured. Depending on the sample analysed, different conditions were used, as specified in the relevant chapters. The spectrum at a reference point – often the open circuit potential (OCP) or the initial absorbance spectrum – was subtracted from the other spectra collected to give the difference spectra. These difference spectra are then characteristic of the species evolved or altered as a result of the change in conditions applied.

UV-Visible spectroscopy

UV-Vis absorption spectra were either collected from transmission measurements in the Cary60 spectrometer machine used for SEC (Agilent Technologies), or calculated from integrated sphere measurements performed in a Shimadzu UV-Vis 2600 spectrometer (Shimadzu). In the latter case, the percentage transmitted and reflected light was measured and Equation 3.9 used to calculate the percentage absorption, where A is the absorption, T is transmittance and R is diffuse reflectance.

$$\%A = 100 - \%T - \%R \quad (3.9)$$

3.3.3 Stepped-voltage absorption spectroscopy

The other technique used to study the Ni and Fe electrocatalysts in Chapter 6 is a version of a potential step/UV-Vis measurement, herein named stepped-voltage absorption spectroscopy (SVAS). This technique, adapted by the Durrant group to afford examination of 'dark' catalysts,¹⁵¹ works by applying a square-wave potential and tracking the change in sample absorbance at a specific wavelength as a function of time. Although stepped-potential/UV-vis measurements have been reported previously on numerous occasions, the use of a synced square-wave input with high time resolution to calculate rate laws makes SVAS unique. The information obtained is similar to that gained from a SEC experiment but, by following a specific wavelength, SVAS

allows for calculation of extinction coefficients, which may then be used to convert the $\Delta O.D.$ signal into a concentration of accumulated species. These calculations are described in detail in Appendix A.6.

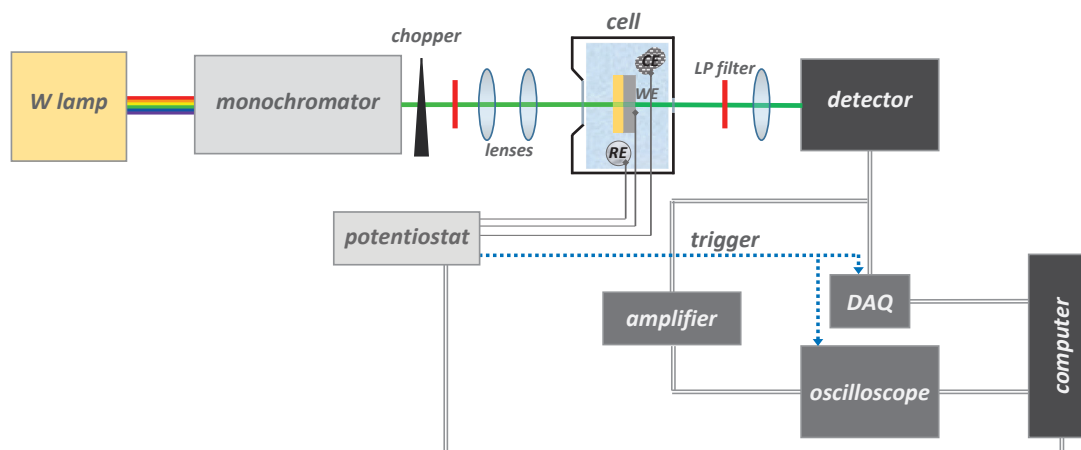


Figure 3.5 – Schematic representation of the stepped-voltage absorption spectroscopy (SVAS) setup used to monitor charge carriers under steady-state conditions.

SVAS setup

The setup for this technique, shown in Figure 3.5, is rather similar to that of photo-induced absorption spectroscopy, which is described in several publications.^{112, 119, 152, 153} However, rather than use an optical pump to photogenerate charge carriers, a sufficiently large potential (positive, in the case of photoanodes) is applied to alter the occupancy of states within the space-charge layer. For Ni/FeOOH, this entails applying a positive enough potential such that catalytic current is produced, with valence band (VB) ‘holes’ generated through depopulation of VB-edge states. These holes are then probed similarly to the method described for TAS (Section 3.3.1), using monochromated light from a 75 watt W-arc lamp, which passes through the sample and a number of optical filters before reaching a Si photodiode detector (FDS100-CAL, Thorlabs). The PalmSens3 potentiostat (PalmSens) was essential for this experiment for three reasons: (i) it could generate the square-wave potential needed to produce an ‘excited’ state and a ‘resting’ state from which a difference could be calculated; (ii) the potentiostat allowed for the transient photocurrent to be monitored by the DAQ (see Section 3.3.1); (iii) after specific modification of the PS-Trace software used by the potentiostat, the PalmSens3 was able to trigger data acquisition at the correct time (usually corresponding to a step in the resting potential to allow for the rise

and fall of the optical signal under catalytic bias to be observed). The resting potential was usually selected to be just below the catalytic onset potential, whereas the step in potential was altered during the experiment to determine the effect of applied potential on the signal monitored. Typical step sizes varied between 0.02 V and 0.50 V. Each SVAS data point presented in the thesis corresponds to the average of approximately 25 up-down step cycles per stepped potential. Within one cycle, the 'resting' time was eight seconds and the 'stepped potential' was applied for five seconds. Data was acquired for ten seconds of each cycle, allowing three seconds before the next cycle. This relatively long measurement time allows for equilibria to establish such that the steady-state under the specified conditions is reached, and the species monitored are those that accumulate under these conditions. Only the optical data acquired by the DAQ was analysed, as the optical data from the oscilloscope was subject to over-filtering effects. The cell time constant was deemed insignificant in both the SVAS and TPC experiments as calculated by Dr Pendlebury.¹⁵⁴

Chapter 4

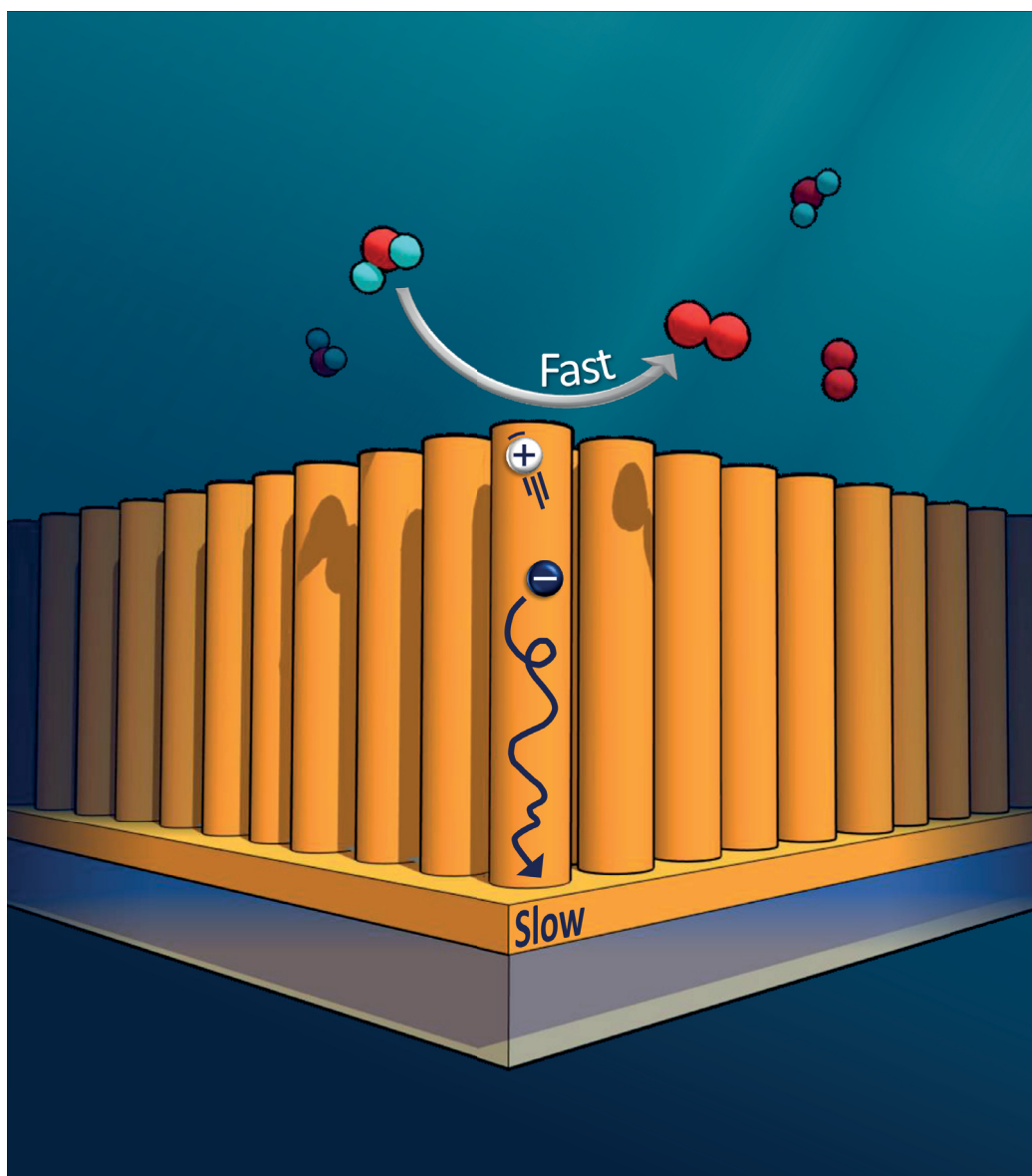


Illustration by author

4 Tungsten oxide photoanodes for water oxidation

This chapter presents the physical characterisation of AA-CVD synthesised WO_3 photoanodes for water oxidation. The films have a nanoneedle structure and a high Faradaic efficiency for oxygen evolution (<85%) with a photocurrent onset that is close to the flat-band potential. In order to understand if these performance properties are related to the charge carrier dynamics, the films were examined by transient diffuse reflectance spectroscopy and correlated with transient photocurrent data for electron extraction. Under anodic bias, efficient hole transfer to the aqueous electrolyte is observed within a millisecond. In contrast, electron extraction is found to be comparatively slow (≈ 10 ms), increasing in duration with nanoneedle length. The relative rates of these water oxidation and electron extraction kinetics are shown to be reversed in comparison to other commonly examined metal oxides (e.g., TiO_2 , $\alpha\text{-Fe}_2\text{O}_3$ and BiVO_4). Studies were conducted as a function of applied bias and film processing to modulate oxygen vacancy density and these indicate that slow electron extraction kinetics result from electron trapping in shallow WO_3 trap states associated with oxygen vacancies. Despite these slow electron extraction kinetics, charge recombination losses on the microsecond to second time scales are observed to be modest compared to other oxides studied. It is proposed that the relative absence of such recombination losses, and the observation of a photocurrent onset potential close to flat-band, result directly from the faster water oxidation kinetics of WO_3 . I conclude that these fast water oxidation kinetics are correlated with the highly oxidising valence band position of WO_3 , thus highlighting the potential importance of thermodynamic driving force for catalysis in outcompeting detrimental surface recombination processes.

Most of the results presented in this chapter have been published in the following article:

Corby, S. et al., "Water oxidation and electron extraction kinetics in nanostructured tungsten trioxide photoanodes", *Journal of the American Chemical Society*, **2018**, 140, 47, 16168–16177

4.1 Introduction

WO₃ is often reported to have a high electrical conductivity,^{60, 138, 155} which has led to its frequent implementation as an electron transport layer in various heterojunction photoanodes, including junctions formed with α -Fe₂O₃ and BiVO₄, in which conductivity is significantly poorer.^{95, 134, 135, 156–159} It has been proposed that high electrical conductivity improves water splitting performance by aiding the separation of photogenerated charges such that competing recombination processes are retarded.¹⁶⁰ High conductivity in WO₃ is considered to be a result of a large density of charge carriers, caused by intrinsic oxygen vacancies, which act as n-type dopants.^{161–163} Carrier concentrations in the range from 1×10^{17} to 1×10^{22} cm⁻³ have been reported, depending on stoichiometry (WO_{3-x}).^{134, 139, 140} Similarly, changes in the stoichiometry of single crystals have been shown to modulate electrical conductivity between 10 and 1×10^{-4} S/cm.¹⁶¹ However, such deviations from stoichiometry have also been suggested to introduce chemical defects that can result in increased charge trapping, which, rather than boost performance, can often introduce additional recombination pathways.^{164–168} For example, the presence of defect states in the band-gap of α -Fe₂O₃ has been shown to enhance electron-hole recombination kinetics that can outcompete water oxidation.⁶⁸ In addition, high carrier densities can also result in shorter minority carrier lifetimes and thus also accelerated recombination losses.^{169, 170} Water oxidation is a kinetically slow process, requiring the accumulation of multiple holes. As such, kinetic competition between water oxidation/electron extraction and surface charge recombination (sometimes called back electron-hole recombination) can severely limit the efficiency of photoelectrochemical water oxidation.^{96, 117, 144, 171} Using sacrificial reagents, Amano et al. found that the size of suspended WO₃ particles affected the frequency of surface recombination with concurrent effects on oxygen evolution rate.¹⁷² However, this competition has received limited attention to date for WO₃ photoanodes under photoelectrochemical conditions.

Reported herein is an analysis the dynamics of photogenerated charges in tungsten oxide photoanodes synthesised by chemical vapour deposition (CVD). The synthesis method generates highly oxygen deficient, monoclinic WO_{3-x} nanoneedle-structured films that are intensely blue in colour, which are then annealed in air at elevated temperature to remove most of the oxygen vacancies. These photoanodes exhibit an early photocurrent onset potential (ca. 0.5 V vs reversible hydrogen electrode (RHE)) and a high Faradaic efficiency for water oxidation ($\geq 85\%$). The rate of water oxidation is analysed by transient diffuse reflectance spectroscopy and transient photocurrent measurements and is found to be faster than other commonly used transition metal oxides and much faster than electron extraction. The effect of interband defects on electron transport is then investigated. I find that electron trapping in the WO₃ needles is significant and propose a

trap-mediated mechanism of electron transport to the back contact (fluorine-doped tin oxide (FTO)). To examine how the density of traps may affect this electron transport, the annealing time and the needle length is altered and I find that this has profound effects on extraction time. This study thus provides unique kinetic insight on the charge carriers of WO_3 , a material growing in popularity for solar fuel-related applications,^{144, 173–176} and highlights the direct impact these kinetics have on photoelectrochemical performance.

4.2 Results

4.2.1 Sample characterisation

Tungsten oxide samples were prepared by aerosol-assisted chemical vapour deposition (AA-CVD) according to a previously established synthesis,¹⁴³ as detailed in the Chapter 3.

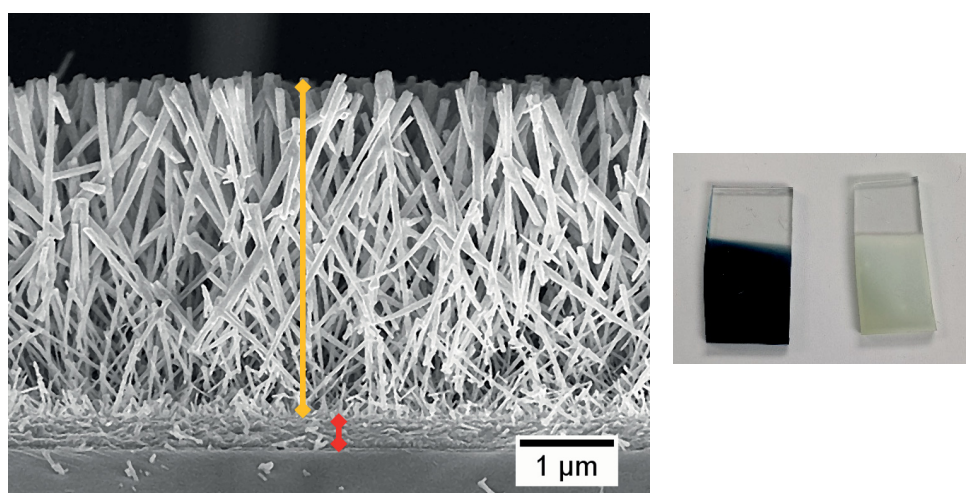


Figure 4.1 – *left*: Cross-sectional SEM image of annealed WO_3 needles (3.6 μm , yellow line) on 400 nm dense WO_3 seed layer (red line) deposited on FTO-coated glass, $\times 53000$ magnification. *right*: A photograph demonstrating the difference in colour of the WO_3 samples before (left) and after (right) annealing in air for 2 hours at 500°C.

Figure 4.1 (*left*) shows the cross-sectional scanning electron microscopy (SEM) image of an annealed WO_3 sample, indicating the 4 μm long needles (yellow line) on top of the dense seed layer (400 nm, red line). X-ray diffraction data confirm the crystalline monoclinic nature of these WO_3 films, with the (002) peak most prominent due to the preferential growth perpendicular to this plane, as shown in Figure 4.2. Samples were also characterised by X-ray photoelectron spectroscopy (XPS). The XPS spectra of WO_3 samples before and after annealing indicate the

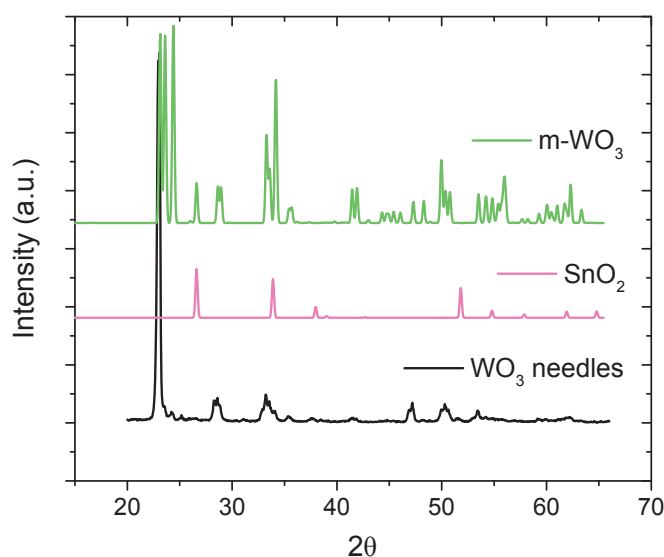


Figure 4.2 – XRD of WO₃ needles compared to monoclinic reference and FTO, performed by Dr Andreas Kafizas. Mostly the diffraction peaks from the [002] Miller plane are visible in the needles due to the strongly preferred growth orientation.

films are of similar purity, with adventitious carbon the only detectable impurity (Figure 4.3, *top*). By focusing on the W 4f peaks, we can obtain information about the W oxidation state in the sample. In both lower graphs in Figure 4.3, five peaks can be observed. The small peak at higher binding energy is known to be a W loss feature, a residual effect from the XPS experiment environment, and can be ignored. The remaining four peaks show two sets of doublets; a high spin (7/2) and a low spin (5/2) peak corresponding to tungsten in its completely oxidised form (W⁶⁺) and the same two peaks for reduced W atoms (W⁵⁺), which shift the peak-maxima to lower binding energy.¹⁷⁷ In the non-annealed, blue sample (Figure 4.3, *left*) the reduced tungsten peaks are much more pronounced as a result of a larger number of W⁵⁺ species present, which can be directly correlated with oxygen vacancies. Gaussian-Lorentzian functions (fixed at 40% GL) were used to fit all the peaks and the full-width-half-maximum (FWHM) of each chemical environment was kept approximately constant. The binding energy gap between the W 4f (7/2) and W 4f (5/2) was also kept constant. The proportion of W⁵⁺ to W⁶⁺ analysed with this surface-sensitive technique is ~30%, calculated by integrating the respective peaks. Figure 4.3 (*right*) shows that after annealing in air at 500°C for 2 hours, the number of these reduced states is dramatically decreased to ~10% of the tungsten atoms probed. Photographs of the annealed and unannealed samples are given in Figure 4.1 (*right*).

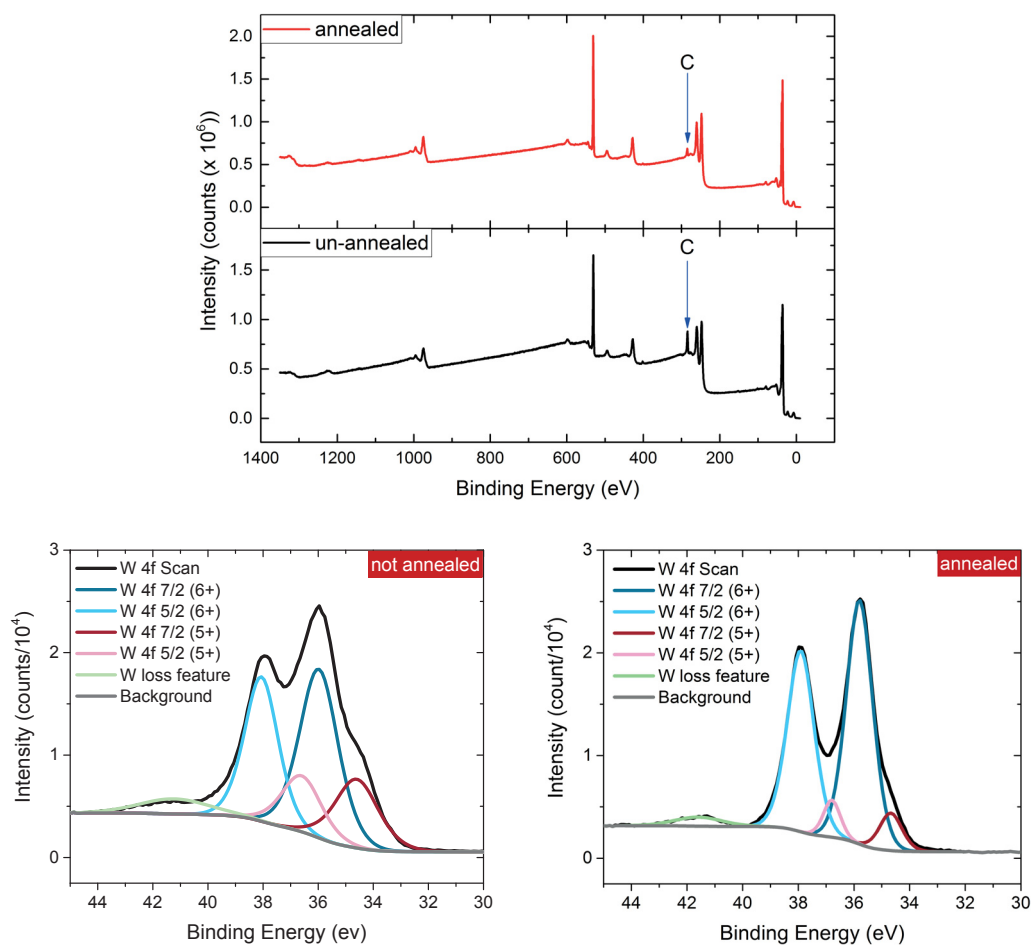


Figure 4.3 – *top*: Full XPS spectrum of blue and yellow WO_3 showing no impurities (adventitious carbon peak is indicated with blue arrow). *left*: High-resolution W 4f XPS scan of the as-synthesised sample (blue) showing the clear presence of W^{5+} states (30% of the W atoms probed), which are associated with oxygen vacancies. *right*: the same W 4f scan after annealing 2 hours at 500°C in air.

4.2.2 Photoelectrochemical water splitting performance

The current/voltage characteristics of annealed WO₃ were examined by linear sweep voltammetry (LSV) under simulated 1 sun irradiation from the front side of the sample (electrode-electrolyte, EE), as shown in Figure 4.4.

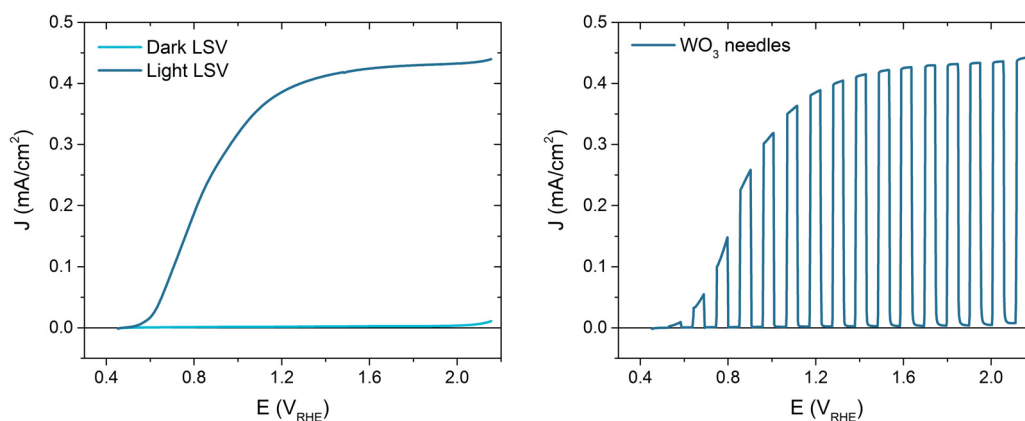


Figure 4.4 – Linear sweep voltammetry of WO₃ needles under simulated 1 sun irradiation in 0.1 M H₂SO₄, indicating early photocurrent onset and reasonable maximum (10 mV/s scan rate). Details of the three-electrode setup can be found in the Chapter 3. *left*: continuous illumination, *right*: chopped illumination.

Under both chopped and continuous illumination, the photocurrent reaches an approximate plateau by 1.23 V_{RHE} of ~0.45 mA/cm², and the onset potential (ca. 0.5 V_{RHE}) is only ~100 mV above the calculated flat-band of such nanostructured WO₃.¹⁷⁸ The left graph in Figure 4.4 clearly highlights that the dark current was negligible over the voltage range examined. Unlike photoanodes of several other transition metal oxides, there is an absence of transient spikes when the light is turned on (positive spikes) or off (negative spikes) in the chopped LSV (Figure 4.4, *right*). Such photocurrent transients are indicative of current loss from recombination processes at the surface, typically the recombination of surface accumulated holes with bulk electrons, which compete with hole transfer to the electrolyte (e.g. by water oxidation).^{117,179} These transients are readily observed in α -Fe₂O₃ and BiVO₄, for which this recombination can be a significant loss pathway.^{69,101} The early photocurrent onset observed for the WO₃ needles, combined with the lack of transient current spikes, suggests that there is very little such surface recombination occurring, which may be a result of slower surface recombination or a faster reaction of accumulated holes (discussed further below).

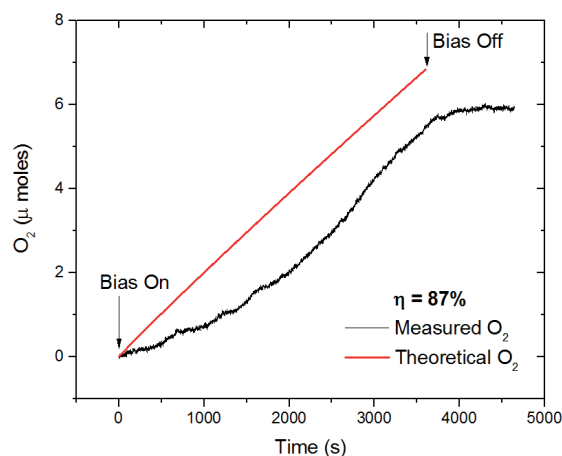


Figure 4.5 – Oxygen evolution measurements with theoretical yield calculated from the photocurrent (red line) and measured oxygen using the Clarke electrode (black line) over 3500 seconds. The calculated Faradaic efficiency is 87%. Continuous 1 sun irradiation and 0.1 M H_2SO_4 were used for the measurement and the bias ($1.45 \text{ V}_{\text{RHE}}$) turned on and off.

Oxygen evolution was measured with a calibrated Clark electrode as detailed in Chapter 3. Figure 4.5 demonstrates the high Faradaic efficiencies obtained, which were consistently between 85 and 90%. It is noted that this value is higher than a large proportion of the Faradaic efficiency values reported in the literature for this material.^{138,163,171} This high Faradaic efficiency may be related to the high crystallinity of the WO_3 needles and/or preferential crystal orientation, reported by others to be significant.^{172,180} Further analysis on this aspect is beyond the scope of this chapter, but mentioned briefly in Chapter 5. In addition, measurements of Faradaic yield were performed at 1 sun equivalence (or greater in some cases), whereas transient optical studies used lower excitation densities. Due to the difficulties in accurately measuring evolved oxygen at low current densities, I have assumed the Faradaic efficiency of the needles to be constant across all intensities examined, although this may not be the case.

4.2.3 Dynamics of electrons and holes

Transient diffuse reflectance spectroscopy (TDRS) measurements were performed on the microsecond to second timescale to monitor the kinetics of photogenerated charges under water oxidation conditions (see Chapter 3 for experimental details). Previous studies have shown that WO_3 exhibits two main spectral features: a broad transient signal centred at $\sim 800 \text{ nm}$ that, by use of chemical scavengers, has been assigned to photoexcited electrons; and a hole signal, which may be probed below 550 nm .^{111,181} The transient diffuse reflectance (TDR) spectra for the

WO₃ needles in this work, Figure 4.6 (*left*), are in agreement with these previous assignments. The stronger electron absorbance signal spans most of the visible spectrum down to ~550 nm. Monitoring the electrons at 800 nm, we observe a long-lived transient signal that decays by ~1 s (red trace, Figure 4.6, *right*). The transient photocurrent (TPC) was measured simultaneously and integrated to give the extracted electron density as a function of time delay (dashed red trace, Figure 4.6, *right*). On the one hand, by comparing the TDR electron signal at 800 nm with the integrated TPC signal, it is clear that the integrated TPC signal rises as the 800 nm signal decays, supporting the assignment of the 800 nm signal to WO₃ electrons. On the other hand, the hole signal, monitored at 500 nm presents a much faster decay, implying faster kinetics for the hole reaction with the electrolyte. Given the high Faradaic efficiency exhibited by the photoanodes, this hole reaction can be assigned primarily to water oxidation. If we take approximate half-lifetimes for these decays with respect to the signal amplitude at 10 μ s, $t_{1/2}$ (electron) is ~10 ms, and $t_{1/2}$ (holes) is ~0.5 ms. These values indicate that holes react an order of magnitude faster than electrons are extracted from the electrode. As highlighted further in the following sections, this timescale of water oxidation is much faster than those observed for other commonly studied transition metal oxides.^{91,92,118} All kinetics are assumed to result predominantly from optical excitation, i.e. laser-induced heating during TDRS measurements is assumed negligible, although a temperature dependence study, such as that by Selim et al. on BiVO₄,¹⁸² could have been used to support this assumption.

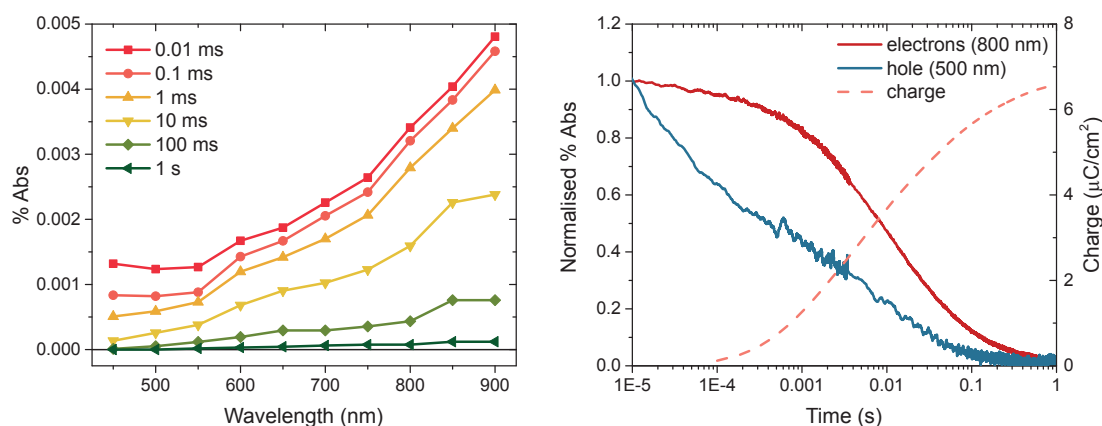


Figure 4.6 – Transient diffuse reflectance data of WO₃ photoanode at 1.45 V_{RHE} in pH 1 electrolyte, 355 nm excitation at 0.3 mJ/cm² and 0.4 Hz. *left*: transient spectra for time delays after photoexcitation from 0.01 ms to 1 s. *right*: kinetic traces at 800 nm (red) and at 500 nm (blue), assigned to electron and hole signals, respectively, alongside integrated transient photocurrent data (dashed red) corresponding to the kinetics of electron extraction.

4.2.4 Hole kinetics in water and propylene carbonate

To further examine the rapid water oxidation kinetics evident from the TDR decay at 500 nm in Figure 4.6, the same kinetic measurement was repeated in inert organic solvent (propylene carbonate). As seen in Figure 4.7 (pale blue trace), when there is no water present, a longer-lived transient signal is observed at 500 nm. This trace still decays within the timescale of the measurement due to some oxidation of the solvent and/or other recombination processes. When a small percentage of water (pH 1 electrolyte) is added to the propylene carbonate, the rate of signal decay is increased, thus confirming that the fast decay observed at 500 nm is due to surface holes reacting with water. Although the poor miscibility of water in propylene carbonate limits the comparisons to low water concentrations, a clear trend of increasing rate with increasing water content is observed, with 100% aqueous electrolyte displaying the fastest oxidation kinetics.

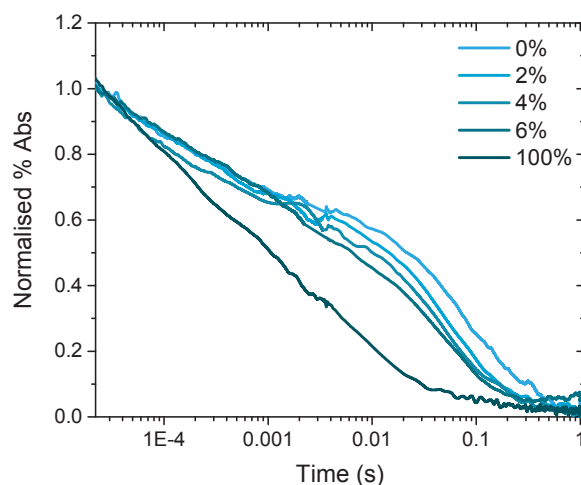


Figure 4.7 – TDR decays for WO_3 needles at $1.45 V_{\text{RHE}}$ in propylene carbonate TBA SO_4 with increasing aqueous electrolyte volume fraction (0.1 M H_2SO_4 , %), probed at 500 nm.

4.2.5 Kinetics of electron transport

To further investigate the relatively slow electron extraction kinetics shown in the 800 nm TDRS and TPC data in Figure 4.6, a series of transient diffuse reflectance decays were recorded at a range of potentials, along with integrated transient photocurrent signals, to determine the effect of applied bias (Figure 4.8, *upper left*). With progressively larger anodic bias, the magnitude of the initial optical and final extracted charge signals increase simultaneously. The rise in these signal amplitudes indicates an increase in the density of photogenerated long-lived electrons that can be extracted from the film and fed to the external circuit. This can be rationalised as a consequence of greater band-bending in the material under higher bias, creating a larger

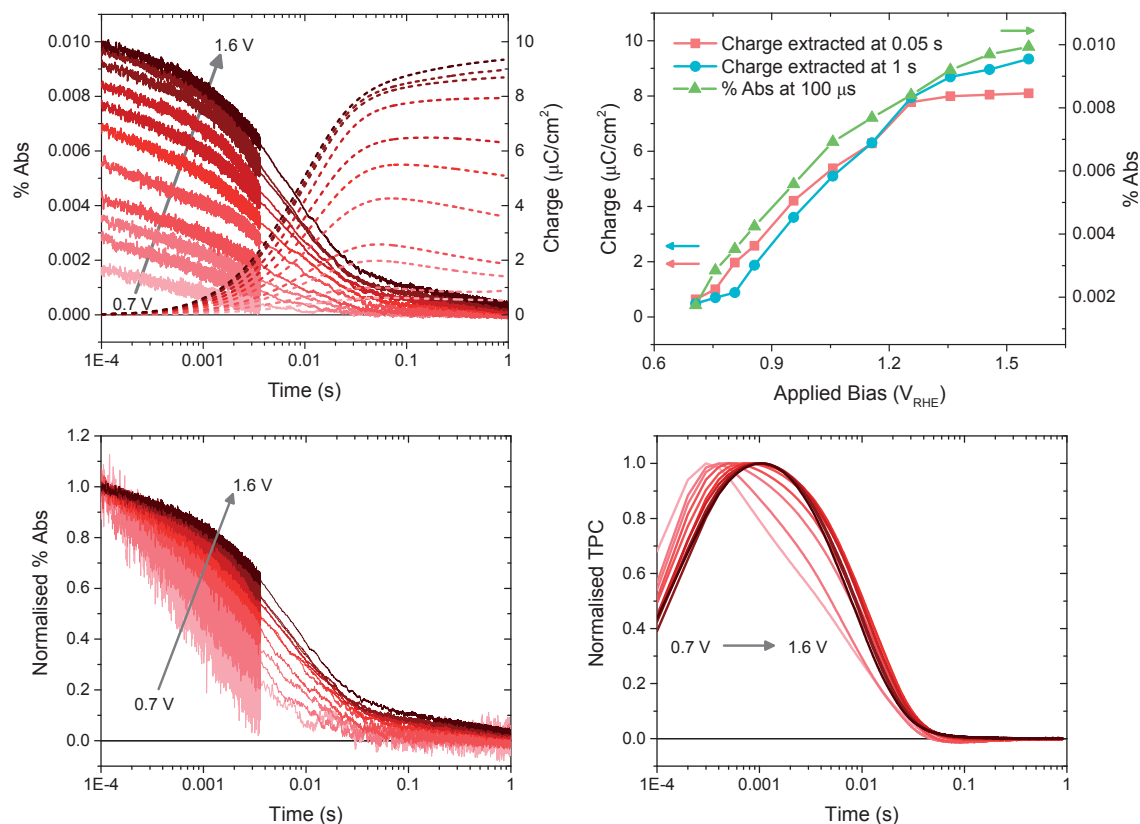


Figure 4.8 – *upper left*: TDR decays at 800 nm and the integrated transient photocurrent at a range of different applied potentials (0.7–1.6 V_{RHE}). *upper right*: The initial magnitude of the optical signal (*triangles*), and the extracted charge measured at 50 ms (*squares*) and at the end of the measurement, 1 s (*circles*). *lower left*: Normalised optical decays shown above. *lower right*: Normalised transient photocurrents for the same applied potentials.

space-charge layer to separate charges and thus a higher yield of electrons. In other words, the magnitude of the optical signal directly correlates with the number of electrons that remain in the electrode after any ultrafast bulk recombination occurs. In Figure 4.8, *upper right*, the correlation between the initial optical TDRS assay of long-lived electrons (green triangles) and the integrated photocurrent assay of extracted electrons (blue circles) versus applied potential is given. The close agreement between these two assays indicates that, despite the slow electron extraction kinetics, the electrons observed on these time scales are still extracted reasonably efficiently by the external circuit; that is, relatively few of the electrons monitored on the microsecond to second timescales studied herein are recombining on this timescale. This is in agreement with the early photocurrent onset and lack of transient spikes observed in the chopped J-V curve (Figure 4.4). If we consider the extracted charge density at both 50 ms (Figure 4.8, *top right*, pink squares) and 1 s (blue circles), we observe a small difference at low bias indicative of modest back

electron-hole recombination losses. Back electron-hole (surface) recombination occurs over long timescales as a result of charge accumulation at the electrode-electrolyte interface. This build-up of charge draws electrons in the opposite direction of normal current flow, diminishing the total charge collected.¹¹⁷ By 1.15 V_{RHE}, a large enough field is maintained to successfully prevent this slow timescale recombination process. This ‘surface recombination turn-off’ potential is lower than for α -Fe₂O₃ and BiVO₄ photoanodes,^{92, 117, 183, 184} most probably due to the faster competing water oxidation reaction kinetics reported above, although the sample morphologies may also play a role. Applied potentials of at least 1.15 V_{RHE} result in increased charge extraction with time, as the majority of electrons are collected.

The lower left and right panels of Figure 4.8 give, respectively, the normalised optical and photocurrent (without integration) transients for a series of applied biases. It is noted that increasing bias results in longer-lived optical signals and slower charge extraction kinetics. This could be a result of improved charge separation, although, as mentioned, there is little bimolecular recombination at these timescales across the potential series, as most charges are extracted. As such, small changes in recombination are unlikely to account for the differences in decay kinetics, which are dominated by extraction. Alternatively, and more likely, these slower kinetics under stronger anodic bias could result from increased trapping of charges with larger bias, resulting in hindered transport. It is widely acknowledged that WO₃ has a large propensity to form electronic defects within the band-gap.^{162, 165, 185–187} With the conduction and valence band energies pinned at the electrolyte interface, increases in applied potential could empty, and thus make available for electron trapping, an increasing density of unoccupied shallow defect states within the space-charge layer. This would slow extraction, as electrons would encounter a greater number of progressively deeper states with increasing positive bias. This is analysed further in the discussion section below.

Incident photon-to-current efficiency (IPCE) measurements were conducted at 1.23 V_{RHE} with front (EE; electrolyte-electrode) and back (SE; substrate-electrode) irradiation to probe whether slow electron extraction is limiting performance, as shown in Figure 4.9, *left*. With FTO absorption accounted for in both cases, higher efficiencies were obtained under SE irradiation (36% vs 22% at 350 nm), with charges generated closer to the extraction point. This correlates with the slow extraction times observed by TDRS and suggests that the small amount of surface or back electron-hole recombination observed (Figure 4.8) has some effect on performance. The trend in IPCE also agrees with the relatively large diffusion length of holes (150 nm) in WO₃, which has previously been reported to be significantly larger than for other popular metal oxides (e.g. 4 nm in α -Fe₂O₃), sometimes larger than the depletion width.^{60, 95, 164} Since the WO₃ needles

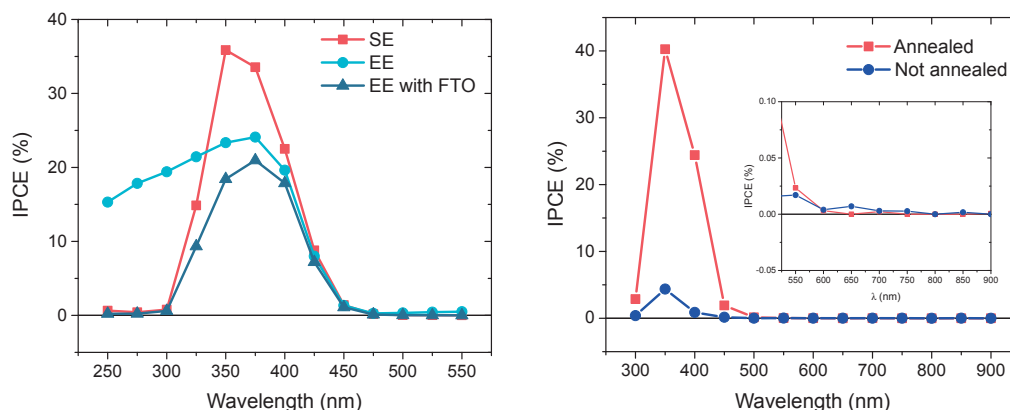


Figure 4.9 – *left*: Incident photon-to-current efficiency (IPCE) of the WO_3 needles from back (SE; pink) and front (EE; blue), 1.23 V_{RHE} , 0.1 M H_2SO_4 . SE illumination gives higher currents when $\lambda > 325$ nm. Below 325 nm, performance drops due to light absorption by the FTO substrate. When FTO is placed in front of the sample to account for this absorption under EE illumination (dark blue), it is evident SE illumination is more efficient. This indicates that higher currents are attainable when electrons are generated closer to the substrate, suggesting that electron transport is limiting. *right*: IPCE of annealed (pink) and not-annealed (blue) WO_3 films under the same conditions, SE illumination. There is no enhanced photocurrent due to improved visible light absorption from the oxygen vacancy states, which give an absorption band from 550 nm that stretches towards the near IR.

are ~ 100 nm in diameter, holes should readily diffuse to the surface regardless of whether the electrode is irradiated from the front or the back. IPCE data were also collected over longer wavelengths (Figure 4.9, *right*) to confirm that any absorption from oxygen vacancies does not contribute to enhanced visible light harvesting. These data were also collected for a sample prior to annealing and thus with a larger concentration of vacancies. The effect of oxygen vacancy states on photoanode performance are discussed in detail in Chapter 5.

4.2.6 WO_3 modifications

To aid confirmation of the cause of such slow electron extraction kinetics, various alterations were made to the WO_3 needles. The first was to grow shorter needles (2 μm) through modification of the same AA-CVD synthesis (see Chapter 3).¹⁴³ As is apparent in Figure 4.10 (*left*), the shorter WO_3 needles give a faster optical electron signal decay (pink line) and earlier charge extraction kinetics (dashed lines), indicating that electron extraction is kinetically limited by electron transport through the WO_3 needles. Front and back IPCE, converted here to an APCE (absorbed photon-to-current efficiency) are more comparable for these shorter needles, as the electron

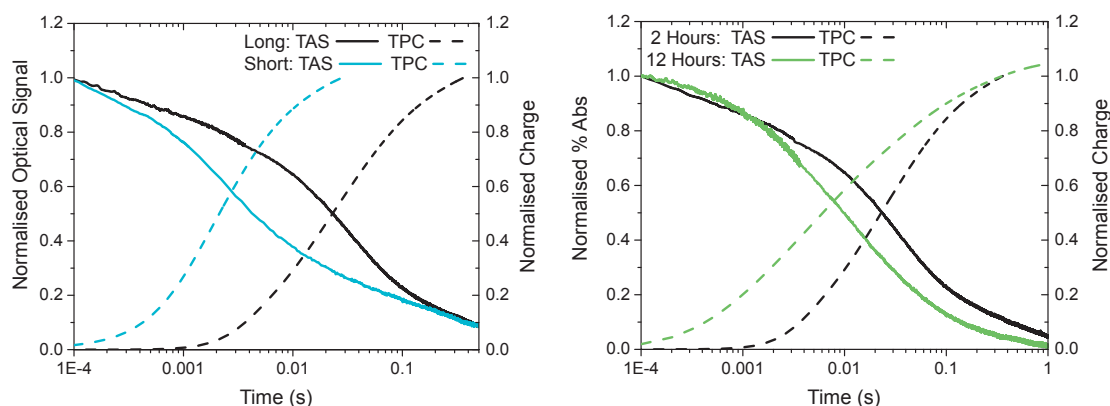


Figure 4.10 – TDR decays at 800 nm (solid lines) and corresponding TPC data (dashed lines) at 1.45 V_{RHE} , pH 1 electrolyte. *left*: Comparison of WO_3 needles with shorter WO_3 needles grown by the same method. *right*: Comparison of WO_3 needles to those annealed in air for a longer time to remove/fill more oxygen vacancies.

transport distance has been reduced (Figure 4.11). The second modification was to anneal the as-synthesised blue WO_{3-x} needles in air for a longer period of time. Previous XPS data already confirmed that annealing in air reduces the number of oxygen vacancies (see Figure 4.3). Similarly, observations in literature show that the converse approach of annealing under oxygen-poor atmosphere (hydrogen or argon) increases the number of oxygen vacancies,¹³⁷ which may act as electron trap sites.¹⁸⁸ Although the nature of any trap sites discussed herein has not been probed directly, it is reasonable to assume that these would be associated with oxygen vacancies as evidenced by our XPS measurements (Figure 4.3) and the wealth of data on WO_3 .^{185, 186, 189, 190} Figure 4.10 (*right*) compares the electron decay of a long needle sample annealed in air at 500°C for two hours to one annealed for 12 hours, and thus with a reduced population of oxygen vacancies. This subtle change in oxygen vacancy density was determined by an increase in sub-band-gap absorption (Figure 4.12), as previously reported in the literature.^{139, 191, 192} As can be observed, the half-lifetimes of both the TDR and photocurrent decays are reduced for the sample that was annealed for a longer period of time, consistent with the idea of trap states associated with oxygen vacancies slowing electron extraction.

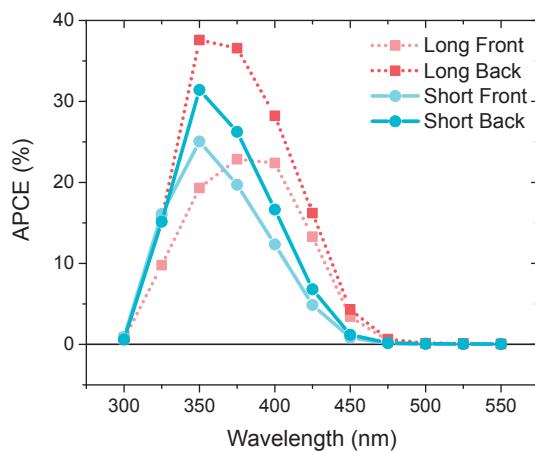


Figure 4.11 – Absorbed photon-to-current efficiencies (APCE) for 4 μm long (pink) and 2 μm short (blue) WO_3 needles at 1.23 V_{RHE} . Samples examined under front illumination have an FTO slide in front to give the same FTO absorption under both front and back illumination. Efficiencies of the shorter needles are not too dissimilar from the long needles, and there is much smaller disparity between front and back illumination, owing to the shorter electron transport distance required.

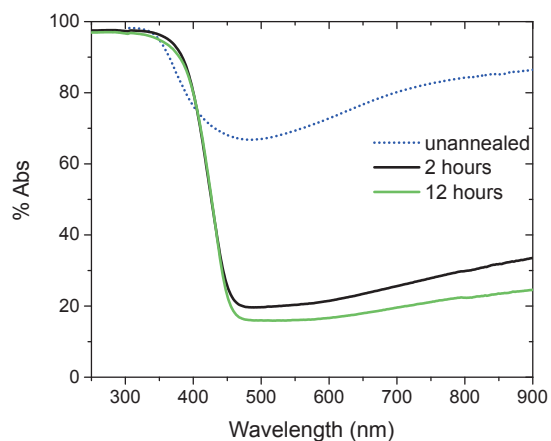


Figure 4.12 – UV/Vis absorbance from integrated sphere measurements comparing WO_3 needles annealed for 12 hours (green) to those annealed for 2 hours (black), thus highlighting the difference in polaron absorption from oxygen vacancy states. The absorbance of an non-annealed sample is given for reference (blue).

4.2.7 Comparison with other transition metal oxides

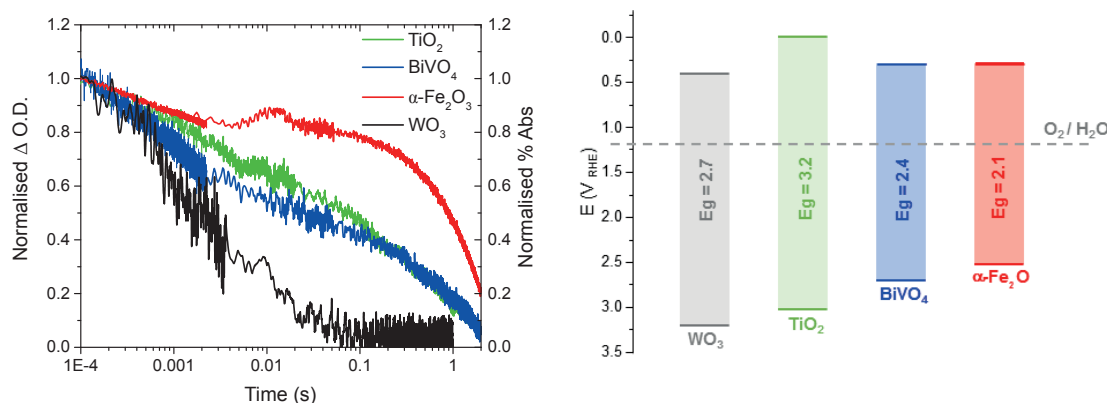


Figure 4.13 – *left*: TDR decays for holes in the WO_3 needles (black), studied at 500 nm (pH 1, 1.45 V_{RHE}), compared to transient absorption measurements of hole decays in other metal oxides at similar applied bias, equating to the photocurrent plateau: BiVO_4 in blue (550 nm, pH 7, 1.5 V_{RHE}), TiO_2 in green (500 nm, pH 13, 1.15 V_{RHE}), and $\alpha\text{-Fe}_2\text{O}_3$ in red (650 nm, pH 13, 1.5 V_{RHE}). *right*: Valence band alignments for the different metal oxides.^{156, 158, 193}

Finally, the kinetics of water oxidation and electron extraction reported herein for WO_3 are compared against other transition metal oxides frequently employed as photoanodes for water splitting (see Appendix A.1 for further details on these samples). In Figure 4.13, the transient optical signal for water oxidation by surface holes is compared between transition metal oxides commonly studied as photoanodes for water oxidation. Often considered the kinetic bottleneck of photoelectrochemical water splitting, the oxidation of water occurs on the timescale of 100 ms to seconds for titania (TiO_2), hematite ($\alpha\text{-Fe}_2\text{O}_3$), and bismuth vanadate (BiVO_4) but is significantly faster for the WO_3 needle sample under similar applied bias. Factors such as sample morphology and solvent may alter these values, but to a rough approximation, this trend can largely be correlated with the depth of the valence band (Figure 4.13, *right*). Comparing values taken from literature, WO_3 displays the most positive valence band energy and thus the largest thermodynamic driving force for water oxidation. The pH at which each decay was collected corresponds to the conditions of best performance for each sample and the mechanism is presumed to be similar in each case, as supported by a recent publication examining rate law analyses.¹²⁰

The electron extraction kinetics of the WO_3 needles studied herein, observed both optically and by integrated photocurrent transients, were also compared to TiO_2 needles of similar length (Figure 4.14).¹⁹⁴ Clearly, the electron extraction is much faster for the TiO_2 sample, with a reduction in half-life of the decay from ~ 20 ms in WO_3 to ~ 1 ms in titania. Figure 4.14 (*right*)

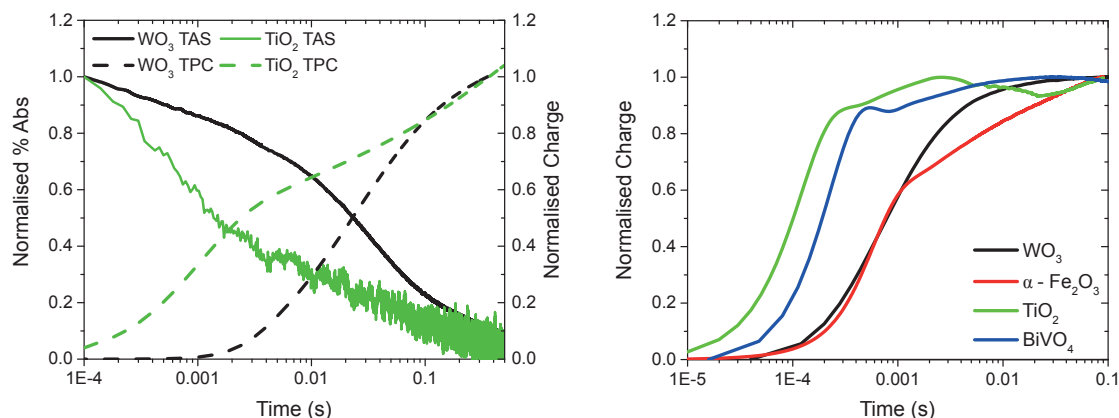


Figure 4.14 – *left*: Comparison of TDR decays at 800 nm (solid lines) and corresponding TPC data (dashed lines) at 1.45 V_{RHE}, pH 1 electrolyte for WO₃ needles (black) against TiO₂ needles (green) of similar length, also grown by CVD. *right*: Comparison of flat, dense WO₃ (black trace, pH 1) with similar thicknesses of dense TiO₂ (green trace, pH 13), Fe₂O₃ (red trace, pH 13), and BiVO₄ (blue trace, pH 7).

gives a similar charge extraction comparison for dense WO₃, TiO₂, α-Fe₂O₃, and BiVO₄ (flat for ease of synthesis). Once again, the slowest extraction times are observed for the WO₃ sample, with similar kinetics to α-Fe₂O₃, which is known to have low conductivity across such thicknesses when undoped (ca. 500 nm).^{95, 195, 196} This strongly suggests that slow electron transport is an intrinsic property of WO₃. As proposed above, this is most likely related to its propensity to become oxygen-deficient, forming vacancies that can trap charges.^{164, 197}

4.3 Discussion

In the majority of photoelectrochemical systems examined for water oxidation, the water oxidation reaction itself is considered the kinetically limiting step, whereas the extraction of the majority carrier (electrons) is comparatively fast.^{41, 118, 198} However, in this work on WO₃ photoanodes, we find the converse to be true. Direct analysis of the transient photocurrent alongside the correlating optical decay of the electron signal has highlighted the extraction of electrons to be particularly slow, slower than the rate of water oxidation (Figure 4.6). Rather surprisingly, we find evidence that holes in these nanostructured samples react faster at the electrolyte interface than for any other transition metal oxide we have previously investigated (Figure 4.13, *left*), with an optical half-lifetime under bias of less than a millisecond ($t_{1/2}(h^+) \approx 0.5$ ms). Such a rapid decay of the hole signal in WO₃ has been observed previously by Cristino et al. but was assigned to non-Faradaic oxidation processes rather than water oxidation.¹⁷¹ Water oxidation was confirmed to be the dominant oxidation process at the surface of our WO₃ needles through oxygen evolution measurements yielding greater than 85% Faradaic efficiency.

The importance of fast water oxidation kinetics is most apparent in the early onset of the photocurrent for this material (Figure 4.4), requiring a much smaller overpotential for water oxidation compared to α -Fe₂O₃ and BiVO₄.^{92, 199} In the case of α -Fe₂O₃, it has been suggested that the requirement for overpotentials as large as 0.6 V above flat-band is the result of poor water oxidation kinetics,^{179, 183, 200} necessitating the use of co-catalysts to lower the onset potential.^{67, 179, 201} In this study, the earlier onset of WO₃, presented herein and observed by others,¹³⁴ correlates with faster water oxidation kinetics. Rapid reaction kinetics at the interface allow an increased proportion of the holes that reach the surface to perform useful chemistry over competing back electron-hole recombination processes. This is true for these WO₃ nanoneedles without the need for co-catalysts or passivating overlayers. As shown in Figure 4.13 (*right*), the valence band edge is more positive in WO₃ than in BiVO₄, α -Fe₂O₃, and TiO₂,^{135, 156, 158, 193, 202} which may explain the origin of the faster water oxidation kinetics observed, given the excess thermodynamic driving force then available for the reaction to occur on WO₃. This relationship between valence band depth and kinetics has been proposed in other work,^{118, 203} and would then suggest that there exists a valence band energy dependence on photoelectrochemical water oxidation that is analogous to the overpotential dependence often found in electrocatalytic water oxidation systems. The high crystallinity of the sample, the preferential growth orientation of the needles, or effects of pH on the water oxidation mechanism may also contribute to the faster kinetics observed for our WO₃, though further investigation on these aspects was beyond the scope of this study.

In stark contrast to the hole kinetics, a parallel comparison of electron dynamics between WO_3 and those of the other common transition metal oxides yields the opposite trend, as WO_3 displays slow electron extraction (Figure 4.14). This difference in extraction time is as large as an order of magnitude when comparing TiO_2 and WO_3 needles and is still evident when comparing the dense films, demonstrating that slow electron extraction is a property of WO_3 . Considering that good electron conductivity is often presented as a promising feature of WO_3 ,^{60, 138, 155} this result was surprising. It suggests that the main benefit of adding WO_3 as an electron transport layer in various heterojunctions is to aid charge separation and thus increase charge carrier lifetime (see Chapter 2, Section 2.2.2), rather than rapidly transport electrons to the contact. Irradiated from the front, it is observed that longer WO_3 needles give slower charge extraction than shorter needles (Figure 4.10, *left*), confirming that the issue is related to transport through the material, rather than interfacial defects at the contact. I propose that this slow electron extraction is due to the trapping of electrons below the conduction band and suggest that the mobility of electrons is thereby reduced. The negative correlation of rate of extraction with increasing anodic bias (Figure 4.8, *lower*) supports a trap-mediated transport mechanism. As the anodic bias is increased, an increasing number of progressively deeper states below the conduction band are emptied and thus become accessible to trap photoexcited electrons. With greater applied bias, both the density and the depth of these available electron traps in the space-charge layer increases. It follows that the electron extraction is slowed because electrons trap and de-trap to reach the back contact, effectively hopping through the needle. This model is consistent with the observation that shorter needles have a faster extraction time, as the distance to the contact is reduced, and so fewer trapping/de-trapping steps are required. The fitting of the TDR electron decay to a stretched exponential gives further analytical grounding that supports this transport mechanism, as it represent a pseudo-first order decay, reflecting that trapping is determined by an excess of only one carrier, in this case the electrons (Figure 4.15).²⁰⁴ Furthermore, this fitting indicates the dispersive time range in which electrons are extracted due to multiple trapping events.²⁰⁵ This trapping and de-trapping form of transport has previously been explored with stretched exponential functions or power law decays in other metal oxide-based systems.^{206, 207} It has also been tentatively proposed by Lindquist's group,¹⁶⁶ and is consistent with the presence of interband states in WO_3 as confirmed in other studies.^{165, 189}

As previously acknowledged, tungsten trioxide has a large propensity to form numerous oxygen vacancy defects.^{185, 187, 197, 208} It is therefore highly probable that these chemical defects form the interband states responsible for trapping electrons. This is supported herein by the improvement in extraction time observed when the WO_3 is subjected to prolonged annealing in air (Figure 4.10, *right*): with increased opportunity provided for oxygen to permeate the WO_3 structure

and fill/remove such oxygen vacancies, longer annealing results in fewer trap sites to hinder the transport of electrons to the contact. Furthermore, the lack of photocurrent in the non-annealed sample (Figure 4.9, *right*) suggests that excessive concentrations of oxygen vacancies trap electrons so strongly and impede the charge carrier mobility to such an extent that most charges recombine. A model of electron dynamics for WO₃ needles is summarised in Scheme 4.16.

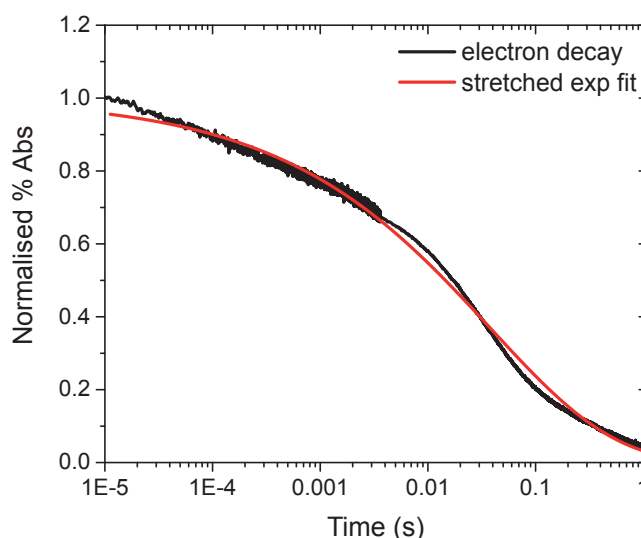


Figure 4.15 – Stretched exponential fit to the TDR electron decay probed at 800 nm for WO₃ needles under 1.45 V_{RHE}. The fitting has the form $(t) = ae^{-t^b}$, with the dispersive factor $b = 0.38$ and an R^2 value of 0.998.

As evidenced in the bias dependence study (Figure 4.8), it is shown, depending upon applied bias, that the majority of electrons observed on these microsecond-to-second time scales are eventually extracted, negating the possibility that a slow, trap-mediated recombination is predominantly being monitored. The lack of substantial recombination losses observed in the electron kinetics across these time scales (0.01 ms to 1 s) is supported by consideration of the internal quantum efficiencies obtained for the longer and shorter WO₃ needles (Figure 4.11), which remain similar under front illumination, despite the difference in electron extraction times shown in Figure 4.10. Modest back electron-hole (surface) recombination is observed for anodic potentials close to flat-band; however, this is readily removed by applied potentials greater than 1.15 V_{RHE}. The lower back electron-hole recombination losses compared to other metal oxide photoanodes such as BiVO₄ and α -Fe₂O₃ are most likely due to the faster water oxidation kinetics by WO₃ holes, as discussed above, which will result in less hole accumulation at the surface under conditions of steady-state photoelectrochemical water oxidation.^{92, 117} However, the extensive electron

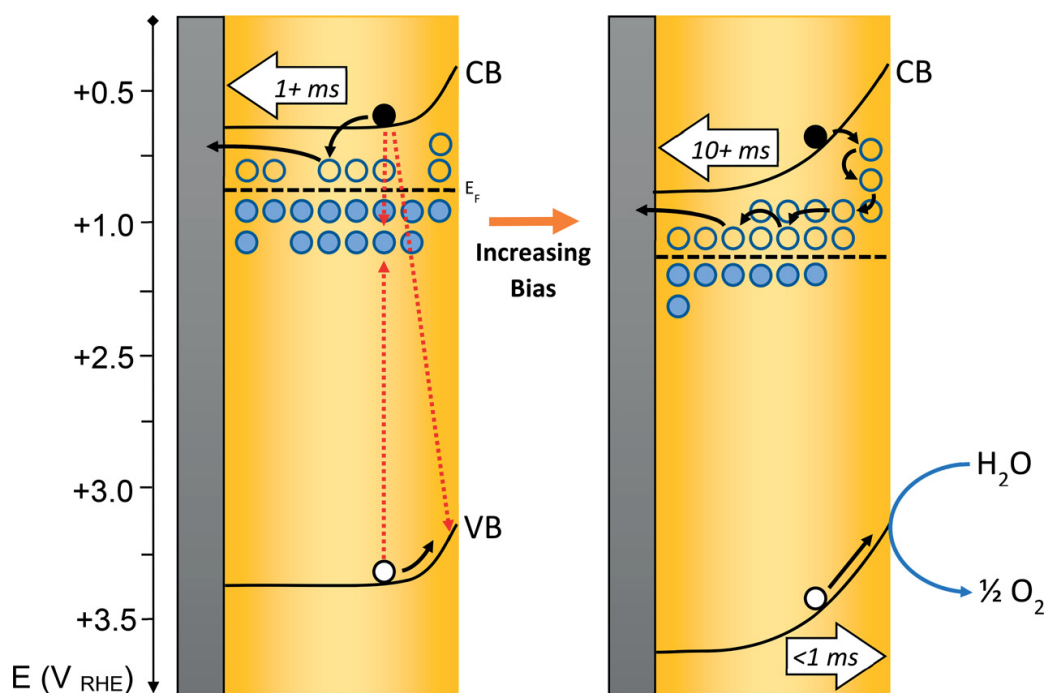


Figure 4.16 – Photogenerated electrons (black) have different extraction times depending on the applied potential, *left*: $0.8 V_{\text{RHE}}$, *right*: $1.45 V_{\text{RHE}}$. This is due to the increased number of traps that are empty under bias and hence can accept electrons (open circles). Electrons navigate through these states to the external circuit as indicated by the black arrows. Little recombination, either from the surface or via the trap states (red arrows), is observed on the time scales of the experiment as photogenerated holes (white) are rapidly transported to the surface to oxidise water within milliseconds.

trapping and associated slow electron transport kinetics observed for the WO_3 photoanodes studied herein can be expected to lead to internal resistance losses, which will limit the fill-factor of the J-V curve in a tandem cell device. Given the relatively efficient electron extraction observed for these WO_3 photoanodes, one can conclude that ultrafast bulk recombination is the most probable factor limiting device internal quantum efficiency. This is discussed further in Chapter 5.

4.4 Conclusion

In summary, I have shown these WO_3 needles to be rapid water oxidation photoanodes, with high Faradaic efficiency and faster hole injection into the electrolyte than in other commonly studied transition metal oxide photoanodes. These rapid water oxidation kinetics improve catalytic performance by suppressing competing surface recombination and enabling photocurrent onset close to flat-band without added co-catalysts; it is proposed that the kinetics correlate with the depth of the valence band. The extraction of electrons, by comparison, is observed to be particularly slow, which is assigned to trapping of electrons into vacant defects below the conduction band. I propose that these trap sites are unoccupied oxygen vacancy states which form the primary intrinsic dopants in the material. Annealing for longer in air therefore increased the rate of charge extraction by reducing the number of oxygen vacancies. I thus conclude that the density of intrinsic chemical defects, such oxygen vacancies, can have a significant effect on charge transport through nanostructured WO_3 , with potential implications for other heavily doped materials.

Chapter 5

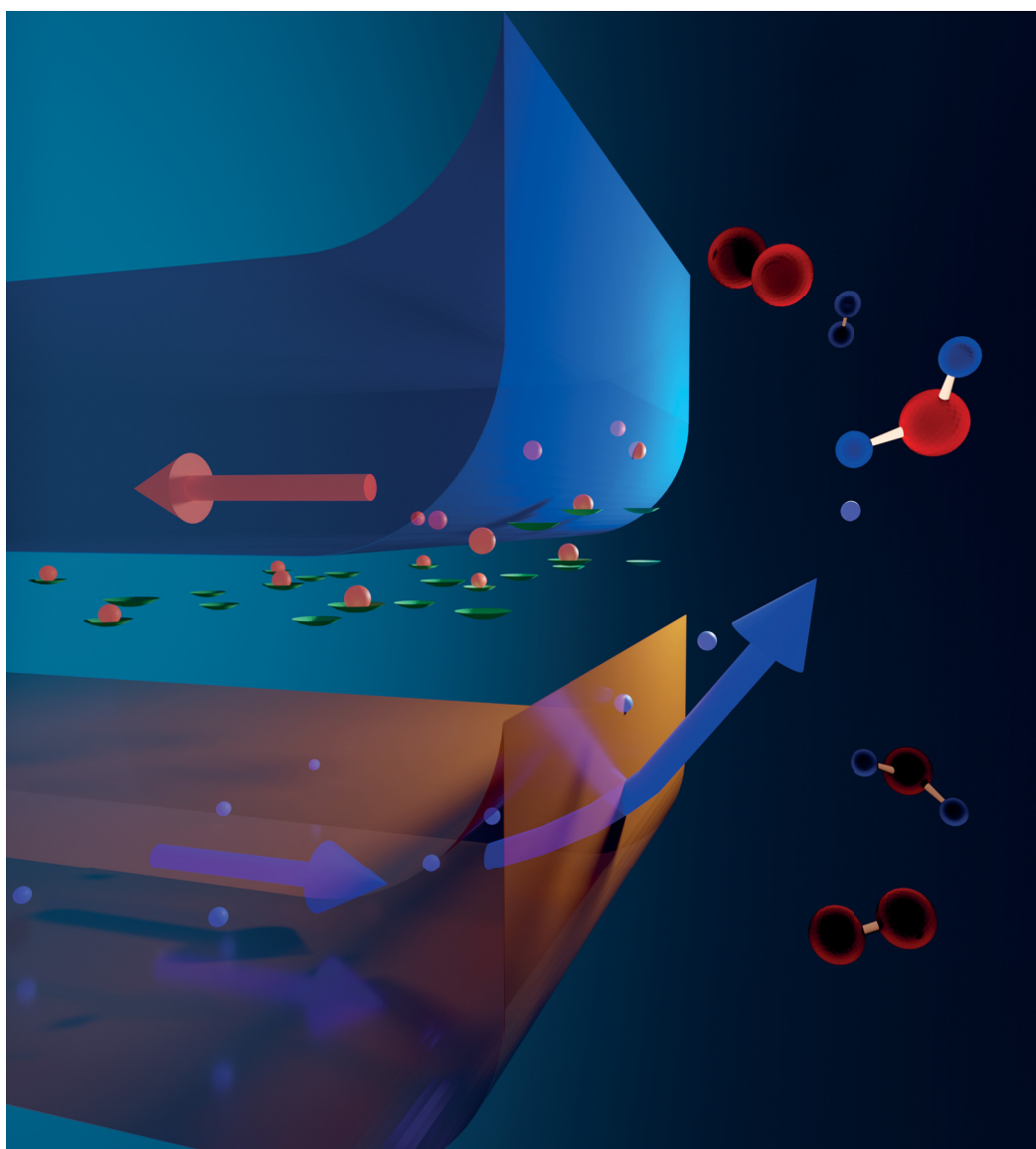


Illustration by author

5 Charge separation, band-bending and trapping in tungsten oxide

In this chapter, we take a closer look at the WO_3 photoanodes examined in Chapter 4 to understand how fundamental processes such as charge separation and recombination are affected by intrinsic doping and space-charge layer formation. As mentioned in Chapter 2, the spatial separation of photogenerated electrons and holes in metal oxides is typically attributed to band-bending at the metal oxide/electrolyte interface. However, direct evidence of such band-bending impacting upon charge carrier lifetimes in metal oxides at early timescales has been very limited to date. In this chapter, the effect of band-bending on charge carriers dynamics in the WO_3 photoanodes is directly observed. Using ultrafast transient spectroscopy, the rapid relaxation of holes in the space-charge layer and their recombination with trapped electrons is tracked. I find that applied bias can significantly increase carrier lifetimes across all timescales measured, and attribute this to enhanced band-bending correlated with changes in oxygen vacancy state occupancy. Analogous enhancements in charge carrier lifetimes are observed following sample immersion in electrolyte, and changes in electrolyte composition, even in the absence of applied bias, again assigned to variations in surface band-bending. This study directly demonstrates how band-bending increases charge carrier lifetimes at early times, how this correlates with oxygen defect-state occupancy, and the importance of this for photoelectrochemical function. I then take this further by modulating the bulk oxygen vacancy concentration over a series of WO_3 photoanodes. I find that samples with intermediate quantities of vacancies pertain to the highest photocurrents, with transient kinetics revealing that both higher and lower concentrations of vacancies lead to increased incidences of recombination across all timescales. Ultimately, this chapter presents new material insight that is relevant for all metal oxide photoanodes, demonstrating how band-bending increases charge carrier lifetimes at early times, and the importance of intrinsic defects, sometimes overlooked.

Chapter 5. Charge separation, band-bending and trapping in tungsten oxide

Most of the results presented in this chapter are included in the following articles for publication:

Corby, S. et al., "*Charge separation, band-bending and recombination in WO₃ photoanodes*", The Journal of Physical Chemistry Letters, **2019**, 10, 18, 5395–5401

Corby, S. et al., "*Determining the role of oxygen vacancies in the photocatalytic performance of WO₃ photoanodes for water oxidation*", submitted

5.1 Introduction

As discussed in Chapter 2, most models of oxide photoelectrode function assume that charge carrier longevity, and the ability for slow surface chemistry to compete against faster recombination processes, is the product of surface band-bending.^{170,209,210} However, actual studies of the role of band-bending and concomitant space-charge layer (SCL) formation on the dynamics of photogenerated charge carriers at early times are very limited. Long-lived holes (microsecond-to-second timescales) with lifetimes capable of driving water oxidation catalysis have been observed under anodic bias in several systems.^{64,211,212} However, the yield of these long-lived holes, and thus the final quantum yield for a device, is primarily determined by the efficiency of charge separation that occurs on much faster timescales. Despite many studies of charge carrier dynamics on ultrafast timescales in such photoanode materials, there is, to the best of my knowledge, only one report demonstrating any relation between applied field and carrier lifetime,²¹³ even with the widely accepted importance of band-bending-induced charge separation in most models of photoelectrochemical function. The role of band-bending is also of particular importance, and poorly understood, for photocatalyst suspensions, which may evolve oxygen without bias and sometimes without scavenger,^{214,215} thereby suggesting that electrolyte-induced band-bending alone may be adequate to inhibit recombination processes and enable water oxidation. However, the extent to which either bias or electrolyte induced band-bending impacts upon early carrier dynamics, and ultimately device quantum yields, remains unclear.

In this Chapter, I examine the ultrafast kinetics of electrons and holes in nanostructured WO_3 photoanodes, the same promising material for solar water oxidation that was introduced in Chapter 4. As mentioned previously, WO_3 , with a band-gap of ~ 2.6 eV, is generally reported to have a high intrinsic doping density as a result of readily formed oxygen vacancy defects (V_O).^{161,163} Sub-stoichiometric oxygen concentrations are common to most metal oxides and result in two electrons remaining in the lattice for every absent oxygen atom. Thus, in WO_3 , these defects manifest as reduced tungsten centres neighbouring sites absent in oxygen, giving rise to a characteristic broad W^{5+} absorption at red and NIR wavelengths, and interesting material properties such as the photo- and electrochromic effects.^{162,167,216} The exact nature of the electronic states associated with these defects is still debated, although there is some consensus for TiO_2 , BiVO_4 , $\alpha\text{-Fe}_2\text{O}_3$ and WO_3 , that these states reside within the band-gap, with a broad energetic distribution below the conduction band.^{162,204,217–219} However, the significance of oxygen vacancies on the photoelectrochemical performance, particularly at the high concentrations frequently reported for WO_3 , is not well understood and is an area of increasing interest for many oxides. Several reports claim that oxygen vacancies increase the charge carrier density to give improved

conductivity, though there are few direct studies of this correlation.^{73,220,221} Studies conducted by Wang et al. have shown an order of magnitude increase in photocurrent for tungsten oxide films annealed under hydrogen atmosphere to create oxygen vacancies, with the resultant films almost black compared to the yellow, oxidised material.¹³⁷ Zhao et al. reported that the supplementary V_O defects generated in hematite films by N_2 annealing improve charge separation efficiencies.²¹⁸ On the other hand, defect states in the band-gap have been reported to trap charges, resulting in increased recombination pathways and therefore a poorer performance.^{164–166,222} For example, Leshuk et al. demonstrated that bulk vacancy defects generated by hydrogenation of titania resulted in a lower photocatalytic activity for water remediation by increasing trap-mediated recombination.²²³ Similarly, poorer performances in nitrogen and aluminium doped TiO_2 have been attributed to increased recombination through the unintentional creation of oxygen vacancies.^{224,225} The importance of inter-band defects, particularly in charge separation and transport, is thus still in need of clarification.²²⁶ Furthermore, recent studies of ultrafast kinetics in WO_3 have shown that the presence of large numbers of such occupied vacancy states results in rapid trapping of photogenerated holes ($\ll 0.2$ ps after excitation), whereas electrons may trap into unoccupied vacancy states that lie above the Fermi level.²¹⁶ However, the role that band-bending may play on the timescales of these fast processes is unknown. Modulation of the occupancy of these states through band-bending has been demonstrated to significantly affect electron extraction timescales, as was shown in Chapter 4,²²⁷ but the relationship between the electronic occupancy of these defect states, the degree of band-bending and the ultrafast dynamics of photogenerated charges has yet to be directly probed.

The WO_3 films used in the results below were synthesised as discussed in Chapters 3 and 4 and further physical characterisation is given only where specific alterations were made to the photoanodes. As detailed in Chapter 4, the high surface area nanostructures on FTO give good photocurrent onset ($0.5 V_{RHE}$, see Figure 4.4) and reasonable Faradaic efficiencies for oxygen evolution (87%, Section 4.5).²²⁷ However, despite faster water oxidation kinetics than the other commonly studied transition metal oxides, the maximum photocurrent reported to date for WO_3 under 1 sun irradiance and $1.23 V_{RHE}$ is only approximately 70% of the 5.3 mA/cm^2 theoretical maximum.²²⁸ This performance is also an outlier, with more publications reporting photocurrents closer to $\sim 10\text{-}20\%$ of the theoretical limit, and quantum yields far lower than one, indicating severe recombination losses.^{77,110,143,227,229–231} Using transient absorption spectroscopy, I demonstrate herein that space-charge layer formation, achieved through electrolyte contact or applied bias, can significantly retard the ultrafast recombination processes that largely determine the efficiency of photoelectrochemical and photocatalytic performance.

I then examine the performance of my WO_3 films with different concentrations of bulk oxygen vacancies ('low', 'medium', 'high' and 'very high'), and find that an intermediate concentration gives the maximum photocurrent. I determine that an intermediate number of defect states significantly reduces bulk recombination while providing improved electron transport when compared to a poorly doped sample, which shows poor charge separation. On the other hand, a 'high' or 'very high' defect concentration results in a greater probability of trap-mediated recombination, thus lowering performance, with the highest degree of doping giving rise to no photocurrent at all. It is thus that between the extremes lies a so-called "Goldilocks" ratio of oxygen-to-tungsten, equating to an oxygen vacancy density of 2% of oxygen atoms, which is able to balance the doping density required for adequate charge separation and transport while minimising bulk recombination through the defect states generated. With these results, I am thereby able to partially resolve the ongoing dispute in literature as to the role of these chemical defects and stress an important factor for synthetic design of new photoanodes.

5.2 Results

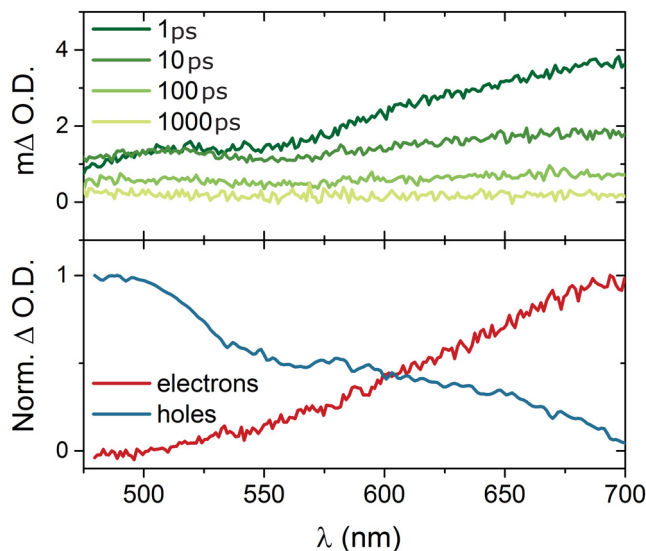


Figure 5.1 – *upper*: Ultrafast transient absorption spectra between 1 ps and 1000 ps in 0.1 M H_2SO_4 under no applied bias after excitation with 355 nm pump at 0.2 mJ/cm^2 . *lower*: Normalised spectra of separated electron and hole signals, obtained using global analysis performed by Ms Yifan Dong (Appendix, A.2).

5.2.1 Transient spectra

Figure 5.1 shows the ultrafast transient absorption (TA) spectra of WO_3 immersed in electrolyte (0.1 M H_2SO_4) in the absence of applied bias at different time delays after exciting with a 355 nm laser. Two features can be determined: a broad absorption spanning most of the visible region, already present within a picosecond of excitation; and a smaller, slower rising feature that peaks around 500 nm. This feature at 500 nm is not always readily apparent due to the varying degree of overlap of the larger signal and thus a global analysis fitting (performed by Ms. Yifan Dong) was used to resolve the two features, shown in Figure 5.1, *lower* (see Appendix A.2 for details). The more dominant feature at long wavelengths is assigned to electrons localised at W^{5+} centres. This assignment agrees with my previous spectral studies on slower timescales, discussed in Section 4.2.3.^{111,227} Furthermore, this spectral range corresponds to the W^{5+} absorption observed in steady-state studies, and typically assigned to W^{5+} species localised adjacent to oxygen vacancies (see also Figure 4.12).^{139,187,232} The second feature at 500 nm is associated with reactive holes in WO_3 , as also discussed in detail in the previous chapter at later timescales.^{111,227} In fact, the spectral shape at 1 ps is remarkably similar to that observed on the microsecond timescale in

Figure 4.6, supporting the assignments given and hinting towards the localised nature of these charges, as discussed herein. Both species can be identified within picoseconds of excitation and are followed herein until the timescales of reaction and extraction (see below).

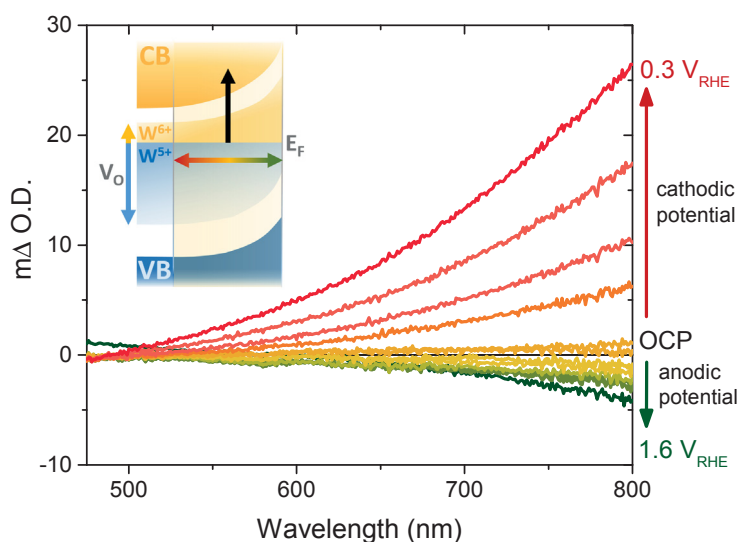


Figure 5.2 – Spectroelectrochemistry with respect to the open circuit potential (OCP), showing the change in oxygen vacancy defect state occupancy with band-bending and the similarity with the TA electron signal. All spectra collected in 0.1 M H₂SO₄. *inset*: schematic showing occupied (blue) and unoccupied (yellow) states, the mid-band oxygen vacancy defects (V_O), the absorption probed by the technique (black arrow) and the changing SCL with bias (coloured arrow).

For further confirmation of these optical assignments, I turned to spectroelectrochemistry (Figure 5.2). With the spectrum at open circuit potential taken as reference (OCP, $\sim 0.5 V_{RHE}$), the space-charge layer (SCL) width was altered using anodic and cathodic variations in potential, resulting in the respective loss and gain of a broad feature at longer wavelengths. This feature, previously reported in photo- and electrochromic studies of WO₃, arises from W⁵⁺ states associated with oxygen vacancies, and therefore highlights that the occupancy of these states and the degree of band-bending in WO₃ are directly correlated.^{232–234} The clear resemblance between the spectral signal observed when a greater number of these states are occupied (Figure 5.2, cathodic potential) and the broad, red-NIR TA (Figure 5.1, red) confirms the assignment of this signal to photogenerated electrons in W⁵⁺ states, and thereby indicates their trapped nature. As such, this correlation suggests that changes in oxygen-vacancy state occupancy as a result of band-bending may also manifest in changes in photogenerated populations that can be monitored transiently, with likely repercussions for performance.

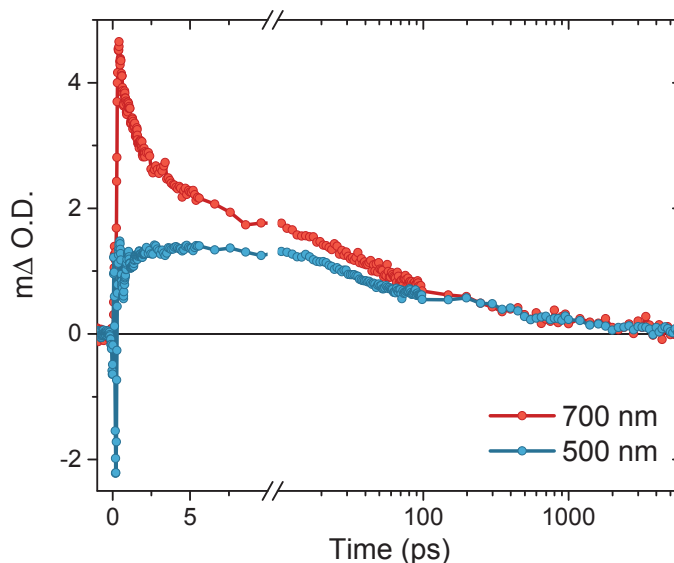


Figure 5.3 – Ultrafast transient absorption kinetics of electrons (700 nm, red) and holes (500 nm, blue) recorded from ~200 femtoseconds to 6 nanoseconds after excitation. (0.1 M H_2SO_4 , no applied bias, 355 nm pump, $0.2 \text{ mJ}/\text{cm}^2$).

5.2.2 Ultrafast carrier kinetics

The kinetics of the electrons (measured at 700 nm) and holes (measured at 500 nm) in the absence of applied bias are given in Figure 5.3. The figure shows that the TA kinetics at early times are markedly different for both species. The electron signal shows an instrument-limited rise, thus reflecting a population generated immediately after photoexcitation. In contrast, the hole signal shows a build-up within the first 6 ps due to the formation of a new state. This can be more readily observed in the close-up given in Figure 5.4 (and also in Figure 5.8 and 5.12). The decay dynamics of both signals overlap at later times, indicating recombination between the two species. I propose that the early-time decay of the electron signal is primarily associated with bulk electron-hole recombination, whereas the relatively slow rise at 500 nm is tentatively assigned to the relaxation/localisation of holes within the SCL. This latter assignment stems from two previous observations. Firstly, outside the SCL (or in the absence of one), photogenerated holes rapidly trap into occupied oxygen vacancy states, resulting in a bleached signal over the W^{5+} absorption range,²¹⁶ consistent with the rapid initial decay at 700 nm in Figure 5.3 indicative of a loss of electron absorption. Secondly, I showed in Chapter 4 that catalytically active holes that absorb at 500 nm oxidise water on slower timescales,²²⁷ thereby indicating that this absorption arises from holes localised within the depletion layer. The data shown in Figure 5.1 and Figure

5.4 are, in essence, optical evidence for the initial separation of electrons and holes, with distinct optical signals and kinetics observed for both photogenerated species.

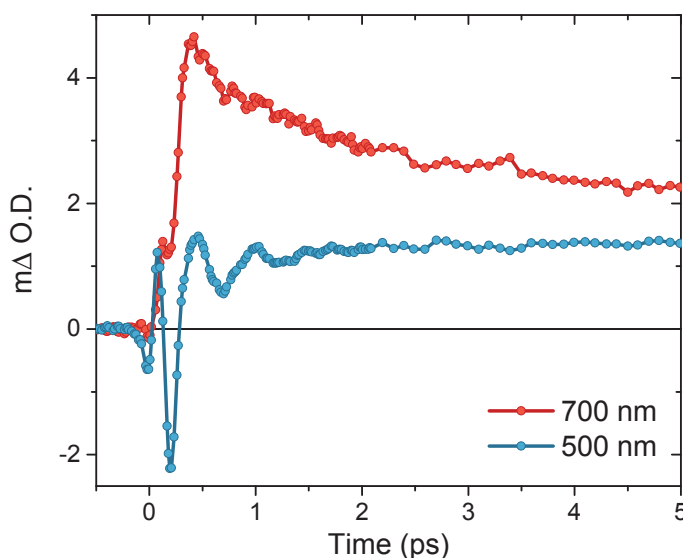


Figure 5.4 – A closer view of the first five picoseconds after excitation from the data in Figure 5.3, showing the rise of the hole signal and an oscillatory feature present.

It is also apparent from Figure 5.4 that the early-time TA data present an oscillatory feature on top of the electron and hole signals that dampens with time. The oscillations were not observed on blank FTO, thereby discounting instrument response artefacts. This feature is strongest at shorter wavelengths though it is present over the entire spectral window as shown in the two-dimensional map in Figure 5.5 (computed by Dr. Ernest Pastor). These oscillations are characteristic of a superposition of optically induced vibronic transitions (vibrations). The lower panels in Figure 5.5 show the averaged Fourier transform (FT) of the oscillatory component at two extremes of the TA spectrum. At shorter wavelengths, where hole absorption dominates, two major peaks are observed at $\sim 60\text{ cm}^{-1}$ and $\sim 75\text{ cm}^{-1}$, also found in the ground state Raman spectrum for WO_3 .²³⁵ Similar photoinduced oscillations have been observed in BiVO_4 and have been assigned to coherent phonons associated with hole trapping.²³⁶ However, given the electronic proximity of the TA signal to the band-gap, the possibility that these frequencies are due to ground-state vibrational wavepackets cannot be discarded. In contrast, at longer wavelengths, a redistribution of peak intensities is observed, with new features below 70 cm^{-1} and at $\sim 100\text{ cm}^{-1}$. Such frequency spread at these wavelengths is suggestive of excited-state vibrational coherences.²³⁷ Though there is scope for further analysis to establish the role of these

vibrations in catalytic activity, the strong coupling between the electronic and nuclear degrees of freedom apparent from the observed oscillations is indicative of the relatively localised nature of the photogenerated electrons and holes, consistent with the discussion above.

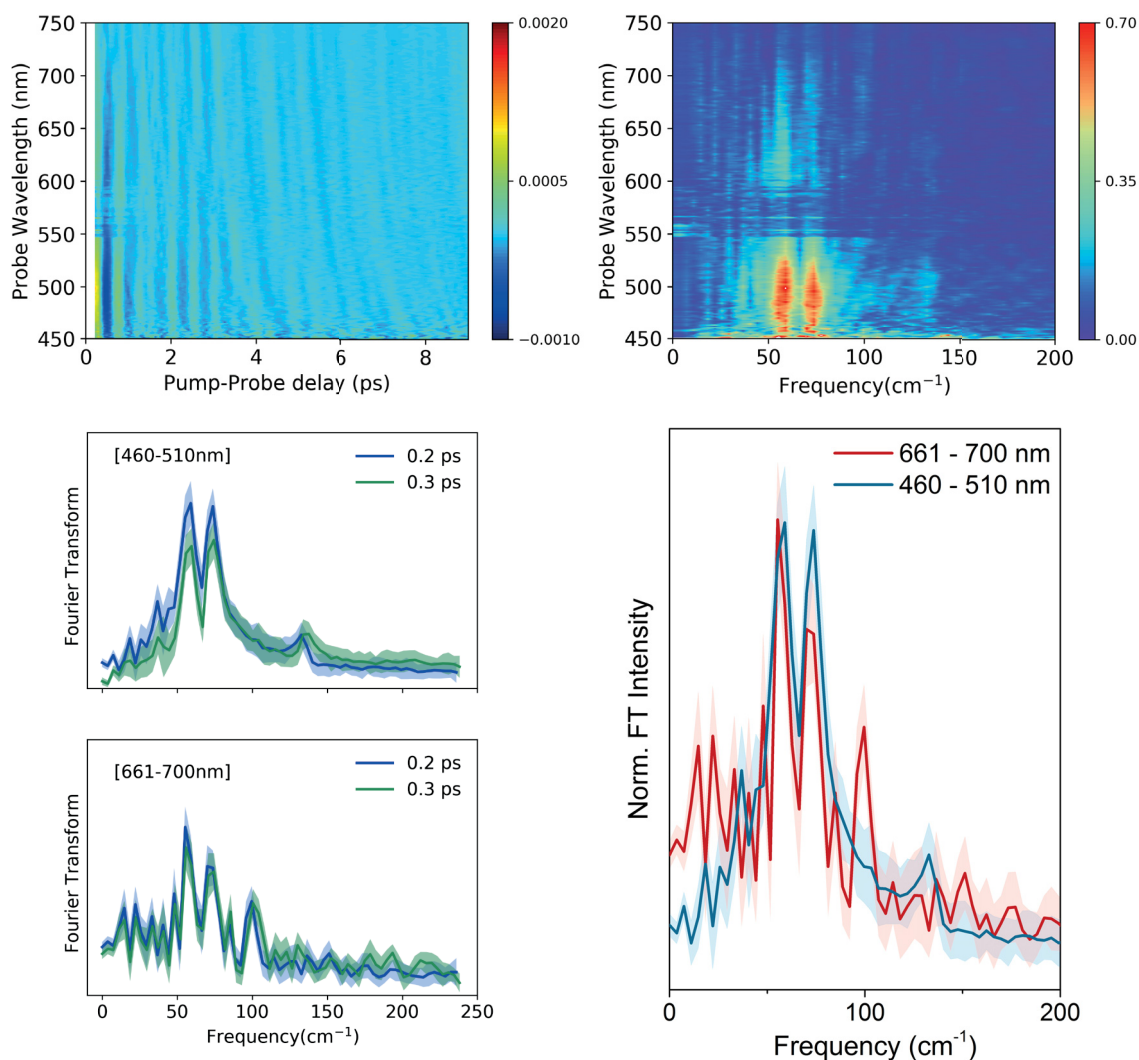


Figure 5.5 – *upper left*: Oscillation map obtained via subtraction of the population component across the TA spectrum. The data was truncated at 0.2 ps to avoid any contamination from coherent artefacts. *upper right*: Fourier transform of the transient oscillations, indicating two main frequencies at 60 cm^{-1} and 70 cm^{-1} , stronger at shorter wavelengths. *lower left*: FT data averaged over different spectral regions (*top* = $\sim$ holes, *bottom* = $\sim$ electrons) and obtained at different data truncation time points. *lower right*: Comparison between the oscillations over the electron and hole regions of the TA spectrum. Faded area gives 95% confidence interval. Figure prepared by Dr Ernest Pastor.

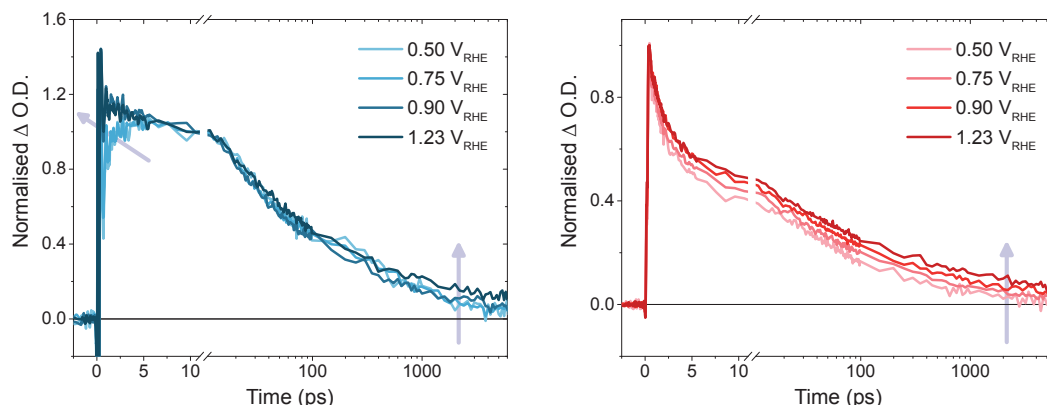


Figure 5.6 – *left*: Normalised hole kinetics (500 nm) under different applied potentials (0.50 – 1.23 V_{RHE}). *right*: Normalised electron kinetics (700nm) under the same applied potentials. Both data sets were measured in 0.1 M H₂SO₄ with a 355 nm pump at 0.2 mJ/cm².

5.2.3 Modulating surface band-bending – bias dependence

To determine how the degree of band-bending affects charge separation and recombination, the ultrafast kinetics were monitored as a function of applied bias. I found that both the hole (Figure 5.6, *left*) and electron (*right*) signals become longer lived as the applied potential increases. This change in kinetics was observed to be reversible, although sample dependent due to variations in oxygen vacancy concentration, and more pronounced with lower excitation densities (see Figure 5.9). Increased carrier lifetime is attributed to an enhancement in the SCL inhibiting recombination processes as band-bending is increased. By taking the half-time of the electron decay at each potential, the rate of change is found to be largest at lower potentials, closer to the OCP, where the dependence of SCL width upon applied potential will be strongest (Figure 5.7). More quantitatively, the increase in carrier lifetime with applied bias correlates with the expected increase in SCL thickness, as demonstrated in Figure 5.7.^{140, 178} A second effect of anodic bias on the hole signal can be noted in Figure 5.6, *left*: as well as increasing hole lifetime (see Table 5.1 for half-lifetimes), applied bias accelerates the initial appearance of the 500 nm hole signal (grey arrow, see Figure 5.8 for a closer view). This trend is consistent with an increase in hole localisation in the broadened SCL. The earlier rise could also result from the increased field driving photogenerated holes towards the surface faster, though the timescale of the rise suggests the holes we observe are those already in, or very near, the SCL.

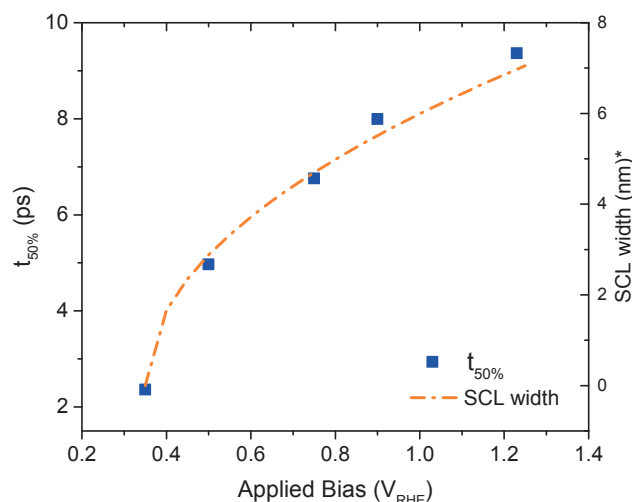


Figure 5.7 – The half-lifetime of the electron decay at 700 nm (blue squares) is plotted against increasing applied potential. This is found to map well with the estimated space-charge layer (SCL) width (orange line).*The SCL width was estimated with $E_{FB} = 0.35 V_{RHE}$, $N_D = 10^{20} \text{ cm}^{-3}$ and $\epsilon_{WO_3} = 50$. These values were taken from literature for similar WO_3 samples.^{140, 178}

Bias (V_{RHE})	$t_{50\%}$ at 500 nm (*from 10 ps)	$t_{50\%}$ at 700 nm (*from 0.5 ps)
0.50	73 ps	5 ps
1.23	88 ps	10 ps

*Different starting points taken to avoid complication from rise in hole signal.

Table 5.1 – Half-lifetimes ($t_{50\%}$) calculated from selected data in Figure 5.6

When the excitation intensity was increased, a smaller dependency of carrier lifetime on applied field was observed, as illustrated in Figure 5.9. This observation is likely related to the relative density (per cm^2) of charge in the SCL compared to the density of photogenerated carriers ($4 \times 10^{14} \text{ cm}^{-2}$ for excitation conditions used in Figure 5.6). At high photon fluxes, the photogenerated charge density becomes comparable to or larger than the SCL density, resulting in screening of the SCL field. Compared to most other metal oxides, WO_3 typically exhibits a higher doping density, associated with a higher number of intrinsic oxygen vacancy states, on the order of 10% of the metal content in these needles (although the electrical doping density will be lower than this chemical doping density).²²⁷ The challenge of undertaking ultrafast TAS experiments at excitation densities lower than the dark doping density is the likely reason for the general absence of bias dependent kinetic data in literature on similar materials, particularly as excitation fluences are often higher than those employed herein.^{135, 238} It is probable that stronger bias dependencies would be observed at even lower excitation densities, more comparable to solar irradiation, although signal to noise limitations prevented such experiments for the study reported herein.

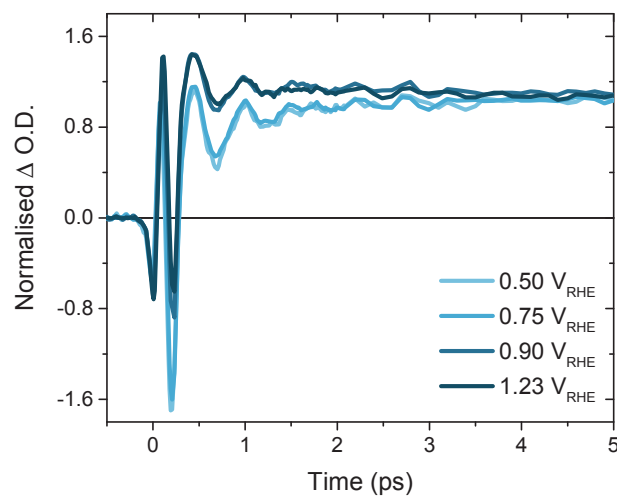


Figure 5.8 – Closer view of the first five picoseconds of the hole dynamics at 500 nm (shown in full in Figure 5.6). A faster rise is observed with increasing anodic bias, which we assign to faster localisation of holes in the wider SCL.

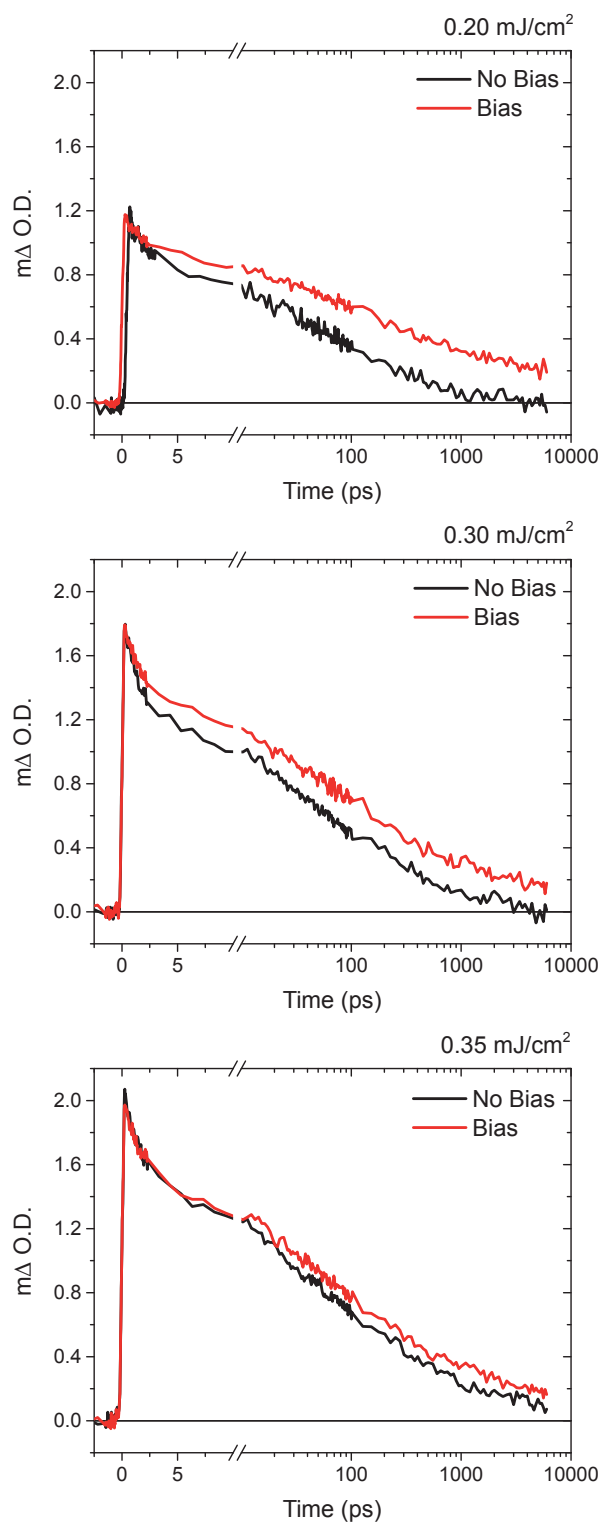


Figure 5.9 – The electron signal (700 nm) shows less strong bias dependence as the laser intensity is increased from (*upper*) 0.20 mJ/cm^2 to (*middle*) 0.30 mJ/cm^2 to (*lower*) 0.35 mJ/cm^2 . Bias is 1.23 V_{RHE} , conditions used were the same as those in Figure 5.6.

5.2.4 Modulating surface band-bending – electrolyte dependence

As the longer carrier lifetimes observed with anodic bias are assigned to increased band-bending, it follows that any method of increasing the space-charge layer should produce a similar result. In particular, immersion of an electrode in electrolyte, even in the absence of applied bias, can result in SCL formation due equilibration of the metal oxide Fermi level with the chemical potential of the electrolyte (see Chapter 2, Section 2.1.1).²¹⁰ Figure 5.10 (*left*) shows a comparison of electron decay kinetics for a WO_3 sample in air and when immersed in the 0.1 M H_2SO_4 electrolyte used throughout this work. In electrolyte, a larger, longer-lived electron signal is observed, which I assign to enhanced band-bending causing an improvement in charge separation. Moreover, the enhancement can be considered an increase in the number of unoccupied oxygen vacancy states available to trap electrons, and a reduction in any hole trapping that may occur without a SCL, which would otherwise lower the signal. Electrolyte-induced SCL formation was supported by UV-visible absorption spectra in air and electrolyte (Figure 5.11), which indicated an electrolyte absorption change reasonably consistent with a loss of W^{5+} states, similar to that shown in Figure 5.2. Furthermore, an accelerated appearance of the hole signal at 500 nm is observed in electrolyte compared to air (Figure 5.12), similar to the effect seen with bias induced band-bending (Figure 5.6), and thus provides further evidence of SCL formation. Longer carrier lifetimes in electrolyte were consistently observed for several samples, although the magnitude of the change differed (Figure 5.13). This is likely due to differences in SCL thickness between samples, which will vary with changes in dark doping density. Oxygen vacancy concentration and energetic distribution is known to vary with factors such as synthesis temperature.^{142, 143} I found that my WO_3 synthesis did not yield consistently doped samples between batches.

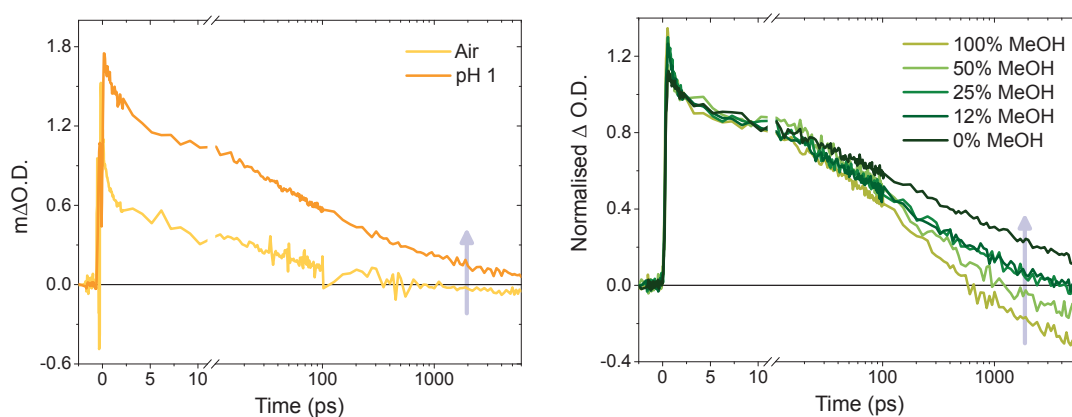


Figure 5.10 – *left*: The electron kinetics in air and in 0.1 M H_2SO_4 with no applied bias. *right*: The electron kinetics in MeOH with increasing percentage of pH 1 electrolyte present (0.1 M H_2SO_4). All data is collected at 700 nm following excitation with 355 nm, 0.2 mJ/cm² pump.

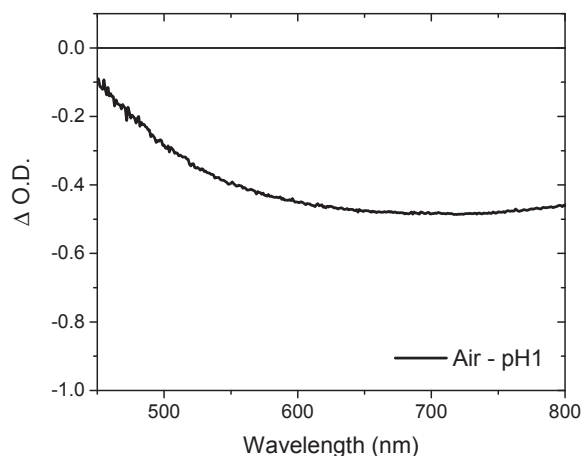


Figure 5.11 – Spectroelectrochemistry of WO_3 in electrolyte ($0.1 \text{ M H}_2\text{SO}_4$) with respect to the spectrum in air. An absorption spectrum was taken in the pH 1 electrolyte and then in air and the latter subtracted from the former to give the difference spectrum as shown. The bleach observed clearly resembles that shown in Figure 5.2, suggesting a loss of absorption from W^{5+} states due to their depletion in the space-charge layer. The differences between this spectrum and that in Figure 5.2 are likely due to changes in oxygen vacancy concentration between samples (see also Figure 5.13).

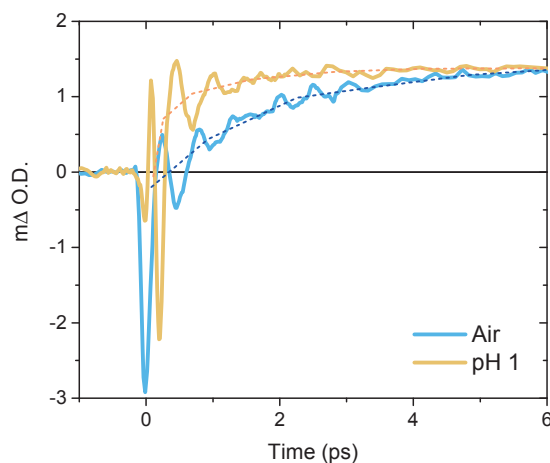


Figure 5.12 – The first six picoseconds of the TA signal at 500 nm, examining the rise-time of the hole signal in air (blue) and pH 1 electrolyte ($0.1 \text{ M H}_2\text{SO}_4$, yellow). The dashed lines are present to guide the eye. The signal rises faster in electrolyte, suggesting that the SCL formed improved the delivery of holes to the surface.

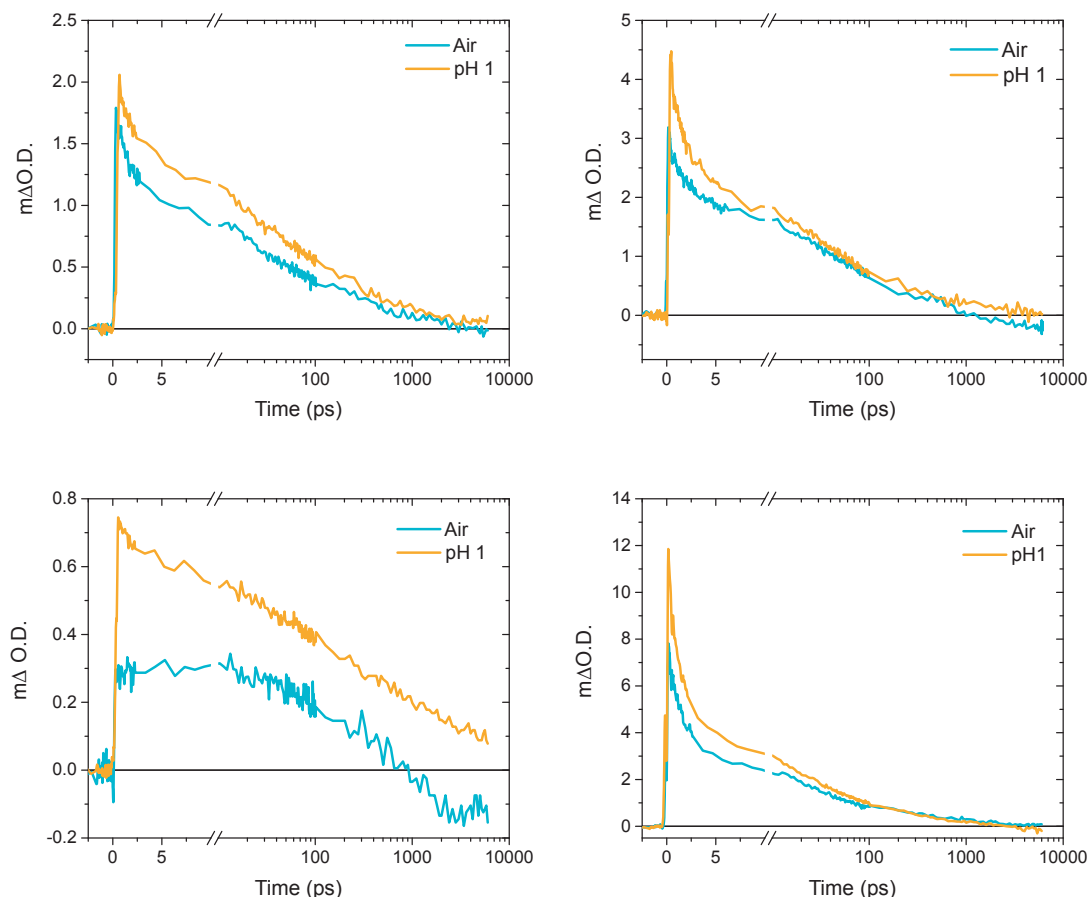


Figure 5.13 – TA decays of electrons at 700 nm for different samples in air and electrolyte, as shown in Figure 5.10. Though electrolyte always increases the electron lifetime, the magnitude of the change varies between samples, presumably due to changes in oxygen vacancy concentration $[V_O]$. All data is collected at 700 nm following excitation with 355 nm, $0.2 \text{ mJ}/\text{cm}^2$ pump.

A similar increase in charge carrier lifetime was observed with changes in the electrolyte composition, as shown, for example, in Figure 5.10 (*right*) for WO_3 in methanol (MeOH) with added aliquots of $0.1 \text{ M H}_2\text{SO}_4$ (pH 1). A faster electron decay is observed in 100% MeOH, with the half-lifetime of the decay increasing as the proportion of pH 1 electrolyte is increased. This suggests that the degree of band-bending following immersion in MeOH is less than in the aqueous pH 1 electrolyte, which may correlate with the less positive redox potential reported for MeOH compared to water.^{239,240} At greater MeOH concentrations, the signal at 700 nm becomes negative at longer times (bleaches). I assign this bleach to enhanced hole trapping into occupied (i.e. unionised) oxygen vacancy states, reducing the trapped-electron count at nanosecond timescales to below the original ‘pre-pump’ concentration. This interpretation complies with the bleached signal observed at these wavelengths in WO_3 samples with greater concentrations of

filled oxygen vacancy states, which can rapidly trap holes.²¹⁶ Figure 5.10 shows that as the ratio of pH 1 electrolyte to MeOH is increased, the electron lifetime increases, consistent with the idea of a greater SCL, which will depopulate potential W^{5+} traps and retard recombination by enhancing charge separation. This electrolyte effect is distinct from any hole scavenging effect of MeOH, which would only be applicable on catalytic timescales and would be expected to increase, rather than reduce, electron lifetime with greater MeOH concentration.

5.2.5 The role of oxygen vacancies

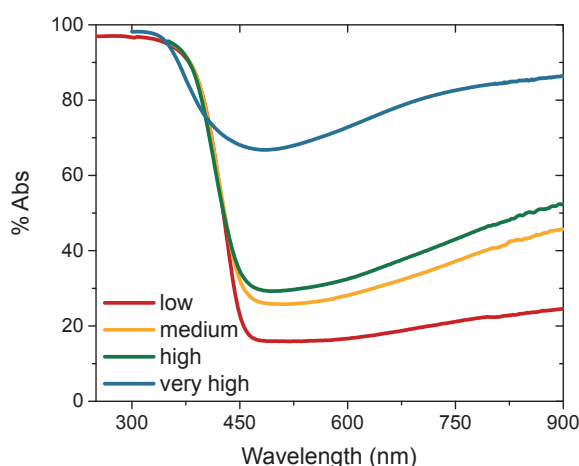


Figure 5.14 – UV/Vis absorption spectra calculated from integrated sphere measurements of transmission and reflectance for WO₃ films after different post-deposition modifications: without annealing ('very high' [V_O], blue), after treatment ('high' [V_O], green), after 2 hour annealing ('medium' [V_O], yellow) and after 12 hour annealing ('low' [V_O], red).

In line with expectations from trends with applied bias at slower times, the results thus far demonstrate enhanced carrier lifetimes in the ultrafast regime with increasing SCL width. Interestingly, there is a strong correlation between increased band-bending and the de-population of W^{5+} states associated with oxygen vacancies, highlighting the potential importance of these defects in performance. In order to study the effect of oxygen vacancies on the WO₃ photoanodes, the films used throughout this thesis were subjected to different post-deposition treatments, mostly involving changes to annealing conditions, all of which are detailed in Appendix A.3. Four sample types with differing oxygen vacancy concentrations were obtained: 'low', 'medium', 'high' and 'very high'. As the films are highly nanostructured, it was not possible to accurately determine the electronic doping densities by electrochemical impedance spectroscopy. The chemical doping density from oxygen vacancy states ([V_O]) could, however, be approximated for each sample

from UV/Vis spectroscopy (Figure 5.14) and by examining the tungsten peaks in the XPS spectra (Figure 5.15 and 5.16), assuming that each oxygen vacancy results in the generation of two W^{5+} species. It is evident in Figure 5.14 that, while the band-edge is comparable between samples, the absorption at longer wavelengths differs substantially. This absorption, as discussed in the spectroelectrochemistry data (Figure 5.2), is the result of W^{5+} centres associated with oxygen vacancies and therefore a larger percentage absorption equates to a higher $[V_O]$. Effects from any potential changes in back-scattering between samples were reduced by use of an integrating sphere setup.

This analysis is substantiated by a closer view of the W 4f envelope in the XPS spectrum for each sample type, which affords a better approximation of $[V_O]$ by examination of the $W^{5+}:W^{6+}$ ratio (Figure 5.16). This ratio was found to be ~ 0.35 in the most heavily doped, as-deposited samples (herein named ‘very high’) and was reduced to only ~ 0.03 through prolonged annealing in the ‘low’ $[V_O]$ samples. By considering that two W^{5+} centres will be formed for each oxygen vacancy, and that there are three oxygen atoms to every tungsten atom in stoichiometric WO_3 , I could convert this $W^{5+}:W^{6+}$ ratio for each sample into an approximate oxygen vacancy concentration as a percentage of oxygen atoms (summarised for each type in Table 5.2). It is clear from both the analogous band-edge absorption between samples (Figure 5.14) and from the high degree of similarity between the XPS survey spectra of each sample (Figure 5.15) – with only carbon and trace sulphur impurities detected – that the band-gap and the core material (WO_3) is not affected by the post-deposition treatments. The close agreement of the UV/Vis and XPS data in determining the oxygen vacancy content is highlighted in Figure 5.17. In addition, XRD analysis was conducted (Figure 5.18), which, in each case, reveals the same growth-oriented monoclinic tungsten oxide that was reported in Chapter 4.^{143,227} Thus, it was confirmed that the four WO_3 film types differ only in intrinsic defect concentration. It is noted that, due to the energetic stabilisation of W^{5+} states adjacent to oxygen vacancies, the percentage oxygen vacancy density (chemical doping) given in Table 5.2 will likely be higher than the electronic doping density caused by dopant ionisation.

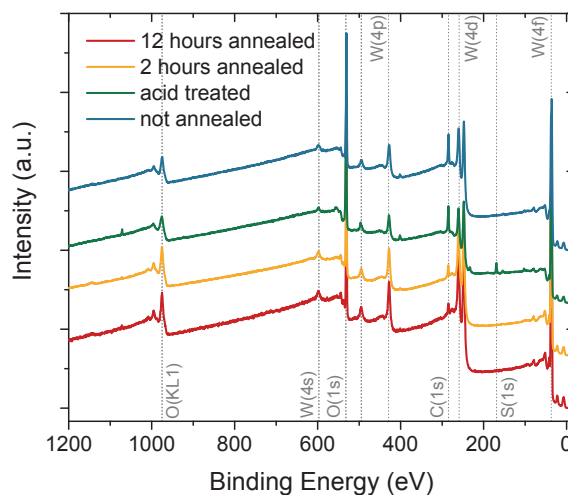


Figure 5.15 – XPS survey scan for each of the WO_3 films after different post-deposition modifications: not annealed ('very high' $[\text{V}_\text{O}]$, blue), acid treated ('high' $[\text{V}_\text{O}]$, green), after 2 hour annealing ('medium' $[\text{V}_\text{O}]$, yellow) and after 12 hour annealing ('low' $[\text{V}_\text{O}]$, red).

WO_3 sample	$\text{W}^{5+}:\text{W}^{6+}$ ratio from XPS	$[\text{V}_\text{O}]$ as % stoichiometric O
very high	0.35	5.8 %
high	0.14	2.3 %
medium	0.12	2.0 %
low	0.03	0.5 %

Table 5.2 – Oxygen vacancy content of each film, determined from XPS data in Figure 5.16

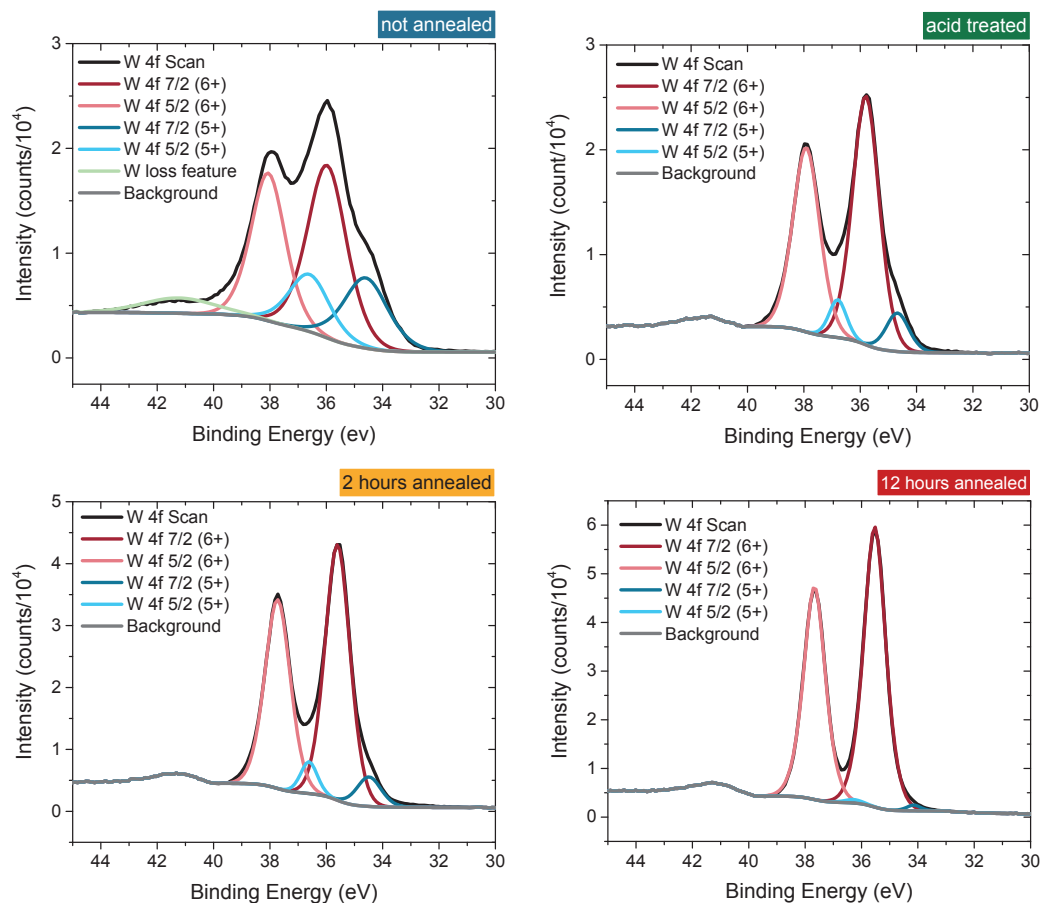


Figure 5.16 – Close up of the W 4f binding region from the XPS spectra in Figure 5.15. The 4f doublet is evident in each case from the two spin states (7/2 and 5/2). The main peaks stem from W^{6+} absorption whereas the smaller shoulders in blue are due to W^{5+} formed from neighbouring oxygen vacancies (V_O). *upper left*: Not annealed (very high $[V_O]$, blue), *upper right*: acid treated (high $[V_O]$, green), *lower left*: 2 hours annealed (medium $[V_O]$, yellow), *lower right*: 12 hours annealed (low $[V_O]$, red). The ratio of $W^{5+}:W^{6+}$ (blue : red peaks) clearly decreases from the upper left to lower right panel (0.35, 0.14, 0.12, 0.03), indicating that fewer oxygen vacancies are present.

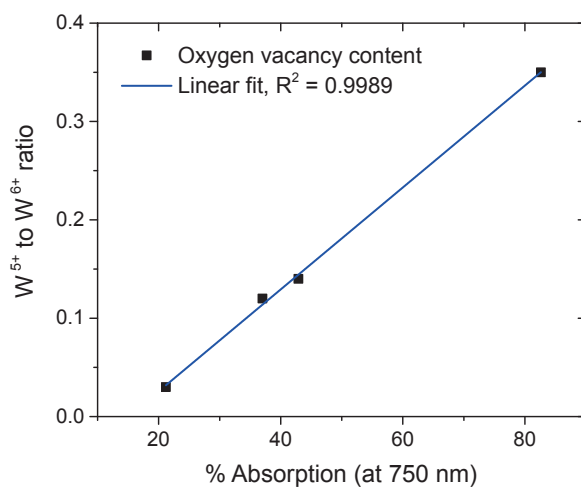


Figure 5.17 – Agreement between the XPS data (Figure 5.16) and UV/Vis data (Figure 5.14) for the determination of the oxygen vacancy content in each of the samples.

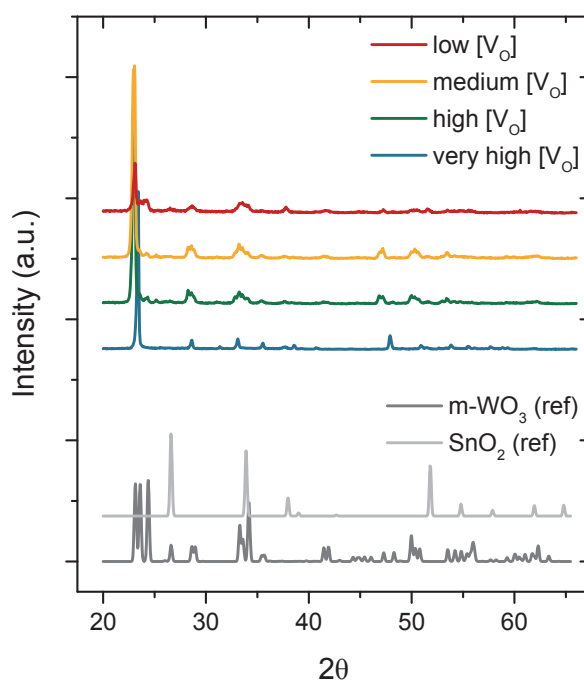


Figure 5.18 – X-ray diffraction (XRD) data for each of the films studied. Monoclinic WO_3 and SnO_2 (FTO) references are also provided in grey. As can be observed, no additional phases could be determined and all samples appeared comparable (not annealed (very high $[\text{V}_\text{O}]$, blue), acid treated (high $[\text{V}_\text{O}]$, green), 2 hours annealed (medium $[\text{V}_\text{O}]$, yellow), 12 hours annealed (low $[\text{V}_\text{O}]$, red)).

The photocurrent performance of each of the treated films was tested, as shown in Figure 5.19, using the same set-up described in Chapter 3. Strikingly, the photocurrent onset is similar for each $[V_O]$ type at $\sim 0.5 V_{RHE}$, but the current plateau is markedly different. The film with ‘very high’ $[V_O]$ gives no photocurrent (blue trace), but the current progressively increases as the defect concentration is reduced, with the highest photocurrent of 0.45 mA/cm^2 at $1.23 V_{RHE}$ for the ‘medium’ $[V_O]$ WO_3 (yellow trace). However, as the defect concentration is decreased further still, the current drops again (red trace), thereby indicating that an intermediate doping density results in the best performance. The same ‘pyramidal’ trend can be seen in maximum photocurrent plateaus in Figure 5.20 for an alternative sample set, as well as in incident photon-to-current efficiency (IPCE) data at $1.23 V_{RHE}$ (Figure 5.21). When FTO absorption is accounted for, back-side illumination results in a better external quantum efficiency than front-side illumination for each sample type (Figure 5.21), though the difference is more extreme for the sample with ‘low’ $[V_O]$. This pyramidal trend in performance with altered oxygen vacancy concentration has been observed previously in ZnFe_2O_4 but not in the most common oxides for water oxidation.²⁴¹ The poor performance in ‘low’ $[V_O]$ samples indicates that electron transport is more limiting than hole transport in these nanostructured films, as observed previously in Chapter 4,²²⁷ and that electron transport is particularly poor in the ‘low’ $[V_O]$ films, likely alluding to conductivity issues as a result of low donor density.

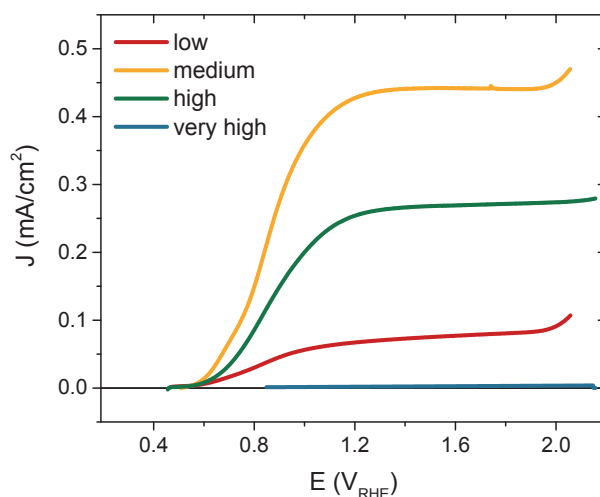


Figure 5.19 – Photocurrent responses for each WO_3 sample under simulated 1 sun illumination from the front side (EE) in $0.1 \text{ M H}_2\text{SO}_4$, scan rate 10 mV/s . Data provided for ‘very high’ $[V_O]$ (blue), ‘high’ $[V_O]$ (green), ‘medium’ $[V_O]$ (yellow), and ‘low’ $[V_O]$ (red).

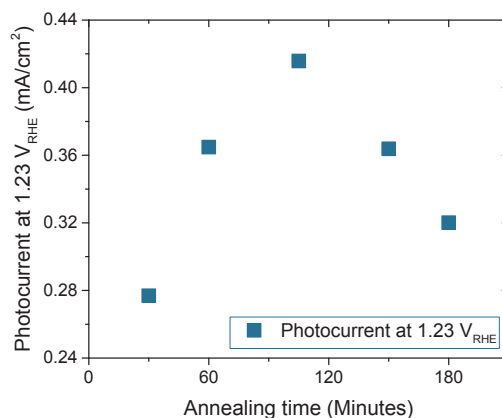


Figure 5.20 – Photocurrent responses under simulated 1 sun irradiation at 1.23 V_{RHE} (0.1 M H₂SO₄) for WO₃ samples annealed for different lengths of time (air, 500°C).

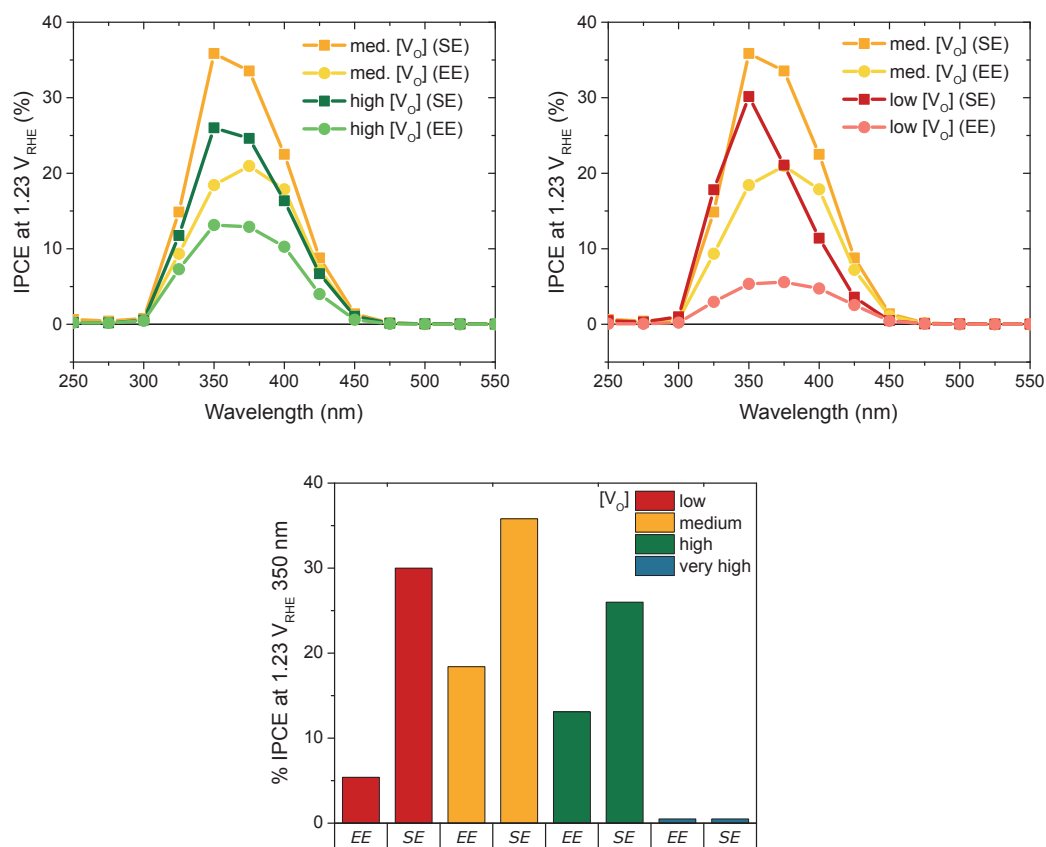


Figure 5.21 – *upper*: IPCE data under EE (lighter shades) and SE irradiation (darker shades) for samples with 'low' [V_O] (red), 'medium' [V_O] (yellow), and 'high' [V_O] (green). *lower*: Bar chart of same data at 350 nm (1.23 V_{RHE}, 0.1 M H₂SO₄)

As presented in Figure 5.3 on ultrafast timescales and in Chapter 4 on slower timescales, I monitored the kinetics of photogenerated electrons in these oxygen deficient samples at red wavelengths (700 – 800 nm), in agreement with the W^{5+} absorption shown in Figure 5.14. Figure 5.22 presents the electron signal for each of the treated samples over longer timescales at 1.23 V_{RHE} . Data for the ‘very high’ $[V_O]$ sample is not of interest as there is no photocurrent for water oxidation and the film self-oxidises under applied bias (see Figure 4.9). The transient charge produced at the back contact as a result of electron extraction was measured simultaneously, which is given by the dashed lines. It is apparent that the highest initial absorption was seen for films with ‘medium’ $[V_O]$ – the films that produced the highest photocurrent (Figure 5.19). It is equally evident that the rate of decay of this signal matches the rise in transient charge, confirming the electron assignment and indicating that predominantly electron extraction, rather than any recombination, is monitored at these times ($\sim \mu s$ to s) and under these conditions, as was noted in Section 4.2.3. By comparison, both the ‘high’ $[V_O]$ sample (green) and the ‘low’ $[V_O]$ sample (red) give a smaller initial amplitude and less accumulated charge over the same time-window, in agreement with the trend in photocurrent shown in Figure 5.19. The smaller initial amplitude of the optical signals for the highly and poorly doped samples suggests that the differences in photocurrent performance are, in part, determined by processes occurring before 10 microseconds. However, the drop in final charge extracted in these samples is quantitatively larger than the variation in initial optical signal, indicating additional carrier losses during electron extraction in both the ‘high’ and ‘low’ $[V_O]$ samples.

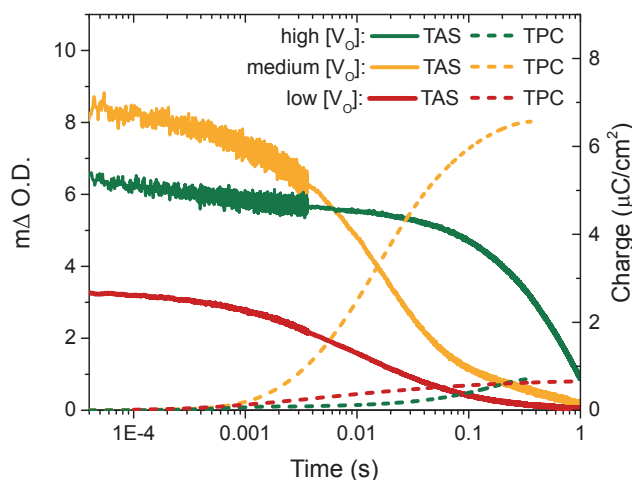


Figure 5.22 – Electron decays (solid lines, 800 nm) under bias ($1.23 V_{\text{RHE}}$) from transient absorption spectroscopy measurements in 0.1 M H_2SO_4 , exciting at 355 nm with $0.25 \text{ mJ}/\text{cm}^2$. The transient photocurrent was measured simultaneously and then integrated to give the transient charge collected (dashed lines). The high performing sample with ‘medium’ doping (yellow) is compared to samples of ‘high’ (green) and ‘low’ doping (red).

The data in Figure 5.22 indicate that the kinetics of electron extraction, as well as the final yield of charges, are also dependent on oxygen vacancy density. The ‘high’ $[V_O]$ sample shows a much slower electron decay with a concomitantly slower charge extraction (optical $t_{50\%} = \sim 0.340 \text{ s}$), compared to the ‘medium’ $[V_O]$ sample ($t_{50\%} = \sim 0.014 \text{ s}$), whereas the ‘low’ $[V_O]$ sample exhibits the fastest kinetics ($t_{50\%} = \sim 0.009 \text{ s}$). These differences in timescales can be clearly noted in the normalisation of these data (Figure 5.23) and are given in Table 5.3. This trend in electron extraction kinetics not only confirms that states associated with oxygen vacancies are directly involved in charge transport, as indicated in Chapter 4,²²⁷ but also reveals a direct correlation between V_O density and effective electron mobility, with a greater number of vacancies resulting in slower electron extraction, attributed to reversible electron trapping on ionised oxygen vacancy sites.²²⁷ This stands in contrast to the increase in conductivity one may have expected from a greater doping density, as discussed in more detail in the Discussion.

WO ₃ sample	Optical $t_{50\%}$	TPC $t_{50\%}$
high $[V_O]$	0.340 s	$\sim 0.1 \text{ s}$
medium $[V_O]$	0.014 s	0.016 s
low $[V_O]$	0.009 s	0.007 s

Table 5.3 – Half-lifetimes from slow timescale TAS (optical) and TPC experiments for the samples in Figure 5.22.

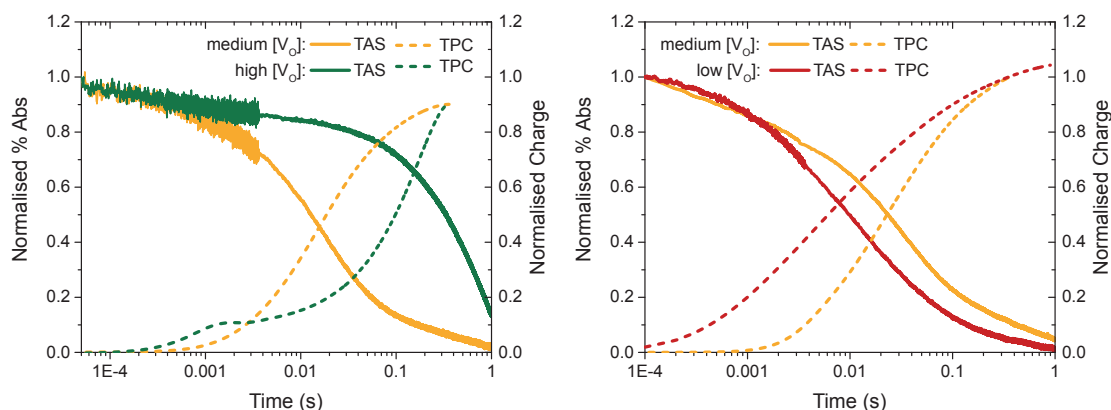


Figure 5.23 – Normalised electron decays (solid lines, 800 nm) and charge measurements (dashed lines) from the data in Figure 5.22. The high performing sample with ‘medium’ doping (yellow) is compared to samples of ‘high’ (green) and ‘low’ doping (red).

To determine the origin of the variations in photogenerated electron yields observed in Figure 5.22 at 10 μ s, I monitored the electron kinetics on faster timescales (fs – ns) under otherwise comparable conditions. This data is given, raw and normalised, in Figure 5.24. Once again, significant differences can be observed between ‘high’, ‘medium’ and ‘low’ $[V_O]$ doped samples. Most notably, the ‘medium’ $[V_O]$ sample has the highest initial amplitude and the slowest electron decay, with a greater number of charges remaining at 6 ns, consistent with the initial signal amplitudes in Figure 5.22. Both the ‘high’ and ‘low’ $[V_O]$ samples result in optical signals that decay faster and have a smaller initial amplitude, indicating that both excessively high and low oxygen vacancy densities can result in greater charge recombination losses on ultrafast timescales. These results correlate directly with the yields of long-lived charge carriers and photocurrent densities measured under anodic bias.

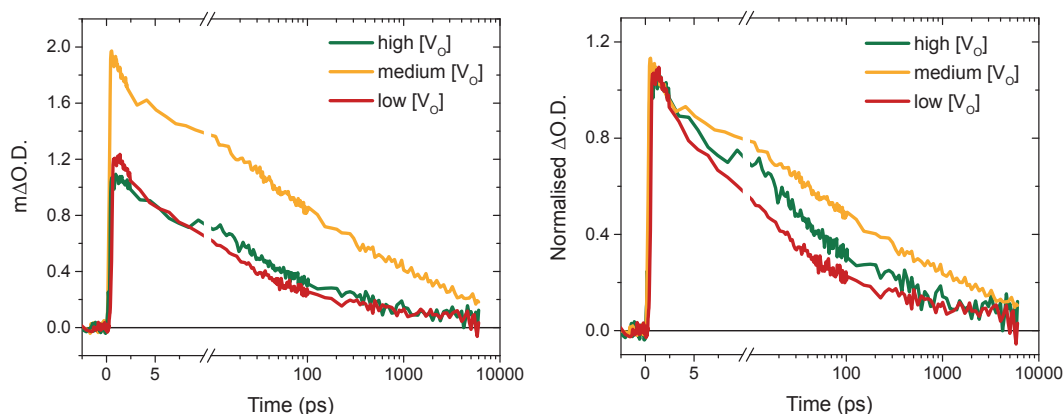


Figure 5.24 – *left*: Ultrafast transient absorption kinetics in 0.1 M H_2SO_4 , probing the electron decay at 700 nm from ~ 200 fs to 6 ns after excitation with 355 nm ($0.2 \text{ mJ}/\text{cm}^2$) for ‘high’ (green), ‘medium’ (yellow) and ‘low’ (red) $[\text{V}_\text{O}]$ doping concentrations. *right*: The same data, normalised at 2 ps after excitation. Measuring absolute amplitudes in highly reflective samples can be challenging, but this data suggests that the ‘high’ $[\text{V}_\text{O}]$ and ‘low’ $[\text{V}_\text{O}]$ samples suffer immediate recombination losses at timescales faster than can be resolved. I assign this recombination loss to poorer charge separation, leading to increased trapped-mediated losses in the highly doped sample, and increased ‘geminate-style’ recombination in the poorly doped sample, as discussed in the text.

5.3 Discussion

As discussed in the introduction to metal oxides in Chapter 2, there are several possible processes to which photogenerated carriers in semiconducting materials may fall fate, most of which are loss processes that reduce the maximum attainable quantum yield. However, there are also multiple ways by which the scientific community is innovatively trying to improve charge carrier lifetimes, from addition of dopants to Z-schemes. In Section 5.2.3, I find that applied bias can limit recombination losses from as early as a picosecond onwards. Perhaps more surprising still, in Section 5.2.4, increased electron lifetimes merely from SCL formation at the semiconductor–electrolyte interface can be observed, highlighting the importance of this depleted region in the separation of photogenerated charges. As discussed in Chapter 4 and emphasised schematically in Figure 5.2, the SCL in WO_3 is generated in conjunction with the ionisation of oxygen vacancy states (V_O) and their associated neighbouring W^{5+} centres. As such, understanding the role that these defects may play in charge carrier lifetimes is of significant interest, particularly as the concentration of oxygen vacancies may (to some extent) be controlled, allowing for potential improvements in the development of new materials.

Notably, from the J-V data in Figure 5.19, the maximum photocurrent in these nanostructured WO₃ samples does not correlate with either the highest or lowest concentration of oxygen vacancies studied herein ($[V_O] \sim 5.8\%$ and $\sim 0.5\%$, respectively) but with an intermediate value, equating to an oxygen vacancy density of *ca.* 2% of the stoichiometric oxygen content. This indicates that these intrinsic defects can enhance performance, but that there is a limit to this enhancement beyond which additional oxygen vacancy states are detrimental. This result affords a bridge between the seemingly contradictory reports in the literature on the influence of additional oxygen vacancies in such metal oxide photoanodes – both positive^{73, 137, 188, 242–244} and negative^{68, 160, 164, 166} trends with increasing defect concentration appear plausible depending on the defect density regime one begins with.

Front and back IPCE data shown in Figure 5.21 also follow the same pyramidal trend in photocurrent generation with increasing oxygen vacancy concentration, as the ‘medium’ $[V_O]$ films show the greatest external quantum yields. This can be rationalised, to some extent, as an effect of improved conductivity from increased doping, as proposed by others.^{73, 221} In particular, this provides plausible explanation for the disparity between front and back illumination currents in the ‘low’ $[V_O]$ sample, for which the iR loss resultant from low conductivity may have become a significant factor. However, conductivity arguments cannot be used to rationalise the drop in IPCE with further increases in doping. In Chapter 4, I demonstrated that oxygen vacancies have a role in electron transport through the WO₃ nanostructure,²²⁷ and the decay kinetics shown herein (Figures 5.22 and 5.24) further emphasise that these chemical defects have a strong influence on carrier mobility and recombination kinetics. Interestingly, two different effects of oxygen vacancies on the electron dynamics can be discerned, with each dominating on a different timescale. In Figure 5.22, we find the initial optical amplitude of the electron signal for each sample correlates with the trend in the steady-state photocurrent between samples (Figure 5.19). As the optical amplitude is proportional to the number of species probed, the smaller amplitude in samples with ‘high’ or ‘low’ defect state concentrations indicates the presence of fewer electrons on these timescales, thereby suggesting an effect of oxygen vacancies on electron loss (recombination) at early times. This is one effect, which I will discuss in detail momentarily. The other effect of these vacancy states is apparent at later times in Figure 5.22, and in the normalised data in Figure 5.23. As the concentration of defects is increased from ‘low’ to ‘high’, we observe a 100-fold decrease in the electron decay rate and, in accordance, a slower extraction of charge (Figure 5.23, dashed lines). This trend clearly exemplifies the trap-mediated electron transport mechanism proposed previously,²²⁷ with increasing numbers of vacancy states limiting the carrier mobility due to electron trapping on ionised vacancy sites. Similar changes to transport times were shown in Chapter 4 with increasing anodic bias, as this resulted

in a greater number of available trap-sites through the ionisation of occupied oxygen vacancy states. The low mobility in highly doped samples also incurs a penalty on the performance, with the quantum yield/extracted charge significantly lower than may have been expected from the optical amplitude (see Table 5.4). In other words, not all of the electrons observed on slow timescales in ‘high’ $[V_O]$ samples are contributing to current, with the large number of defects likely invoking trap-mediated recombination, as suggested by others.^{164,222} Considering the nanoneedle nature of these films, electron transport will be proceed in close proximity to holes accumulating at the WO_3 surface, such that recombination losses during extraction are plausible. This is depicted schematically in Figure 5.26.

WO_3 sample	External Quantum Yield
high	1.7 %
medium	9.4 %
low	1.0 %

Table 5.4 – External quantum yields, calculated from TPC data (Figure 5.22) as detailed in Appendix A.3

In contrast to the highly doped sample, the ‘low’ $[V_O]$ sample presents a faster electron decay on $\mu s - s$ timescales, and earlier charge extraction (Figure 5.23). Once again, this can be rationalised by considering electron transport through the WO_3 nanoneedle: with fewer oxygen vacancy sites in the sample (and the atomic distance between those remaining likely larger), electrons will go through fewer trapping and de-trapping events before reaching the back contact and are therefore extracted faster. Furthermore, the ‘low’ $[V_O]$ sample is expected to exhibit a wider SCL as a result of its lower doping density, which may also contribute to faster extraction kinetics as a greater proportion of photogenerated electrons can be expected to experience drift fields, driving more of them to the centre of the needle where they may shield one-another. However, the extraction efficiency remains low for this film, as indicated by the quantum yield. This could be due to increased ‘free carrier’ recombination as a result of inadequate trapping and localisation, a concept I discuss further below. This positive contribution of electron trapping to performance has seldom been considered in previous studies examining variations in oxygen vacancy concentration.²⁴¹

As mentioned previously, the initial electron population observed in Figure 5.22 is determined by loss processes occurring on earlier timescales. The ultrafast carrier dynamics for these samples are shown in Figure 5.24. Strikingly, significant differences in electron decay kinetics between the samples are observed from just a couple of picoseconds after excitation. As predicted from the optical signal amplitude in the slow data (Figure 5.22), the ‘low’ $[V_O]$ sample shows the fastest decay on ultrafast timescales, indicating greater bulk recombination losses, which eventually

result in the poor photocurrent observed for this sample (Figure 5.19). Similarly, the ‘high’ $[V_O]$ sample also shows faster recombination kinetics than the best performing sample. Since charge separation and geminate and non-geminate recombination processes dominate the kinetics at these timescales, it can be concluded that oxygen vacancy states are affecting these processes. Moreover, it can be determined that the nature of their effect on charge longevity must be both beneficial and detrimental, as an intermediate number of vacancies still produces the best performance, even at these early times. Firstly, a detrimental effect of increasing defect concentration is observed going from ‘medium’ to ‘high’ $[V_O]$, which is largely assigned to the trapping of photogenerated valence-band holes into filled oxygen vacancy states, in excess in this sample. This assignment stems from previous observations that a very high population of occupied defect states (those below the Fermi level) results in bulk hole trapping with 300 femtoseconds, leading to a loss in the W^{5+} absorption from electrons in these states.²¹⁶ Indeed, the non-normalised data reveals a smaller initial amplitude for the higher doped sample, indicative of electron loss from rapid hole trapping (Figure 5.24). This assignment is also supported by Figure 5.25, which shows that the ultrafast kinetics of the highest doped sample, ‘very high’ $[V_O]$, give only a negative signal (bleach) at the same examined wavelength, due to a transient loss, rather than gain, of trapped electrons. Holes that trap deeply or recombine with electrons are unable to contribute to water oxidation, and thus higher incidences of trap-assisted recombination result in lower photocurrents. In the extreme case of the very highly doped sample, the overwhelming degree of trapping from early times results in no photocurrent at all, as shown in Figure 5.19.

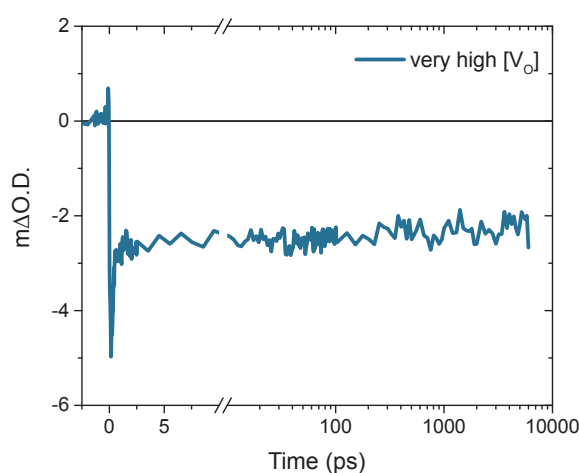


Figure 5.25 – Ultrafast transient absorption kinetics probing the electron decay from ~ 200 fs to 6 ns after excitation with 355 nm (0.2 mJ/cm^2) for ‘very high’ $[V_O]$ WO_3 sample (700 nm, 0.1 M H_2SO_4). A bleach is observed over all timescales measured due to trapping of photogenerated holes into the large number of available (occupied) oxygen vacancy states.

The beneficial effect of intermediate oxygen vacancy densities on early timescale processes is arguably more surprising. When comparing the electron kinetics of the ‘low’ $[V_O]$ sample with the ‘medium’ $[V_O]$ sample, a retardation of bulk recombination is observed in the latter, which cannot easily be rationalised as a reduction in charge trapping, considering the ‘medium’ $[V_O]$ sample is more doped. It appears more likely that the retarded recombination losses of the ‘medium’ sample over the poorly doped sample arise from improved charge separation as a result of enhanced electron localisation on ionised oxygen vacancy sites. In other words, the relative absence of oxygen vacancy states in the ‘low’ $[V_O]$ sample could be expected to increase the proportion of electrons in the conduction band, accelerating their recombination with valence band holes. This ‘free-electron – hole’ recombination could account for the lower electron amplitude at ~ 200 fs in the ‘low’ $[V_O]$ sample (Figure 5.24) and also reconcile the faster electron decay across the entire ultrafast window, as electrons will spend proportionally more time moving between trap states due to there being fewer of them. This stands in contrast to the oxygen vacancy study on ZnFe_2O_4 , which attributes the poor performance of lower $[V_O]$ solely to reduced conductivity.²⁴¹ The idea of improved charge separation through carrier trapping has been proposed previously in other materials,^{245,246} but, to my knowledge, has not been observed directly in the most common oxide photoanodes for water oxidation. For example, in their examination of $\text{Zr-Bi}_2\text{WO}_6$ for organic photodegradation reactions, Zhang et al. determined that ‘an appropriate’ oxygen vacancy concentration leads to the temporary trapping of photogenerated electrons, thereby enhancing charge separation.²⁴⁷ This reversible electron trapping observed herein, even from pre-picosecond timescales, may thus be applicable to many similar photoanodes for a multitude of applications. As such, the vital role of these intrinsic defect states in early-time processes such as charge separation in these materials cannot be overstated, and cannot be adequately described by comparison of two extremes.²¹⁶ The role of oxygen vacancies in charge separation and electrons transport in WO_3 is summarised in Scheme 5.26.

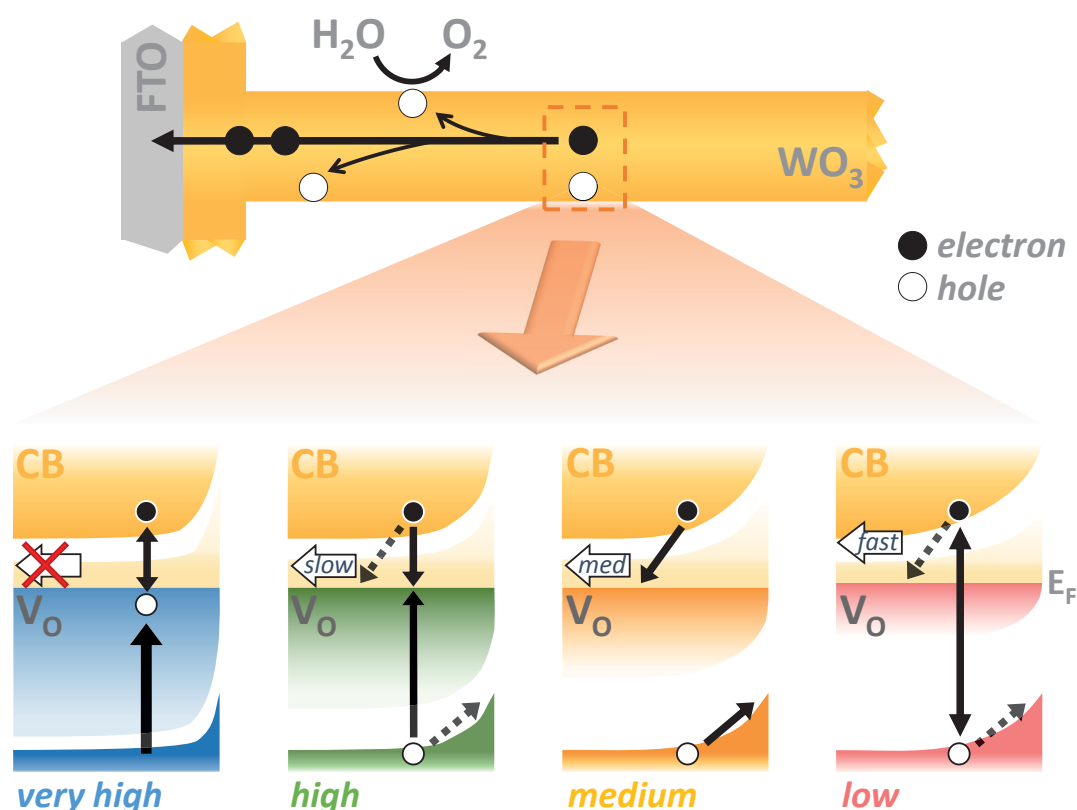


Figure 5.26 – *upper*: Illustration of a single nanoneedle of WO₃ (yellow) on FTO (grey), indicating electron (black) transport (black arrows) and possible recombination pathways with holes (white) on route to extraction. *lower*: Indication of the dominant kinetic pathways immediately following charge separation in each of the samples examined; ‘very high’ [V_O] (left, blue), ‘high’ [V_O] (centre left, green), ‘medium’ [V_O] (centre right, yellow) and ‘low’ [V_O] (right, red). Filled V_O states are given in colour, empty/ionised states able to trap electrons are given in yellow. ‘Very high’ [V_O] shows hole trapping faster than instrument detection (heavy arrow). The ‘high’ doped sample has the greatest bulk trap recombination, particularly from hole trapping, so later carrier collection is limited. With too few defect states (‘low’, red), charge separation is hindered and the probability of geminate and bimolecular recombination increases. The best performing sample has the optimal amount of defects to aid charge separation without losing carriers to trap-mediated recombination.

Whether the trends with varied oxygen vacancy concentration reported herein are specific to WO_3 as a product of this material's infamously high doping densities, or are general to all metal oxides cannot be concluded from this study alone. For example, Forster et al. have shown there to be a fine balance between enhanced electrical properties and trap-mediated losses in $\alpha\text{-Fe}_2\text{O}_3$ films with high oxygen vacancy densities, but their study focuses solely on slow timescales, so the effects of oxygen vacancies on the initial charge separation in hematite remain unclear.²⁴⁸ Further studies are required to elucidate whether the optimum oxygen vacancy concentration is similar between different metal oxides, and whether all equally benefit from enhanced carrier trapping (rather than simply increased conductivity). Likewise, the nanostructured nature of the WO_3 samples, while known to be key to enhanced performance, may also play a negative role in enabling recombination with surface holes at later times during electron extraction parallel to the nanorod surface; in a dense film such losses would be less important due to electron extraction proceeding perpendicular to film surface (Scheme 5.26, *upper*). On the other hand, nanostructuring allows for an increased quantity of a photoanode to be within the SCL and minimises the bulk material, which I also determine to improve charge carrier lifetimes.

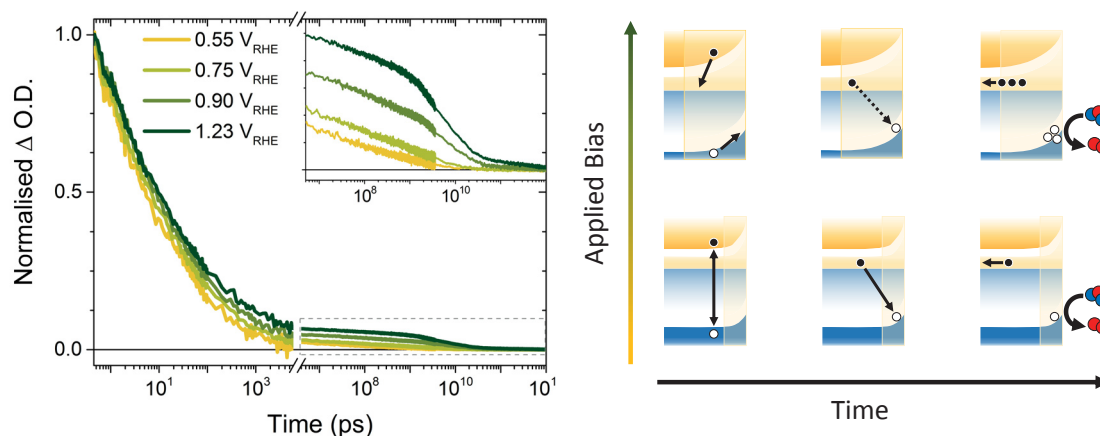


Figure 5.27 – *left*: Kinetics of electrons (700 nm) under different applied bias from 0.5 ps to 1 s. A break in the x-axis (6 ns to 1 μs) is present as those timescales could not be probed (355 nm, 0.2 mJ/cm^2). *right*: Schematic to describe the electron kinetics in WO_3 at high and low bias, showing charge separation, trapping, recombination and extraction/reaction (0.1 M H_2SO_4). Black arrows indicate movement of electrons (black circles) and holes (white circles). At early times and low bias, bulk recombination dominates and many holes that reach the surface face recombination with bulk electrons before catalysis. With increased bias, initial charge separation improves due to increased electron trapping into ionised V_O states, giving way to less recombination within the SCL (dashed arrow), and enhanced performance. Top schematics are 1.23 V_{RHE}, bottom are 0.55 V_{RHE}. Blue represents occupied states, yellow empty states, with V_O states as shown in Figures 5.26 and 5.2 inset.

Figure 5.27 (*left*) plots the electron kinetics at 700 nm for different applied potentials from ultrafast timescales up to 1 second for the best performing WO_3 sample (normalised for the difference in excitation conditions used for later times). It is apparent that the increased proportion of long-lived charge carriers observed with more anodic bias on ultrafast timescales correlates well with the improved charge longevity seen at times relevant to catalysis. The magnitude and decay kinetics of the signal on the millisecond timescale correlate with transient photocurrent measurements of electron extraction (Chapter 4, Figure 4.8), consistent with the assignment to long-lived electrons, and specifically to electrons trapped at oxygen vacancy states. By mapping the increase in charge extracted with anodic bias, a dependency strikingly similar to the increase in electron half-time with anodic bias observed on ultrafast times is found (compare Figure 5.7 with Figure 4.8). Such correlating trends clearly indicate that the positive effects of SCL formation in retarding fast recombination processes are carried through to later times, and, in fact, account for most of the improved performance seen with bias, with strong repercussions on maximum attainable performance. It is therefore evident, that the beneficial charge separation in the SCL, aided by ionised oxygen vacancy states, is key to the success of this material. The kinetics of the charge carriers in WO_3 , from their generation to reaction and extraction, are summarised in the schematics in the right hand panel of Figure 5.27.

5.4 Conclusion

In summary, I have determined that increased space-charge layer formation with applied bias is directly correlated with increased charge carrier lifetimes in WO₃ photoanodes. Often assumed, though never previously directly demonstrated, I have also shown that the space-charge layer formed upon contact with electrolyte, in the absence of applied bias, also can increase the lifetime of charge carriers on the ultrafast timescale. In this work, the separate localisation of electrons and holes could be observed from the first few picoseconds, with the former trapped into oxygen vacancy defect states and the latter observed in the SCL. Through alteration of the oxygen vacancy density, I found that an intermediate density gives the best photocurrent, resulting from the fine balance between trap-assisted charge separation and trap-mediated recombination. The observation of rapid holes trapping into bulk oxygen vacancies in heavily doped samples, in conjunction with the rapid localisation of ‘active’ holes in the SCL highlights that only holes that are localised in the SCL are likely to participate in water oxidation. This gives likely rationale for the lower external quantum efficiencies reported for this material,^{227,231} and suggests that tighter control of these defects and their occupancy may significantly boost performance. Analysis of electron kinetics from generation to extraction reveals the extent of charge loss due to bulk-recombination and the importance of adequate SCL width in inhibiting recombination if greater photocurrents are to be obtained. It is therefore important for the next generation of photoanodes to be engineered such that bulk material is minimised (i.e. adequate nanostructuring), and suitable doping levels are obtained to balance charge transport properties and charge separation with vital SCL formation.

Chapter 6



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6 Nickel-iron oxide electrocatalysts for water oxidation

While Chapters 4 and 5 have detailed the photoelectrochemical approach to water oxidation with WO_3 photoanodes, in this chapter dark electrocatalysis is examined using Ni/Fe oxyhydroxides. These metal oxyhydroxides are the best performing Earth abundant electrocatalysts for water oxidation at alkaline pH, with the smallest reported overpotentials for this notoriously difficult reaction. However, the origin of their remarkable performance is still not well understood. Herein, I employ spectroelectrochemical techniques to analyse the kinetics of water oxidation catalysis on a series of Ni/Fe oxyhydroxide films: FeOOH (100% Fe), FeOONiOOH (79% Fe), and Ni(Fe)OOH (5% Fe). Two optically distinct oxidation processes are observed, the second of which is correlated with the onset of catalysis. The concentrations and reaction rates of the states accumulated during water oxidation catalysis are determined as a function of applied potential. Ni(Fe)OOH is found to exhibit the fastest water oxidation kinetics but accumulates fewer oxidised states, resulting in a similar overall J-V performance to FeOONiOOH. The more anodic onset of water oxidation observed for FeOOH is attributed to an anodic shift in accumulation of the oxidised Fe states. A rate law analysis reveals that the rate limiting step of water oxidation for all three materials involves the accumulation of four such oxidised intermediates. Optical difference spectra suggests that these states are Ni-centred for Ni(Fe)OOH but are Fe-centred for the other two materials. To determine where these species accumulate in the film, different thicknesses of Ni(Fe)OOH are examined and it is unearthed that only the upper few nanometres are involved in the catalytic cycle. I conclude by proposing a simple scheme for water oxidation on Ni/Fe oxyhydroxides which highlights the importance of equilibria between the doubly oxidised states and the reactive intermediates in determining the electrocatalytic performance of these materials.

Chapter 6. Nickel-iron oxide electrocatalysts for water oxidation

The results presented in this chapter are included in the following articles for publication:

Francàs, L. and Corby, S. et al., "*Spectroelectrochemical study of water oxidation on nickel and iron oxyhydroxide electrocatalysts*", Nature Communications, **2019**, 10(1), 5278

Corby, S. et al. "*Separating bulk and surface processes in NiO_x electrocatalysts for water oxidation*", submitted

6.1 Introduction

Ni and Fe oxyhydroxides are particularly promising catalysts in both alkaline electrolyzers^{249–252} and photoelectrocatalytic systems.^{144,253–257} Such metal oxyhydroxides have layered structures with significant water permeability and varying degrees of long-range order, and exhibit complex electrochemical properties, including multiple, and relatively localised, redox states.²⁵⁸ For such electrodes, it is therefore challenging to directly probe the densities and reaction kinetics of the oxidised states driving water oxidation under operating conditions using electrochemical data alone. In this chapter, I report a combined spectroelectrochemical analysis of water oxidation on a series of Ni/Fe oxyhydroxides. Employing these data, the concentration of oxidised states driving water oxidation is determined, and the rate constants involved, thus providing new insights into both the reaction mechanism and the role of Fe and Ni centres in driving this catalysis.

NiOOH has been widely used and thoroughly studied as an electrode material in batteries.^{259–263} Since the 1980s the use of NiOOH electrodes for water oxidation has received increasing interest.²⁶³ In particular, Fe-incorporated NiOOH (Ni(Fe)OOH) is the most active earth abundant electrocatalyst for water oxidation under alkaline conditions.^{126,127} It has been reported that even when pure NiOOH is targeted, Fe impurities in the electrolyte can be spontaneously incorporated into NiOOH during the water oxidation reaction and considerably enhance the catalytic performance.^{145,263} The effect of this iron incorporation can vary depending on the content and location of the impurity in the host material, which in turn varies depending on the conditions of incorporation.^{133,264} As a result, there is an intense debate on the identity of the species responsible for oxygen evolution in Ni(Fe)OOH, with no consensus thus far. Most DFT studies suggest that the oxygen-oxygen bond formation takes place at reactive Fe centres.^{133,265–268} One study has reported the experimental detection of Fe(IV) species under catalytic conditions.²⁶⁹ On the other hand, other studies could not detect such Fe species but rather observed Ni(IV) at high applied potentials.^{133,270,271} Recent work has also directly related high valence Ni centres with water oxidation catalysis.²⁷² In addition, Raman studies of Ni(Fe)OOH have detected active oxygen species related to the deprotonation of Ni hydroxylated surfaces.²⁷¹ The environment surrounding Fe atoms also has a structural impact, with a contraction of Fe-O bonds in Ni(Fe)OOH compared to FeOOH,¹³³ which can be expected to affect the electronic and catalytic properties of the metal centre, as was recently reported by Song et al. in comparing the activity of $\text{Ni}_x\text{Fe}_{1-x}\text{OOH}$ with FeOOHNiOOH.²⁷³

Recently, spectroelectrochemical techniques have been used to analyse Fe/Ni oxyhydroxides, reporting a 430 nm spectral feature when > 10% Fe was incorporated into NiOOH.^{274–276} Herein,

I employ in operando stepped-voltage absorption and electrochemical current measurements to assay the concentrations of the oxidised species driving water oxidation catalysis and the resultant water oxidation reaction kinetics. My group has previously demonstrated the potential of analogous photo-induced measurements on photocatalytic systems.^{112, 118, 119, 277–279} In this chapter, such combined optical/electrochemical analyses are applied to elucidate, for the first time, the reaction rate constants for an electrocatalytic system, focusing on high performance Fe/Ni oxyhydroxide electrocatalysts and in particular on the role of Fe/Ni metal centres in these materials. These analyses allow measurement of the absorption spectra and concentrations of different oxidation states of three Fe/Ni oxyhydroxide electrocatalysts with varying Fe/Ni content (Figure 6.3, *inset*), enabling direct determination of catalytic turnover frequencies per accumulated oxidised state under catalytic conditions and thus providing new insights into their water oxidation catalysis.

6.2 Results

6.2.1 Physical and electrochemical characterisation

Three main electrocatalysts were studied in this work and were prepared by collaborators following previously reported methods,¹⁴⁴ the details of which are provided in Chapter 3, Section 3.1.2 and in Appendix A.4. The SEM images of these samples are shown in Figures 6.1 and 6.2. They can most simply be considered as (i) pure FeOOH; (ii) FeOOHNiOOH in which FeOOH and NiOOH layers were deposited sequentially (atomic ratio of Fe:Ni = 0.79:0.21); and (iii) NiOOH with spontaneously incorporated iron – Ni(Fe)OOH (Fe:Ni 0.05:0.95) – as schematically depicted in Figure 6.3 (*inset*). For FeOOHNiOOH, the SEM images indicate that NiOOH deposits inside the voids of the FeOOH layer, resulting in significant mixing of Fe and Ni at the FeOOH/NiOOH interface (Figure 6.2). These electrocatalysts have demonstrated high activity both as electrocatalysts and, when deposited onto BiVO₄ and other semiconductors,¹⁴⁴ as co-catalysts for water oxidation. Herein the focus is only on their electrocatalytic performance at pH 13 (0.1 M NaOH), where they display the best activity.

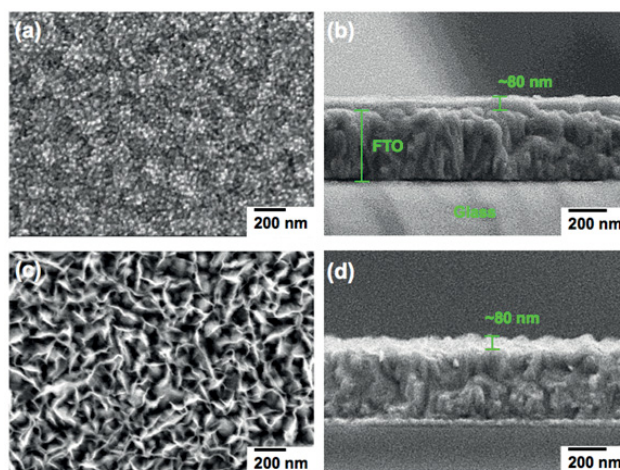


Figure 6.1 – Scanning electron microscopy (SEM) of (a) top and (b) cross-sectional view of FeOOH, and (c) top and (d) cross-sectional view of Ni(Fe)OOH. Performed and analysed in the group of Prof Choi in UWM.

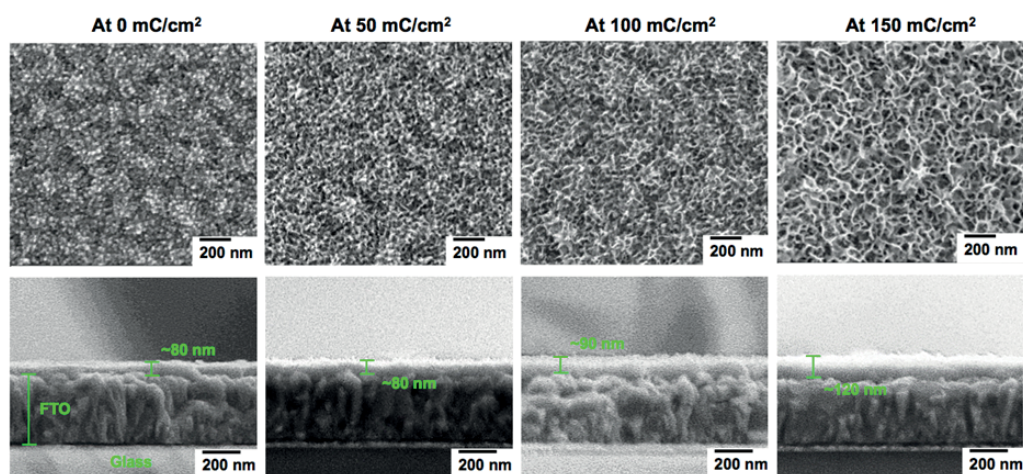


Figure 6.2 – SEM images for the deposition of NiOOH on top of pre-deposited FeOOH to form the FeOOHNiOOH sample. Top (*upper*) and cross-sectional (*lower*) images taken after passing 0 mC/cm², 50 mC/cm², 100 mC/cm² and 150 mC/cm² during the NiOOH deposition. The changes in the morphology and film thickness are not significant until passing 100 mC/cm², suggesting that until this charge is passed, most NiOOH is deposited in the voids of the FeOOH layer, resulting in a significant mixing of iron and nickel. Performed and analysed in the group of Prof Choi in UWM

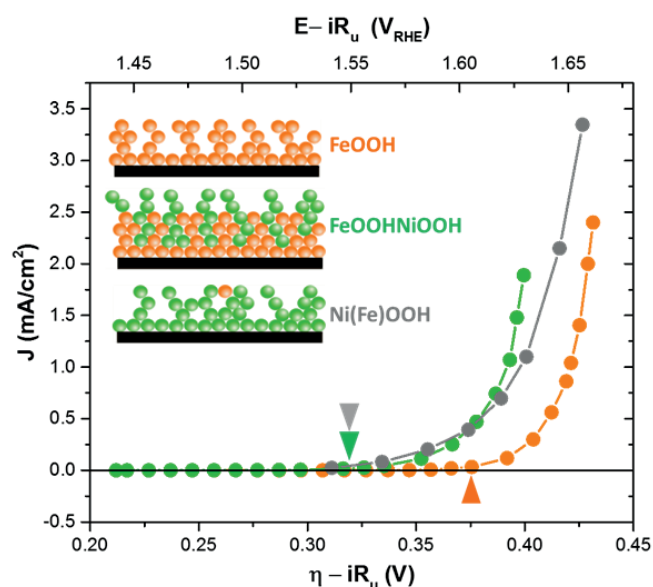


Figure 6.3 – Steady-state J-V curves at pH 13 (0.1 M NaOH aqueous solution) for FeOOH (orange), FeOOHNiOOH (green) and Ni(Fe)OOH (grey). These were recorded by measuring the steady-state current at different applied potential under atmospheric conditions. The FeOOH and Ni(Fe)OOH films are ~ 80 nm thick while the FeOOHNiOOH film is ~ 120 nm thick (Figures 6.1 and 6.2). The overpotential is estimated as: $\eta = E_{\text{RHE}} - 1.23$ V and was corrected by the iR drop estimated by spectroscopic impedance measurements (EIS, performed by Dr Camilo Mesa). Such J-V behaviour is typical of that reported previously for analogous Fe/Ni oxyhydroxide electrodes.^{145,272} Arrows indicate the onset of the catalysis, which has been approximated to the potential at which the current reaches $20 \mu\text{A}/\text{cm}^2$ inset: Schematic representation of the different samples studied in this work. Orange represents an Fe-based group and green a Ni-based group.

Figure 6.3 presents a comparison of the steady-state current as a function of applied potential for the three electrocatalysts studied. The anodic deposition method used in this study produces FeOOH and NiOOH in the as-synthesised forms. While FeOOH is stable, NiOOH gradually converts to $\text{Ni}(\text{OH})_2$ when exposed to air. This change can be easily recognised by the colour change from grey NiOOH to colourless $\text{Ni}(\text{OH})_2$. Accordingly, electrocatalytic J-V data for Ni(Fe)OOH and FeOOHNiOOH were collected after activation to convert $\text{Ni}(\text{OH})_2$ to NiOOH. Activation consisted of five consecutive linear sweep voltammograms (LSV) from the open circuit potential (OCP) to 0.7 V of overpotential (see Appendix A.5 for further details) which restored the grey coloured film (Figure A.1), in agreement with previous reports.^{260,265,270,271} The initial LSV for each film is given in Figures A.2 and A.14. As can be observed in Figure 6.3, the activated Ni(Fe)OOH and FeOOHNiOOH electrodes have a very similar electrocatalytic performance, whilst FeOOH shows a 70 mV anodic shift in catalytic onset.

6.2.2 Spectroelectrochemical characterisation

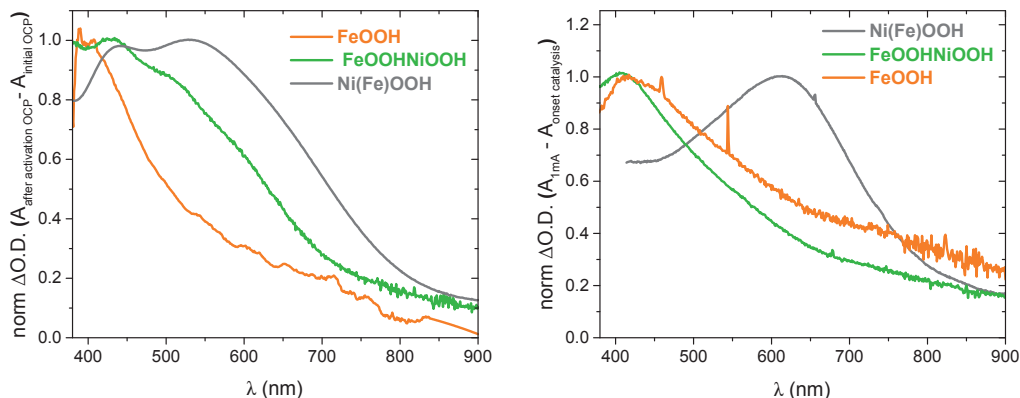


Figure 6.4 – *left*: Normalised Δ O.D. spectra (to 1 at peak Δ O.D.) for the first (0/+), pre-catalytic, oxidation of FeOOH (orange), FeOOHNiOOH (green) and Ni(Fe)OOH (grey), obtained by taking the difference between the spectra at open circuit potential (OCP) after and before activation. *right*: Normalised Δ O.D. spectra for the (+/++) oxidation wave correlated with water oxidation for FeOOH (orange), FeOOHNiOOH (green) and Ni(Fe)OOH (grey), obtained by subtracting spectra at OCP after activation from the spectra at 1 mA/cm² of current density.

Given the complex function of these electrocatalysts, operando optical absorption and electrochemical measurements were used to directly determine the concentration of oxidised species within each sample (see Chapter 3 for experimental details). For all three electrocatalysts, the optical absorption measurements were able to track two distinct oxidation processes. The first, pre-catalytic oxidation process is for simplicity referred to herein as oxidation of MOOH to MOOH(+) (abbreviated to (0/+) where appropriate), and takes place during the activation process described above. The normalised differential absorption (Δ O.D.) spectra for this first oxidation are presented in Figure 6.4 (*left*). Upon applying a more anodic potential, corresponding to conditions of catalytic water oxidation, a further oxidation process occurs, leading to the generation of doubly oxidised states, referred to herein as MOOH(++). Note that this (+) and (++) notation is only intended to describe increased oxidation states and does not give any indication of the absolute oxidation state of the metal centres, which could only be obtained with a suite of complementary techniques beyond the scope of this study. This (+/++) oxidation causes a distinct optical absorption change for each electrocatalyst (Figure 6.4, *right*). It is apparent that the (0/+) and (+/++) Δ O.D. spectra are distinct for each sample, as demonstrated in Figure 6.5. For Ni(Fe)OOH, the first (0/+) oxidation has been assigned to the conversion of Ni(OH)₂ to NiOOH, as observed by others,²⁷⁰ with the associated optical absorption increase assigned to nickel d-d

interband transitions,²⁷¹ although the details of this assignment are not critical for the study herein. For FeOOH, the (0/+) oxidation process is much more limited, oxidising approximately 0.5% of the Fe atoms (see Appendix A.7), and this process is tentatively assigned to oxidation of defects such as metal ions adjacent to oxygen vacancies. Alternatively, this (0/+) process could also involve the adsorption of a water molecule on coordinatively unsaturated surface Fe atoms, which several DFT based studies attribute to the first electron transfer.^{133,280,281} From the spectra in Figure 6.4 (*left*), we can observe that the FeOOHNiOOH (0/+) oxidation results in a $\Delta O.D.$ spectrum that contains features from both the FeOOH and Ni(Fe)OOH (0/+) oxidation. The NiOOH feature is more prominent, suggesting that despite comprising 79% Fe, the (0/+) oxidation process of FeOOHNiOOH is primarily associated with Ni(OH)₂ oxidation.

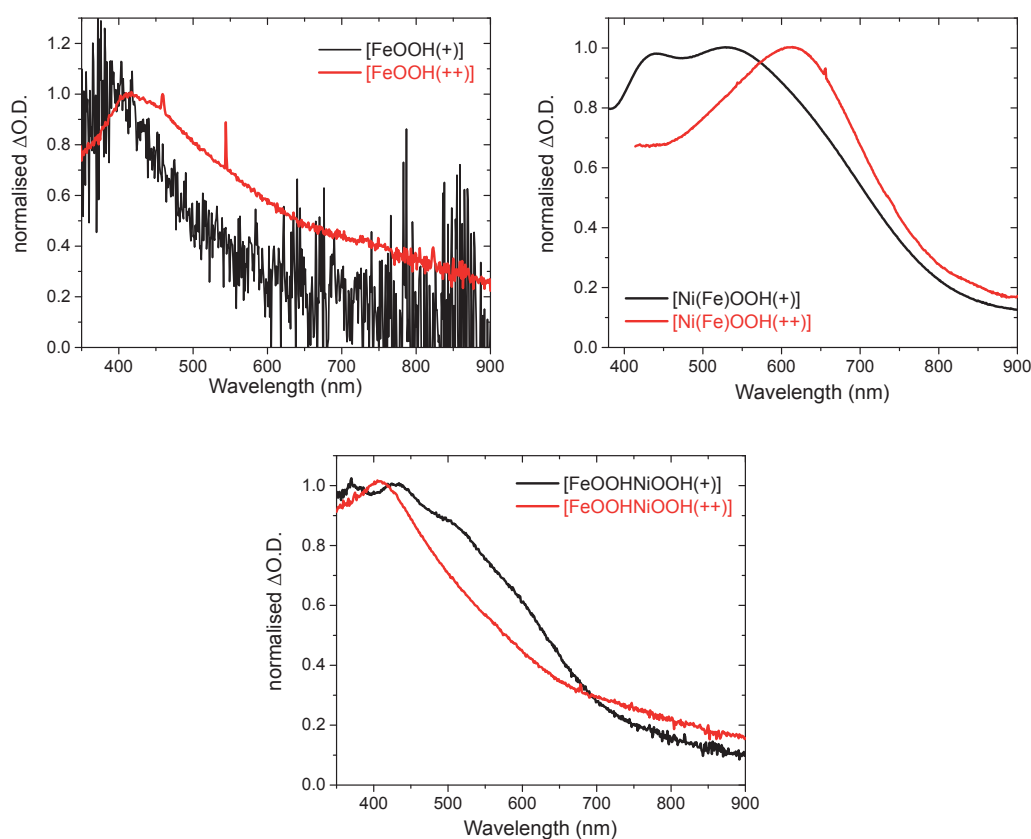


Figure 6.5 – Comparison between the normalised UV-Vis spectra of pre-catalytic (black) and the catalytic species (red) for (*upper left*): FeOOH, (*upper right*): Ni(Fe)OOH, and (*lower*): FeOOHNiOOH. The change in absorption of the pre-catalytic species in Ni(Fe)OOH and FeOOHNiOOH was obtained by subtracting the initial absorbance from the absorbance after the activation. FeOOH pre-catalytic species spectrum was obtained by subtracting the absorbance at the open circuit potential ($\eta = 0.237$ V) from the absorbance at the onset of catalysis ($\eta = 0.307$ V).

In contrast, for the second (+/++) oxidation observed under catalytic conditions, the Δ O.D. spectra are similar for FeOOH and FeOOHNiOOH, both exhibiting a peak around 400 nm (Figure 6.4, *right*), although small difference remain between them, indicating some impact of the presence of Ni on the FeOOHNiOOH(++) states, as discussed below. These spectra for FeOOH and FeOOHNiOOH are clearly different from that for the (+/++) oxidation in Ni(Fe)OOH, which presents a peak *ca.* 650 nm. This suggests that the MOOH(++) species accumulated in FeOOH and FeOOHNiOOH during water oxidation catalysis are similar in nature (and therefore both Fe-centred), whilst those accumulated in Ni(Fe)OOH are distinct, likely alluding to greater Ni character. To better determine whether this is the case, a NiOOH sample free of any Fe impurities was prepared and analysed in a purified electrolyte and otherwise comparable conditions (see Chapter 3, Section 3.1.2 for details). As shown in Figure 6.6, the same two spectral features present for Ni(Fe)OOH are observed for the purified NiOOH sample: a (0/+) oxidation, assigned to the oxidation of any Ni(OH)₂; and a second (+/++) oxidation process, which gives rise to a peak at ~650 nm. As such, it follows that the MOOH(++) species accumulated under catalytic conditions in these mixed metal systems are Fe-centred at higher concentrations of iron, but Ni-centred at low Fe concentrations ($\leq 5\%$). It may be the case that there are intermediate Ni/Fe ratios for which either or both metal centres can accumulate charge. It is also possible that this charge becomes delocalised between centres, which would agree with spectra recently reported by Dau and co-workers for mixed Ni/Fe electrocatalysts, assigned to di- μ -oxo bridged Ni(IV)-Fe(III) motifs.²⁷⁵ It is important to note that the physical nature of the species observed cannot be known without further chemical characterisation and that neighbouring atoms are likely critical for the generation of any (++) species, i.e. metal-centred does not suggest a purely metal-based redox species. Hu and co-workers also propose dual-site water oxidation pathways with certain Ni/Fe oxyhydroxide structures,²⁷³ and a synergistic mechanism remains probable given the improved catalytic onset of FeOOHNiOOH compared to FeOOH, as discussed below.

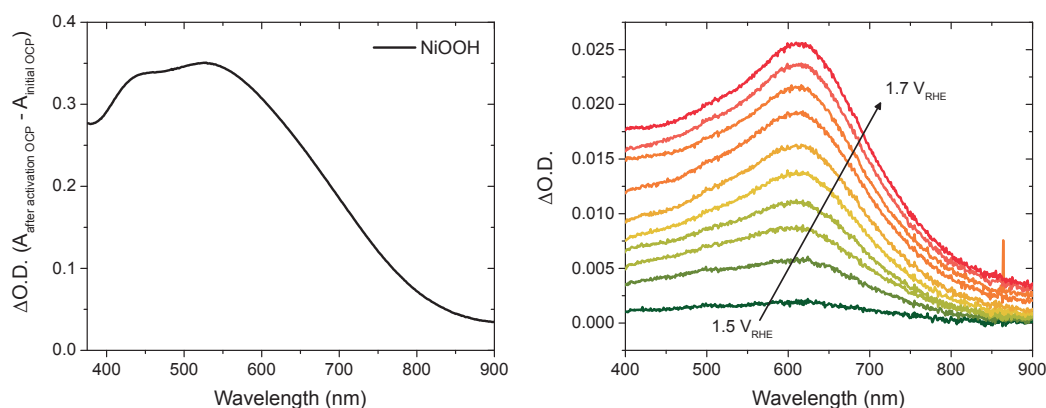


Figure 6.6 – *left*: Δ O.D. spectra for the pre-catalytic oxidation of NiOOH, obtained from the difference between the spectra at OCP before and after activation. *right*: Difference spectra of the catalytic (++) species at different applied potentials for Fe-free NiOOH (purified 0.1 M NaOH). As with the spectra given in Figure 6.4, the Δ O.D. was estimated by subtracting the absorbance at the catalytic onset from higher applied potentials within the catalytic region. The peak matches that found in Ni(Fe)OOH (Figure 6.4, *right*), confirming that the catalytic species is similar in nature and therefore Ni-centred.

The extinction coefficients (ϵ) of all the species involved were estimated from Δ O.D., J-V and stepped-voltage absorption spectroscopy (SVAS) data as detailed in Appendix A.6. Combining these extinction coefficients with the spectroelectrochemical data allows determination of the concentrations of accumulated MOOH(+) and MOOH(++) species (Figure 6.7, *left*). It is noted that the magnitude of (0/+) oxidation is significantly higher in Ni(Fe)OOH compared to FeOOHNiOOH, although these two samples have comparable quantities of Ni atoms (Table A.1). This trend is consistent with previous literature analyses which suggest that the presence of Fe stabilises Ni(OH)₂ relative to NiOOH.^{145,270} Moreover, at current densities equal to 1 mA/cm², Ni(Fe)OOH exhibits the lowest concentration of catalytic MOOH(++) species and FeOOHNiOOH the highest, as discussed further below. The quantity of each MOOH(+) and MOOH(++) species as a percentage of the number of corresponding 'M' metals is also calculated in Appendix A.7, summarised in Table 6.1. This assumes that only one electron is transferred per oxidative step.

Sample	%(+) species per total M-centres*	%(++) species per total M-centres*
FeOOH	0.5	4
FeOOHNiOOH	9	9
Ni(Fe)OOH	85	12

*where 'M' is the relevant active metal in MOOH(+) or MOOH(++) for each sample type.

Table 6.1 – Concentration of (+) and (++) species as a percentage of M-centres, as calculated in Appendix A.7.

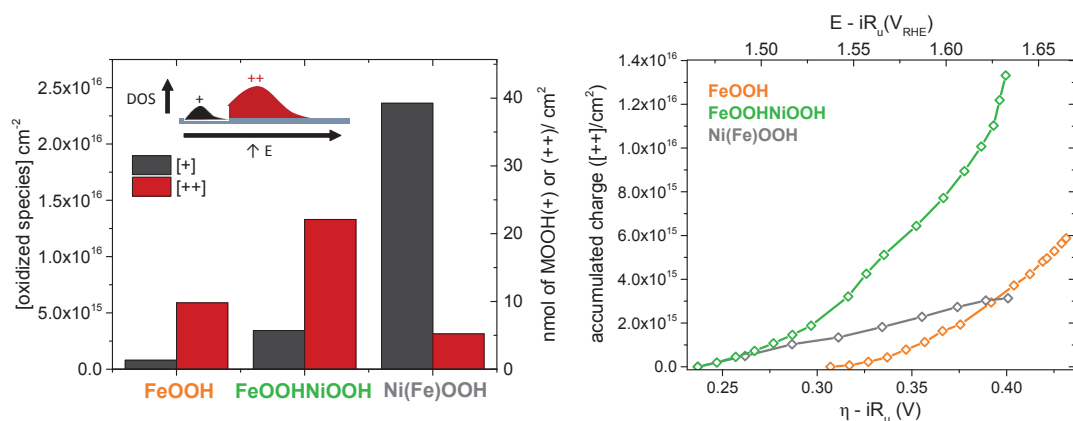


Figure 6.7 – *left*: Concentrations of oxidised MOOH(+) states generated by the activation process (black) and of MOOH(++) states generated at a current density of $1 \text{ mA}/\text{cm}^2$ (red) for each electrocatalyst; (*inset*) schematic representation of the corresponding densities of states (DOS) for these electrocatalysts. *right*: Accumulated concentrations of MOOH(++) states against the applied potential and overpotential for FeOOH (orange), FeOOHNiOOH (green) and Ni(Fe)OOH (grey).

Figure 6.7 (*right*) gives the density of accumulated MOOH(++) species as a function of applied potential for all three samples under conditions of electrocatalytic water oxidation. It is apparent that the Ni(Fe)OOH and FeOOHNiOOH electrocatalysts start accumulating MOOH(++) states ~ 70 mV negative of FeOOH, in agreement with their lower overpotential for current generation (compare this data to Figure 6.3). When comparing the concentrations of accumulated MOOH(++) species, it is also clear that FeOOHNiOOH accumulates the greatest number of MOOH(++) states, far more than both Ni(Fe)OOH and FeOOH. Observe that accumulated charge is not linear with applied potential for any of the catalysts, reflecting the non-uniform density of states found in these materials. Additionally, note that FeOOH(++) states were not generated in non-aqueous electrolytes, highlighting the important role of water molecules and/or proton-coupled electron transfer in the generation of these states (see Figure 6.8). Upon addition of water, a very small oxidative wave can be determined, normally masked by the OER current in aqueous electrolytes, reaffirming the localised, ‘molecular’ style oxidations in these films.

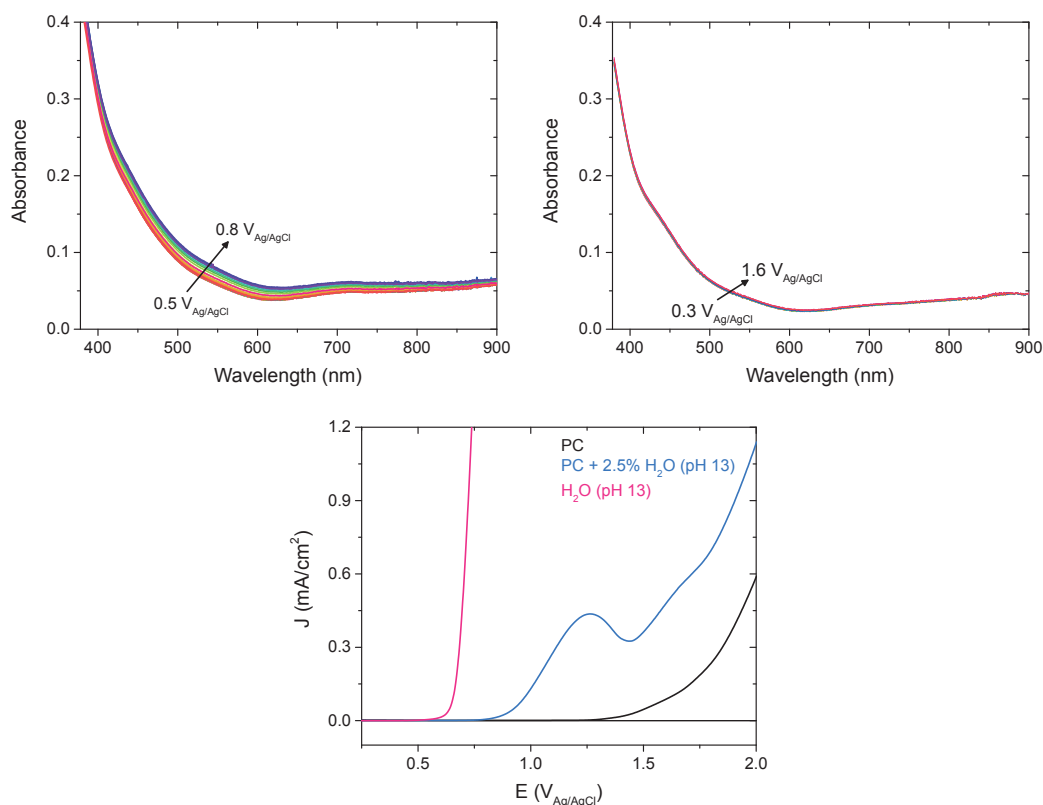


Figure 6.8 – *left*: UV-Vis absorption spectra of FeOOH in (*left*): aqueous electrolyte (pH 13) and (*right*): propylene carbonate (0.1 M NBu₄PF₆ buffer) as a function of applied potential. No change in absorbance can be seen in the absence of water. (*lower*): J-V of FeOOH in pH 13 (pink) and propylene carbonate (black). The addition of 2.5% aqueous electrolyte to PC induces an oxidative process ~ 1.2 V_{Ag/AgCl}, tentatively assigned to the generation of the catalytic FeOOH(++) species, not generated in the absence of water.

The concentrations of accumulated MOOH(++) species, $\sim 10^{16} \text{ cm}^{-2}$, are significantly greater than the density of metals on a flat MOOH surface, consistent with the previously reported permeability of such electrocatalysts to water, with the physical location of these accumulated species extending to some degree into the bulk of the material.²⁸² For example, accumulation of oxidised species beyond the atomic surface has been observed in the well-studied CoPi catalyst. In this case, bulk cobalt atoms were concluded to be catalytically active, leading to a proportionality between catalyst volume and activity.^{283,284} I return to this idea in more detail in Section 6.2.3. The higher concentration of accumulated MOOH(++) states in FeOOHNiOOH, as well as the more negative onset potential, may be associated with extensive mixing of Ni and Fe at FeOOH/NiOOH interfaces (Figure 6.2). As such, in FeOOHNiOOH it is possible that these states are associated with Fe atoms in proximity to Ni atoms of the NiOOH phase that stabilise FeOOH(++)^{265,269}

Before analysing the water oxidation kinetics of these electrocatalysts, the potential dependence of (0/+) and the (+/++) oxidation processes were examined further, as illustrated in Figure 6.9 for each electrocatalyst. The electrode potential and optical absorption decays were measured simultaneously as a function of time, following a switch to open circuit conditions after applying a catalytic overpotential. Switching to open circuit causes a sharp decay in the optical signal (< 5 s), leaving a small residual signal. This rapid decay is assigned to (++) reduction associated with water oxidation, and the small residual signal to persistent (+) states. Consistent with this assignment, the open circuit voltage also shows a rapid decay to a residual potential ($\sim 1.45 \text{ V}_{\text{RHE}}$), which corresponds to the onset of the (+/++) oxidation process. In FeOOH, these residual optical and voltage signals then decay on the timescale of thousands of seconds, consistent with the slow relaxation of the activated FeOOH(+) catalysts back to the FeOOH(0) initial state. The (+) states in FeOOHNiOOH and Ni(Fe)OOH are much more persistent in line with the long-lived NiOOH decaying over days. Overall, these data confirm that the (0/+) process observed in our spectro-electrochemical data is an oxidation process which, though important for catalytic function, is not directly involved in water oxidation catalysis, in accordance with other documentation in the literature for such mixed metal oxides reporting an ‘activation’ or pre-catalytic step to bring the electrode to the catalytic resting state.^{270,285} The relationship between how much of the film is activated, and how many (++) species are formed is, however, thus far unclear.

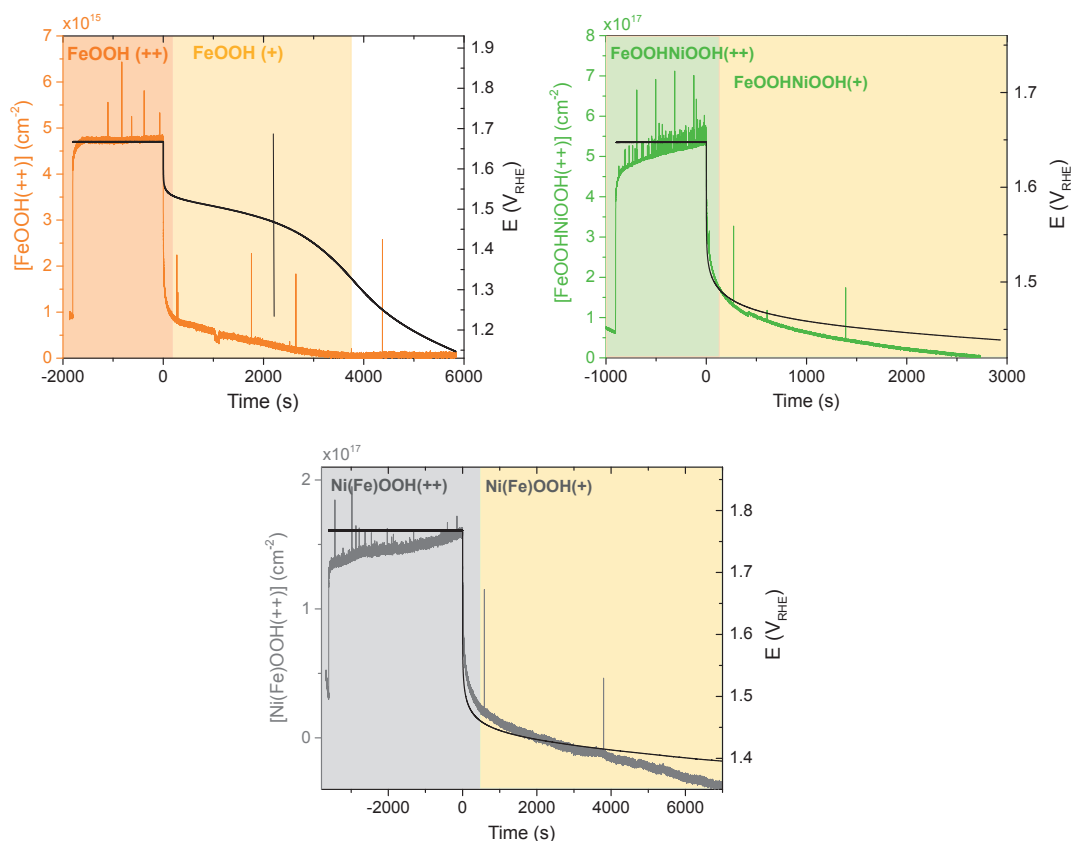


Figure 6.9 – Simultaneous measurement of the optical signal, expressed as concentration of $(++)$ species, and the electrode potential (black trace) at a chosen bias before switching to open circuit ($t = 0$). $FeOOH$ (upper left, orange) shows the clearest distinction between $(+)$ species and rest (0) , whereas $FeOOHNiOOH$ (upper right, green) and $Ni(Fe)OOH$ (lower, grey) show $(+)$ species associated with $NiOOH$ generation that persist significantly longer (days). Note that the y-axis for $(++)$ species concentration cannot afford accurate determination of $(+)$ species concentration owing to the difference in extinction coefficient between these species and as such should be viewed qualitatively.

6.2.3 Thickness dependence study

In order to better define where in these films the (+) and (++) species accumulate, different thicknesses of electrocatalysts were examined. For simplicity, this study was limited to nickel oxide samples which show the greatest (+) species absorption as Ni(Fe)OOH is formed. As control of thickness is clearly essential for this study, NiO_x samples prepared by collaborators by magnetron sputtering were used (rather than the electrodeposited samples), with dense samples of 5 nm, 10 nm, 20 nm and 100 nm examined. The synthetic details for these samples can be found in Chapter 3 and their characterisation is given in Appendix A.8.

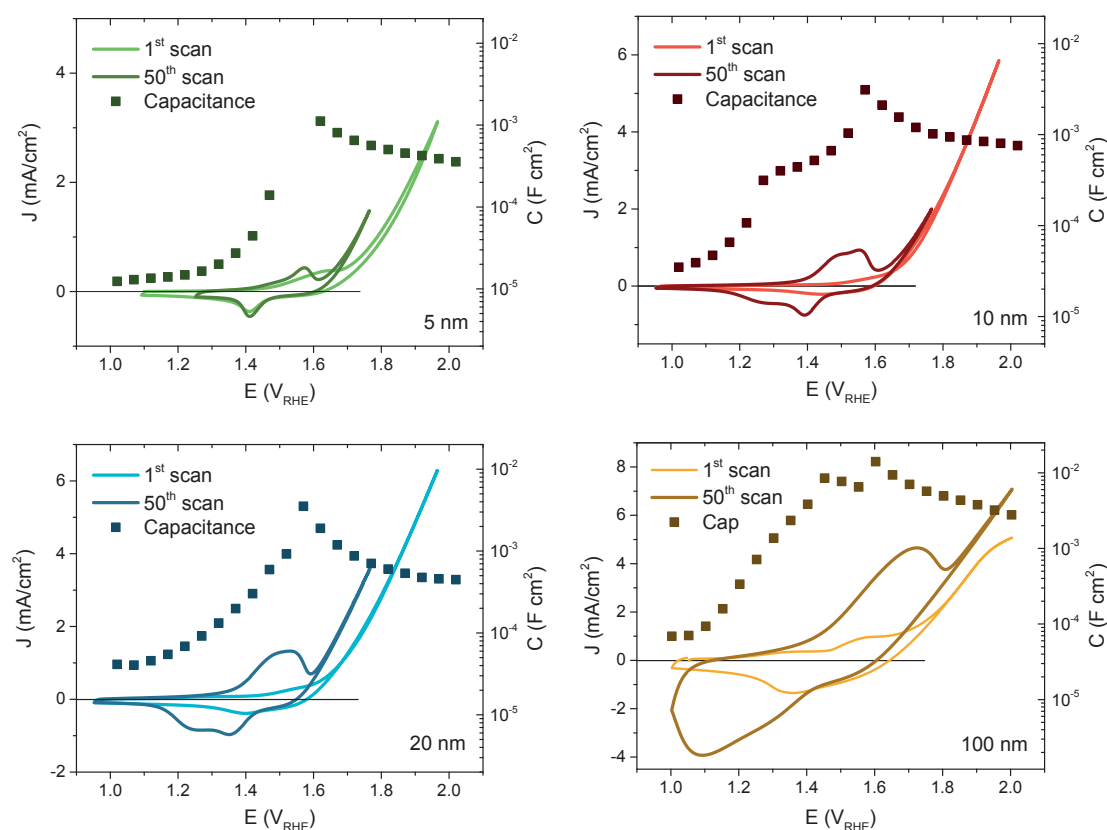


Figure 6.10 – CV scans (lines) and calculated capacitance values (squares) of (*upper left*): 5 nm, (*upper right*): 10 nm, (*lower left*): 20 nm, and (*lower right*): 100 nm thick sputtered NiO_x films. Both the first CV scan (lighter colour) and 50th scan (darker colour) is given for each thickness. The CV scan rate was 50 mV/s and 0.1 M NaOH (pH 13) was used for both impedance and electrochemistry. All electrochemical impedance spectroscopy measurements and subsequent calculations were performed by Dr Miguel Garcia-Tecedor in UJI.

The initial cyclic voltammogram (CV) for each thickness is given in Figure 6.10. A shallow, broad redox wave can be observed approximately 150 mV before the catalytic onset at 1.64 V_{RHE} which is assigned to the oxidation of Ni²⁺ to Ni³⁺ and the concurrent formation of Ni(Fe)OOH, as was observed for the electrodeposited electrocatalysts. As with the electrodeposited samples, the sputtered catalysts required an activation process to obtain the optimal performance. This involved running 50 CV scans over potentials corresponding to this redox wave, resulting in a clear enhancement in the wave amplitude from the oxidation of more Ni centres, as seen in Figure 6.10 for each thickness. An improvement in the catalytic current can also be observed following this activation in agreement with several reports in literature of Fe incorporation from impurities in standard grade alkaline electrolytes.^{127, 145}

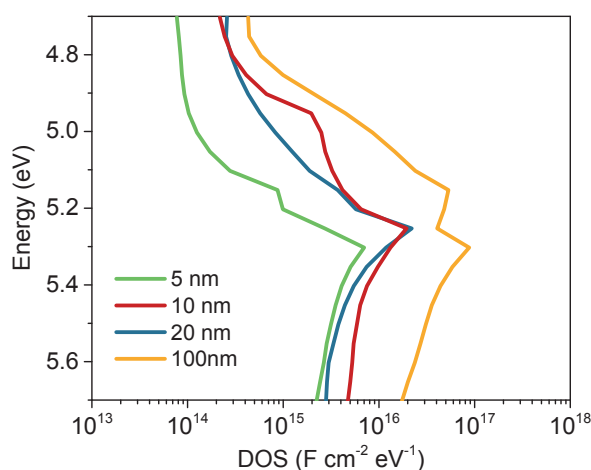


Figure 6.11 – The density of states (DOS) for each NiO_x thickness examined, calculated by Dr Miguel Garcia-Tecedor from the chemical capacitance obtained from EIS using $C = e \times \text{DOS}$.

The capacitance over the same potential range was calculated using electrochemical impedance spectroscopy (EIS) by external collaborators, the conditions for which are outlined briefly in Appendix A.9. EIS is a powerful analytical tool in electrochemistry but strongly relies on use of a suitable equivalent circuit model. The equivalent circuit models used herein and the resultant Nyquist plots at 1.6 V_{RHE} are given in Appendix A.9. As can be observed in Figure 6.10, the capacitance increases with applied potential with a well-defined peak over the redox wave and a gradual decrease over the catalytic region evident at each thickness. This peak in capacitance is thereby associated with the bulk formation of Ni(Fe)OOH, before the onset of catalysis. Furthermore, the capacitance increases with film thickness, and hence the amount of material available. This behaviour is typical of a chemical capacitance, from which an approximate density of states (DOS) may be calculated by dividing by the charge of an electron, as shown in Figure 6.11. Though

the capacitance values obtained, and thus the DOS, will depend on the circuit model used to fit the impedance data, the agreement in energetic maxima of the DOS between samples and the increase in density of states available with thickness strengthens the argument that the same bulk oxidation is required for each film, as expected. A semi-molecular approach in the analysis of these materials is pertinent given the local nature of the oxidation process, requiring direct contact with electrolyte as was shown in Figure 6.8.¹³²

While treatment of these films as semiconductors may not be constructive for understanding their mechanistic activity during catalysis, Mott-Schottky analysis in the pre-redox region ($< 1.2 V_{\text{RHE}}$) reveals a doping density around 10^{21} cm^{-3} (Figure A.13), thereby affirming the highly defective nature of these materials.¹⁴⁶ Higher catalytic activities have previously been associated with highly defective and disordered phases of NiOOH .²⁸⁶ In the case of the 100 nm sample, the relatively large amount of material gives rise to an incredibly large and broad redox wave, which proceeds to grow past 50 CV scans. This therefore indicates that the activation process applied fails to oxidise the entire bulk of this film to Ni(Fe)OOH , as supported by the similarity in Ni 2p and O 1s XPS data for this sample before and after activation (Figures A.9 and A.10). This has been observed in other metal oxide systems and attributed to increasing inhibition of water and hydroxide ion transfer to the inner depths of the oxide layer.²⁸⁷ As such, the DOS is likely to be underestimated for this thickness and this sample was not considered further.

By comparing the 50th CV scan for 5, 10 and 20 nm thick films (Figure 6.12, *left*), a relationship between film thickness and the redox capacitance (size of the redox wave) can be observed. This confirms that this oxidation pre-requisite to catalysis is very much a bulk process, with the electrolyte penetrating deep into the film to form Ni(Fe)OOH throughout the structure. This result correlates with the layered nature of these films, which can swell to incorporate water.^{127,287} The 5 nm and 10 nm films appear to have a similar catalytic onset after the film activation, whereas the 20 nm film has an earlier onset, which I tentatively assign to a greater Fe incorporation. The activation of NiO_x to Ni(Fe)OOH was also probed optical by spectroelectrochemistry, as in Section 6.2.2. By monitoring the change in absorption of the films after activation, i.e. subtracting the initial absorption spectra from those obtained after 50 CV scans, the residual spectra of the oxidised species formed was obtained. This is given in Figure 6.12 (*right*) and clearly displays the same species, Ni(Fe)OOH , as observed in Figure 6.4 for the electrodeposited films. It is equally evident that increasing film thickness results in greater absorption, thereby supporting the electrochemical assignment of this initial NiO_x to a bulk oxidation process. This thickness dependent absorption, alongside the increase in chemical capacitance with thickness is displayed in Figure 6.12 (*lower*).

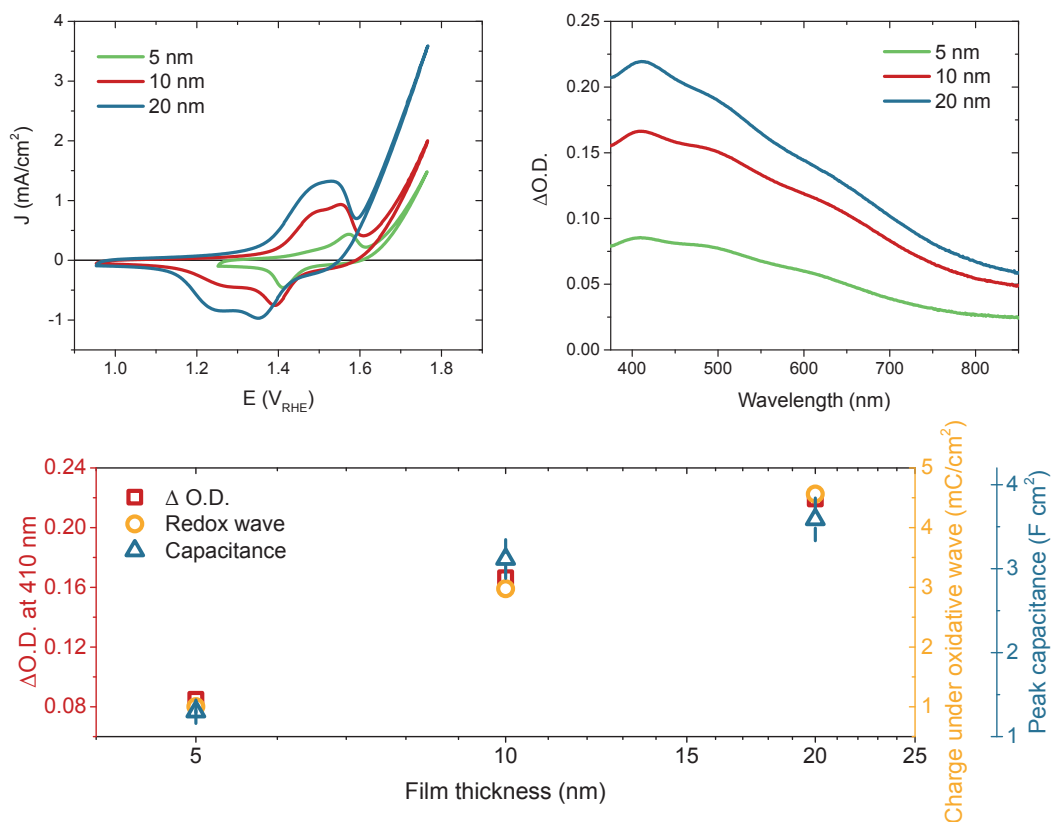


Figure 6.12 – *left*: The 50th CV scan for 5 nm (green), 10 nm (red) and 20 nm (blue) films, with a scan rate of 50 mV/s in 0.1 M NaOH. *right*: Spectroelectrochemistry showing the change in absorbance after activation for each sample, as demonstrated for the electrodeposited samples in Figure 6.4. *lower*: Comparison between sample thicknesses of the area of the redox wave, the peak capacitance value determined by impedance spectroscopy, and the absorbance maximum from spectroelectrochemistry for this first oxidation.

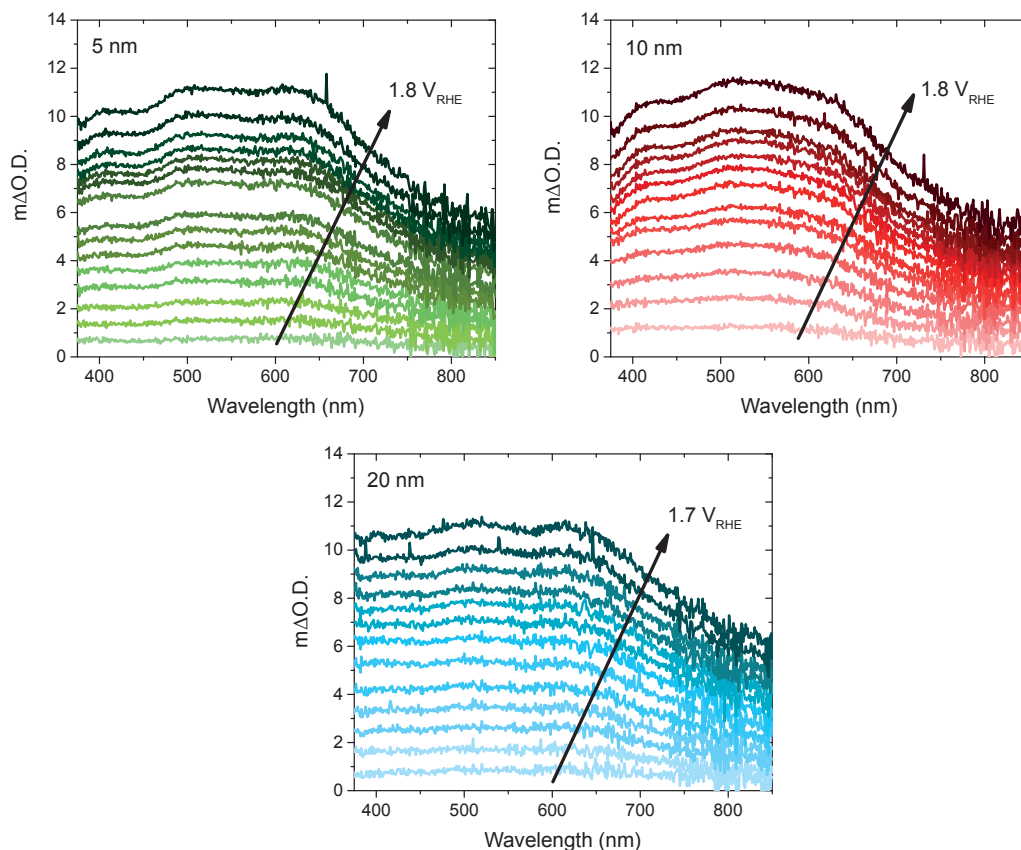


Figure 6.13 – Spectroelectrochemistry over catalytic potentials up to 1.7–1.8 V_{RHE} with respect to the onset potential for each film (*left*: 5 nm (green), *right*: 10 nm (red) and *lower*: 20 nm (blue)). A similar spectral shape and amplitude is observed for each film.

Performing spectroelectrochemistry across potentials that give rise to catalytic current produces a different result, with the appearance of the (++) species (Figure 6.13). This Ni(Fe)OOH(++) species present central peaks at 510 nm and 625 nm, perhaps most similar to the spectra of FeOOHNiOOH(++) from the electrodeposited samples (Figure 6.5). This may be indicative of greater Fe incorporation in these sputtered samples or may result from changes in the morphology (nickel and iron oxyhydroxides are known to exist in several different phases including α , β and γ forms, the more detailed study of which is beyond the scope of this thesis). As with the first oxidation, similar spectra are produced for each thickness (evident, particularly, in the grouped comparison in Figure 6.14, *left*). With increasing anodic potential, these peaks grow steadily due to the increased accumulation of the oxidised species from which they arise. Notably, when comparing the onset of oxidised species accumulation to the current onset (Figure 6.14, *right*), it is once again clear that a degree of accumulation is necessary for catalytic current to be produced,

in line with the multi-step nature of water oxidation and the data from the electrodeposited samples. It is also evident that this accumulation begins ~50 mV earlier for the 20 nm film, in agreement with the earlier catalytic onset of this thicker film, and thereby indicating that current onset is directly correlated with the relative ease of oxidised species accumulation in such materials. The lower overpotential for (++) species accumulation in the 20 nm film is tentatively assigned to a disproportionately larger concentration of Fe atoms in the NiOOH structure. This is supported by comparison of the spectra for each thickness which shows that the 20 nm film has a slightly blue-shifted absorption in relation to the other thicknesses, in-line with the (++) species of the electrodeposited samples that contain greater concentrations of Fe atoms (compare Figure 6.14, *left*, with Figure 6.5, *right*). Enhanced catalytic onsets and improved performances have been widely reported with Fe impurities and can be observed, for instance in comparing the performance of electrodeposited Ni(Fe)OOH against purified NiOOH (Appendix A.11, Figure A.14).^{133,263,288} Lower iron content in the 5 nm and 10 nm films may provide explanation for their later current onsets with respect to their optical onsets (Figure 6.14, *right*), particularly if the MOOH(++) species formed are different in nature, with potentially different rates of catalysis, as we shall examine in Section 6.2.4. Alternatively, the improved onset of the 20 nm film may stem from different proportions of β -NiOOH and γ -NiOOH, which are reported to have different OER efficiencies and different affinities for Fe.^{267,289,290} Unfortunately, the small thickness of the samples inhibited adequate determination of the phases present by XRD and I was not able to reliably determine the concentration of iron in the samples.

Arguably the most striking trend observed in these data is the similarity in optical data at the same current density (Figure 6.14). These data account for the difference in onset, with the Δ O.D. in each case presented 0.1 V after the respective catalytic onset. Indeed, if we were to shift the data in Figure 6.14 (*right*) by the difference in onset between the samples, we would find that both the optical data in the upper panel and current data in the lower panel would overlap at each thickness across the entire potential range measured. The degree of similarity in the species and currents observed between samples over catalytic potentials is highlighted in the comparison in Figure 6.14 (*lower*). Both the steady-state current and peak optical amplitude 100 mV after catalytic onset remain approximately constant across each of the samples examined, independent of thickness. This result stands in direct contrast to the first oxidation (Figure 6.13, *lower*), which demonstrated increasing absorption amplitudes with increasing thickness. The similarity in optical amplitude implies that a similar number of species are accumulating in each sample. The formation of these accumulated species must therefore be limited to the thickness of the thinnest film, i.e. the upper 5 nm or less of Ni(Fe)OOH, despite the initial oxidation of the entirety of the film (Figure 6.13).

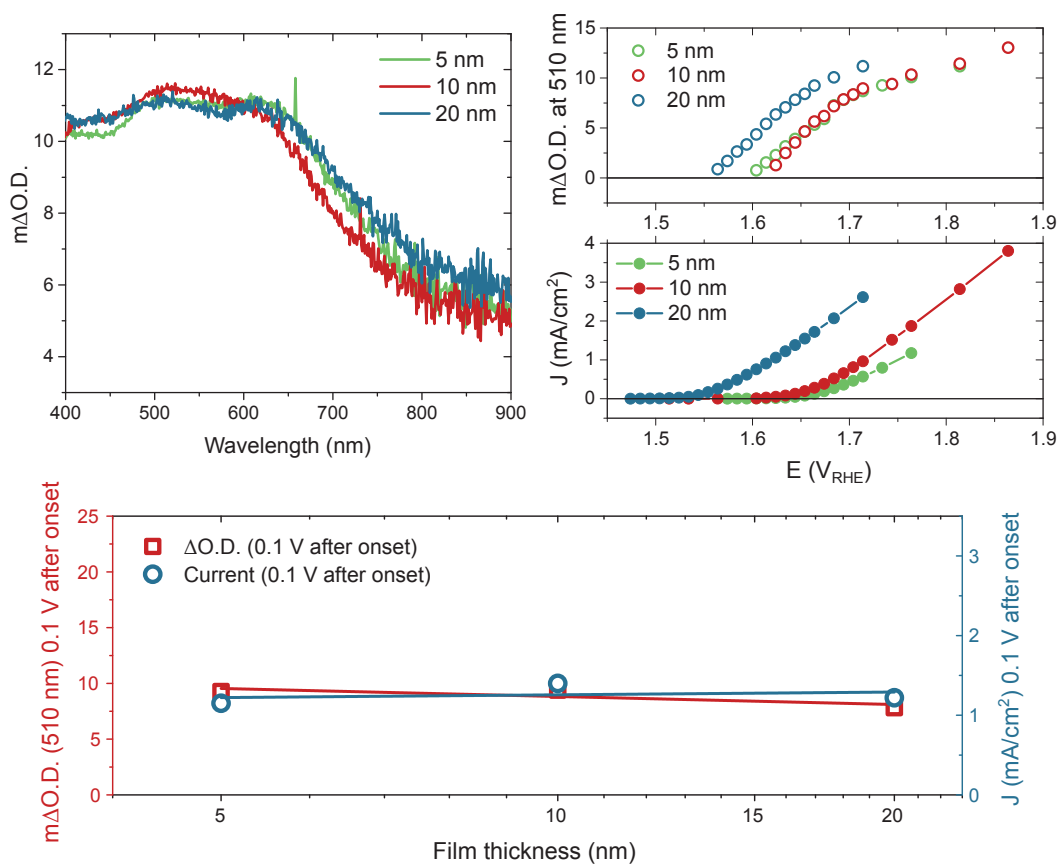


Figure 6.14 – *left*: Normalised absorption spectra of the accumulated species over catalytic potentials for 5 nm (green), 10 nm (red) and 20 nm (blue) NiOOH films, 0.15 V after catalytic onset. *right*: The change in absorption at 510 nm for each film thickness as a function of applied potential over catalytic range (*top*), and the corresponding steady-state current obtained simultaneously from the spectroelectrochemistry measurement (*bottom*) in 0.1 M NaOH. In both panels 5 nm (green), 10 nm (red), and 20 nm (blue) are shown. *lower*: The catalytic current and optical density at 510 nm and 0.1 V after current onset against film thickness, revealing no increase in the population of accumulated species with thickness.

Despite the difference in onset for the 20 nm sample, which could not be elucidated further in this study, a similar oxidised species concentration is apparent from the similarity in optical amplitude, implying that catalysis is limited to within a few nanometres of the surface. Furthermore, this result indicates that the accumulating species is not formed in the ‘bulk’ of the film, presumably due to instability or restricted access to water. With this, it is determined that the hydration of the NiO_x structure observed in Figure 6.13 is essential for the greater oxidative conversion of Ni^{2+} to Ni^{3+} deep into the structure, but that the quantity of NiOOH generated does not directly correlate to the number of active centres in the films, with only those centres ≤ 5 nm of the upper electrode surface able to accumulate the intermediates involved in water oxidation catalysis, as summarised in Scheme 6.15. This result is in agreement with pH dependent data reported by Koper and co-workers which show that the catalytic activity of NiOOH in alkaline media is dependent on surface MO^- and MOO^- species formation,¹³² as has been reported for other similar materials.^{281,291} Likewise a recent investigation using isotope labelling of NiFeO_xH_y particles reports that oxygen evolution is limited to the near-surface region, in line with the conclusions herein.²⁸² By contrast, the DFT work of Doyle et al. reports that, given the hydrated layered structure of these oxyhydroxides, ‘bulk’ sites could contribute to water oxidation catalysis,²⁹² whereas these results indicate that this is not the case. One line of reasoning that could account for the small active thickness of these films is the limitations in mass transport of reactants and products to and from catalytic sites. This would suggest that morphological control of such catalysts could dramatically increase performance.

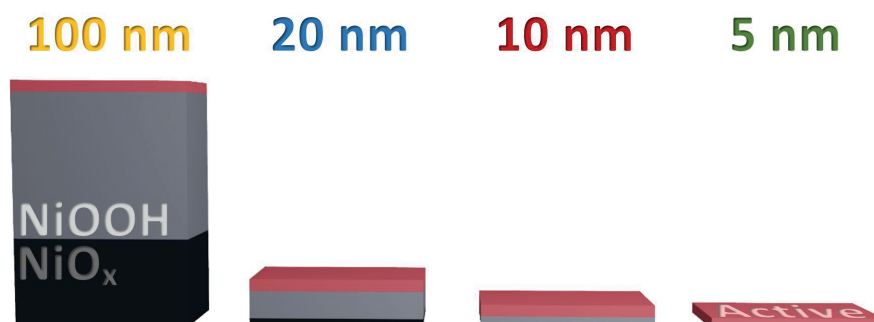


Figure 6.15 – Graphic representation of each thickness of sputtered NiO_x , showing the relative thicknesses of active material to bulk oxidised $\text{Ni}(\text{Fe})\text{OOH}$ and unaltered NiO_x . Only the upper 5 nm or less is active for water oxidation. A small proportion of the 20 nm film is thought to remain NiO_x based on the sub-linearity in Figure 6.12.

6.2.4 Kinetics of water oxidation

With the controversial site of charge accumulation addressed, at least in terms of active thickness if not active site, we return to the electrodeposited samples (FeOOH, FeOOHNiOOH and Ni(Fe)OOH) to determine the kinetics of catalysis on these materials. By varying the potential applied, the concentration of MOOH(++) states can be controlled and the impact on the water oxidation kinetics measured. Akin to previous kinetic analyses reported by the Durrant group,^{112,118,119,277–279} the MOOH(++) state concentrations were measured optically and water oxidation current densities measured simultaneously to determine how the lifetime τ (s) of MOOH(++) states driving water oxidation varies with MOOH(++) accumulation (Figure 6.16, *left*). These data were then used to generate a complementary plot of TOF (s^{-1}) of oxygen molecules per MOOH(++) (taking into account the 4-electron requirement of oxygen evolution) against applied potential (Figure 6.16, *right*) (see Appendix A.10 for details of τ and TOF determination).

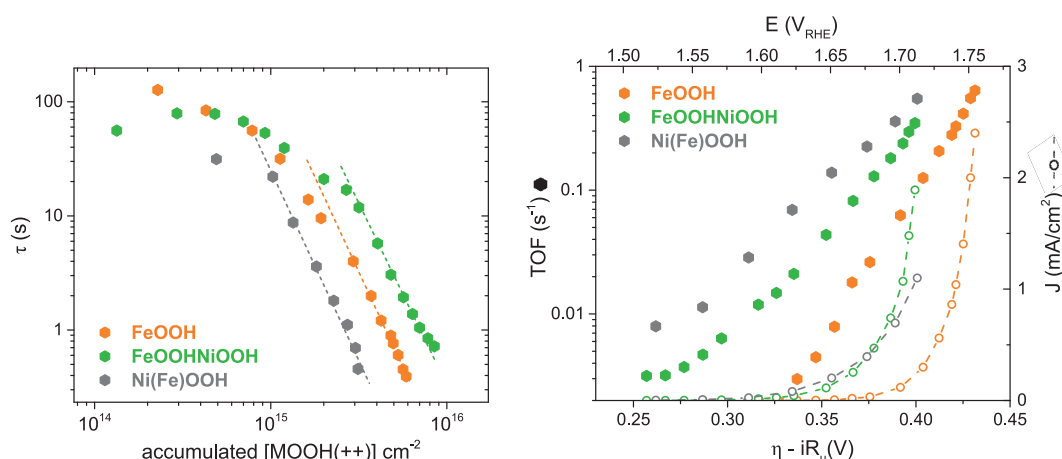


Figure 6.16 – *left*: Plot of the change in decay time (τ) of the accumulated MOOH(++) states as their concentration varies with potential for FeOOH (orange), Ni(Fe)OOH (grey) and FeOOHNiOOH (green). *right*: Corresponding plots of turnover frequency (TOF) per O_2 molecule generated against the applied potential (solid hexagons), overlaid with a plot of current density versus applied potential (empty circles, dashed lines).

Figure 6.16 (*left*) shows the MOOH(++) lifetime, assigned to water oxidation kinetics, decreasing with increasing MOOH(++) concentration. The rapid increase in MOOH(++) concentration for potentials up to 100 mV above the (+/++) accumulation onset potential (Figure 6.7), correlates with a rapid (*ca.* two orders of magnitude) increase in TOF over the same potential range (Figure 6.16, *right*). Note that these studies determine the kinetics of the MOOH(++) species accumulated during steady-state water oxidation catalysis, but cannot resolve the kinetics of any shorter lived

reactive intermediates in the catalytic cycle.

Figure 6.16 (*left*) also shows that at equal accumulated $\text{MOOH}(++)$ concentrations, $\text{Ni(Fe)OOH}(++)$ exhibits the fastest kinetics and $\text{FeOOHNiOOH}(++)$ the slowest by as much as an order of magnitude. The slower water oxidation kinetics for $\text{FeOOHNiOOH}(++)$ provide likely explanation as to why this electrocatalyst exhibits a similar current density to Ni(Fe)OOH , despite accumulating significantly greater concentrations of $\text{MOOH}(++)$ states. In other words, Ni(Fe)OOH has a lower concentration of accessible $\text{MOOH}(++)$ states, but these states drive faster water oxidation catalysis, and the converse is true for FeOOHNiOOH . Up to 0.4 V overpotential, the TOF of Ni(Fe)OOH is faster than FeOOHNiOOH , and FeOOH is the slowest (Figure 6.16, *right*). The TOFs (s^{-1}) at 0.34 V overpotential is given in Table 6.2. From these data, it is concluded that the more positive onset potential for water oxidation of FeOOH , in comparison to both Ni(Fe)OOH and FeOOHNiOOH , does not primarily result from slower water oxidation kinetics by $\text{MOOH}(++)$ states, but rather from the anodic shift in the onset of accumulation of these states.

Similar time constants to those plotted in Figure 6.16 (*left*) were obtained directly from the decay time of the optical signal once the catalytic applied overpotential was turned off (see Figure 6.9 and the fits, calculated by Prof Robert Godin and Dr Camilo Mesa, given in Figure 6.17). This agreement in kinetics between the combined optical/electrochemical data (Figure 6.16) and optical data alone (Figure 6.17) strongly supports the validity of these results, as these two kinetic analyses employ very different experimental and data analysis procedures. The kinetic analysis given in Figure 6.16 relies upon accurate calculation of the extinction coefficient for the $\text{MOOH}(++)$ species such that their concentration may be determined from optical data. On the other hand, the analysis presented in Figure 6.17 does not require such calculations, and the tau values in these cases are obtained only by fitting the raw kinetic traces. Both sets of numbers are given in Table 6.2, alongside other useful comparisons for these samples. The TOF values determined from these data per $\text{MOOH}(++)$ state are higher than those previously reported in the literature, which are typically determined per total mass or metal atom density.^{145, 264, 270, 286, 293} In contrast to those reports, the concentration of the oxidised states driving water oxidation catalysis have been quantified herein, which, in general, is lower than the total content of electrochemically active metals. On the other hand, the TOF values calculated are lower than those reported on Ni(Fe)OOH per Fe atom, indicating that the Fe concentration in this sample is lower than the measured operando $\text{MOOH}(++)$ state density, and as such, reaffirming that the $\text{Ni(Fe)OOH}(++)$ states are Ni-centred, as discussed above.

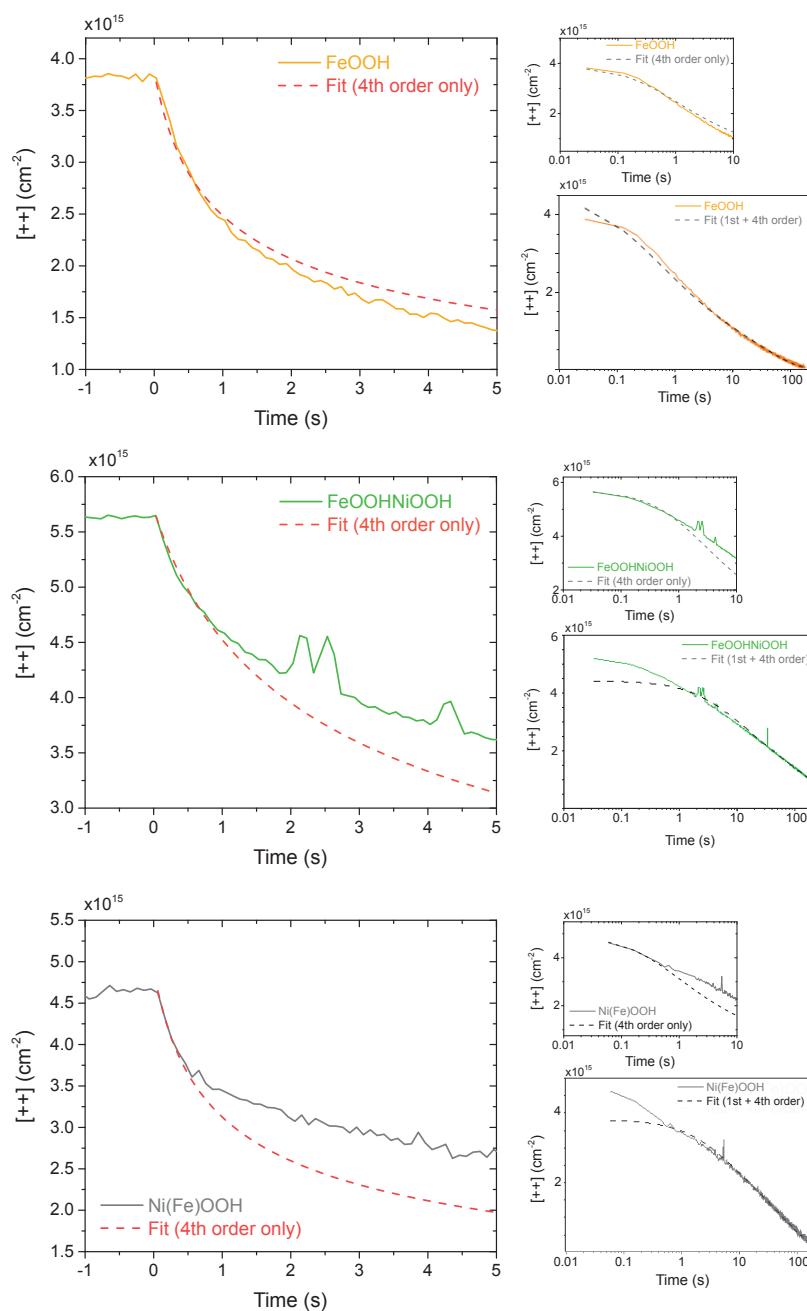


Figure 6.17 – Optical decays from Figure 6.9 after switching to OCP from a catalytic potential, fitted to exponential functions of different orders. (Fittings performed by Prof Robert Godin and Dr Camilo Mesa). The best fit at early times was a 4th order exponential for each electrocatalyst (given on linear scale in largest panel and logarithmic scale in top right panels). This 4th order gives way to 1st order at later times, in agreement with the rate law analyses. *upper*: FeOOH (orange), $k_{obs} = 1.88 \times 10^{-47} \text{ cm}^6(\text{e}^{-1})^{-3}\text{s}^{-1}$, *middle*: FeOOHNiOOH (green), $k_{obs} = 7.63 \times 10^{-49} \text{ cm}^6(\text{e}^{-1})^{-3}\text{s}^{-1}$ and *lower*: Ni(Fe)OOH (grey), $k_{obs} = 1.57 \times 10^{-48} \text{ cm}^6(\text{e}^{-1})^{-3}\text{s}^{-1}$.

Comparative	FeOOH	FeOOHNiOOH	Ni(Fe)OOH
Thickness (nm)	80	120	80
Fe content (at. %)	100	79	1
Fe content after use (at. %)	100	79	5
Catalysis onset* (V_{RHE})	1.60	1.53	1.53
ϵ (+) ($M^{-1}cm^{-1}$)	2400 (500 nm)	8250 (528 nm)	8250 (528 nm)
ϵ (++) ($M^{-1}cm^{-1}$)	2400 (500 nm)	3600 (550 nm)	4000 (650 nm)
τ (s) at 1 mA/cm ² (Figure 6.16)	0.76	1.00	0.46
τ (s) (Figure 6.17)	0.8	1.0	0.6
TOF (s ⁻¹) at $\eta = 0.34$ mV (Figure 6.16)	0.003	0.020	0.070
% MOOH(++) of M-centres**	4%	9%	12%

*catalysis onset approximated to potential at which current reaches 20 $\mu A/cm^2$

**see Appendix A.7 for details

Table 6.2 – Summary of important numerical comparisons between catalysts studied herein

6.2.5 Mechanistic analysis

Considering the synthesis of the catalysts studied in this work, the FeOOHNiOOH film is likely to exhibit the most mixing of Fe and Ni and the largest FeOOH-NiOOH interfacial area. From the results reported above, we find that this higher interfacial area does not improve the kinetics of the catalytic reaction, but does result in a cathodic shift of the onset of MOOH(++) accumulation when compared with pure FeOOH. This observation would agree with a higher degree of stabilization of FeOOH(++) when close to Ni atoms,^{265,269} thus facilitating charge accumulation but decreasing reactivity. The Ni(Fe)OOH sample shows enhanced kinetics and a similar onset of MOOH(++) accumulation to FeOOHNiOOH, although Ni(Fe)OOH is not able to accumulate as large a concentration of MOOH(++) states. The faster water oxidation kinetics of Ni(Fe)OOH in conjunction with the accumulation of fewer Ni(Fe)OOH(++) species results in a similar overall performance to FeOOHNiOOH. These differences in reactivity between FeOOHNiOOH and Ni(Fe)OOH suggest a different nature of the MOOH(++) species, in agreement with the different spectral features, attributed to Fe- vs Ni-centred oxidised species, respectively. The overall result is then a comparable J-V curve for both samples.

Analogous to previous studies in the Durrant group of photoelectrodes such as hematite, these catalysts can be analysed under steady-state conditions using a rate law plot according to the following equation:

$$\log J = \log k_{wo} + \alpha \log[\text{MOOH}(++)] \quad (6.1)$$

where J is the electrochemical steady-state current density (and therefore water oxidation flux), $[\text{MOOH}(++)]$ is the concentration of $\text{MOOH}(++)$ states, k_{wo} is the water oxidation rate constant, and α the order of the reaction with respect to $\text{MOOH}(++)$ concentration.²⁷⁷

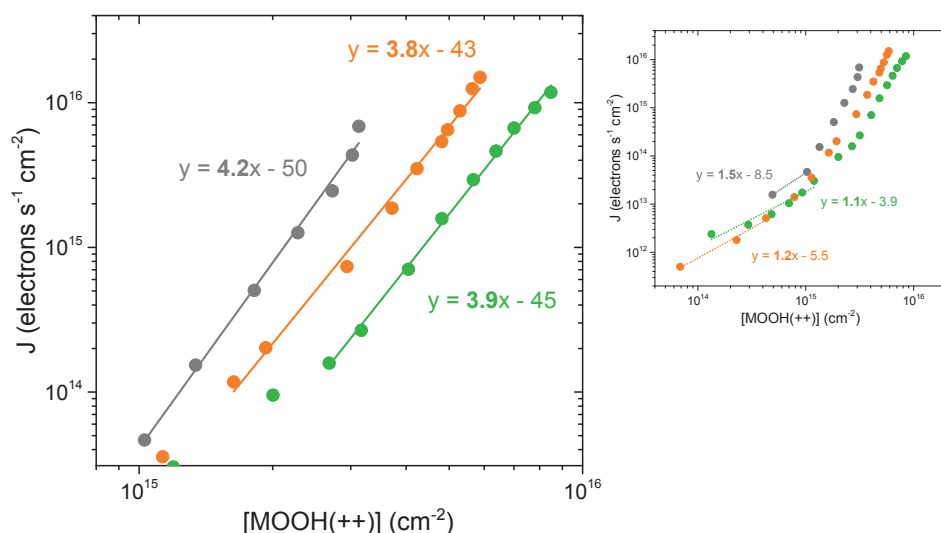


Figure 6.18 – Rate law plots, obtained using Equation 6.1, showing the current density from water oxidation against the concentration of $\text{MOOH}(++)$ states for FeOOH (orange), Ni(Fe)OOH (grey) and FeOOHNiOOH (green). *left*: Catalytic potentials, *right*: entire concentration window measured. Gradient errors are all < 4%.

From the gradient of the plots presented in Figure 6.18, it can be observed that all three electrocatalysts exhibit a reaction order (α) of ~ 4 under conditions of catalytic water oxidation ($20 \mu\text{A}/\text{cm}^2$ to $1 \text{ mA}/\text{cm}^2$). This order decreases at lower current densities (Figure 6.18, *right*), which is tentatively assigned to an overlap with an alternative mechanistic regime of lower order ($\sim$ order 1), as observed in several photoanode materials,^{112,119,279} although it is also plausible that such low current densities are non-Faradaic in origin. In other words, under operational conditions, the current density increases with the 4th power of the concentration of $\text{MOOH}(++)$ states. These reaction orders were further confirmed by satisfactory fitting of the optical decay kinetics presented in Figure 6.9 with a model incorporating 1st and 4th order reactions (see Figure 6.17). This

observation indicates that four MOOH(++) species are required to overcome the rate determining step of the catalysis (RDS). It is interesting that the same order of reaction is obtained for each electrocatalysts, as this implies an inherently similar reaction mechanism between them.

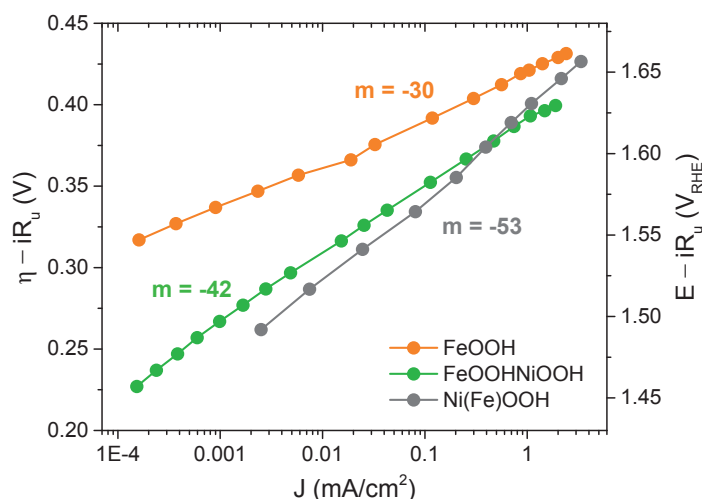


Figure 6.19 – Tafel plots, calculated by Dr Laia Francàs, with slopes indicated (m) for each electrocatalyst FeOOH (orange), Ni(Fe)OOH (grey) and FeOOHNiOOH (green).

This stands in contrast to Tafel analyses (calculated by Dr Laia Francàs) of the same electrodes, shown in Figure 6.19, which yield significantly differing slopes, often interpreted as indicating different reaction mechanisms.²⁹⁴ This disparity can be attributed to charge accumulation in these materials corresponding to multiple, localised redox oxidations at sites of direct electrolyte contact and therefore not behaving as ideal metals. As such, the different Tafel slopes most likely originate from differences in the dependence of charge density upon applied potential (Figure 6.7), rather than being indicative of different reaction mechanisms. The rate law data also confirm the kinetic trends discussed above, with the observed rate constant for these species decreasing in the order Ni(Fe)OOH(++) > FeOOH(++) > FeOOHNiOOH(++). Note that the order of reaction observed for these electrocatalysts was found to be pH sensitive, changing to a lower reaction order when the electrocatalysts were studied at pH 7 instead of the pH 13 used throughout this work. This is consistent with key role of protons in water oxidation as observed for photosynthetic water oxidation, although a full analysis of the effect of pH upon this electrocatalysis is beyond the scope of this study. A simple mechanistic scheme based on our analyses is given in Figure 6.20 for each electrocatalyst.

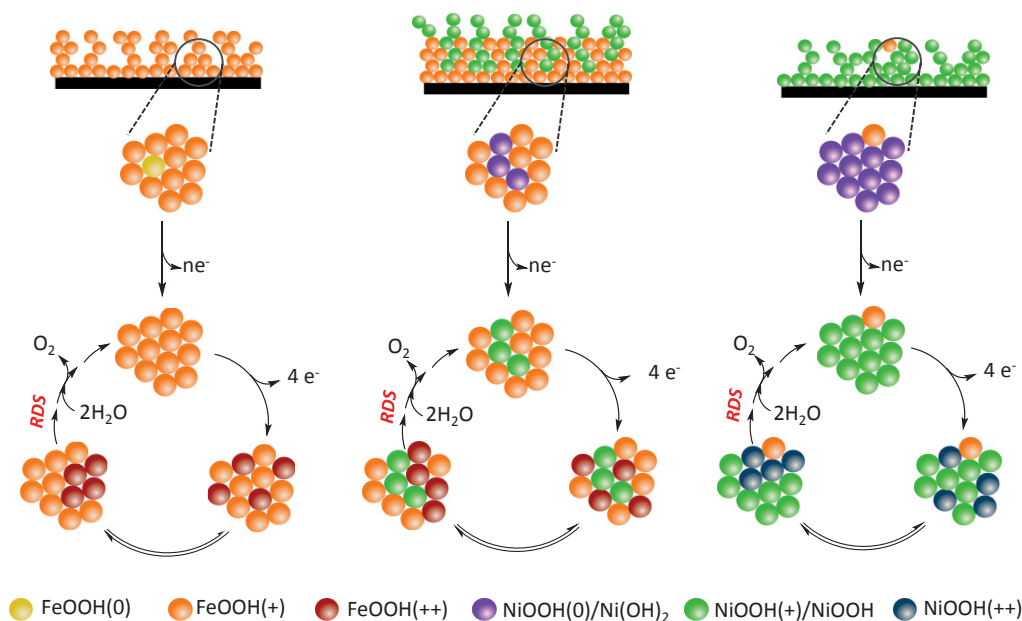


Figure 6.20 – Schematic representations of simple mechanisms for water oxidation on (left): FeOOH, (centre): Ni(Fe)OOH and (right): FeOOHNiOOH. Colour code: FeOOH(0) corresponding to reduced defect states in FeOOH (yellow spheres); FeOOH(+) (orange spheres); FeOOH(++) (red spheres); NiOOH(0) corresponding to Ni(OH)₂ (purple spheres); NiOOH(+) corresponding to NiOOH (green spheres); NiOOH(++) (blue spheres).

6.3 Discussion

The nature of the states driving water oxidation catalysis in Ni(Fe)OOH, and the role of Fe incorporation into NiOOH, is one of the largest controversies in this field. Previous studies have suggested that either Fe^{127, 133, 265, 269, 295} or Ni^{132, 271, 272} centres form the catalytic sites for water oxidation in such electrocatalysts. It is noted that this study focuses only on monitoring the oxidised states which accumulate to drive water oxidation catalysis, rather than directly probing the reactive intermediates involved in oxygen-oxygen bond formation, and the rate constant determined is thus with respect to these accumulated states. As discussed above, the different $\Delta O.D.$ spectra for Ni(Fe)OOH(++) and FeOOHNiOOH(++) states suggest these oxidised species accumulating under catalytic conditions are different in nature between samples. These spectra suggest that Ni(Fe)OOH(++) species are associated either with the oxidation of sparsely incorporated Fe within a NiOOH environment, or with Ni groups. Given the smaller quantity of accumulated (++) species observed in this sample (Figure 6.7), one could assume that these species are Fe-centred, consistent with the smaller concentration of iron present. However, the concentration of Ni(Fe)OOH(++) states is at least twice the total concentration of Fe in the sample

(see Table 6.2), indicating a greater probability that these Ni(Fe)OOH(++) states are centred on Ni atoms. Furthermore, additional analysis of a NiOOH electrocatalyst kept free of any Fe impurities resulted in similar spectral features (Figure 6.6), thus effectively ruling-out any involvement of Fe centres in MOOH(++) species accumulation in samples with low concentrations of iron. This is in agreement with the detection of Ni⁴⁺ (i.e. NiOOH(++) in my nomenclature) in XAS and XANES experiments on this type of catalyst.^{270,271} ¹⁸O-labelling experiments by Hu and co-workers also indicate different active sites for Ni and NiFe oxides (Fe $\approx$ 25%),²⁹⁶ as do light scattering experiments on similar samples by Dau and co-workers, in-line with our conclusions herein.²⁹⁷ However, the Fe concentration at which the favoured MOOH(++) species accumulated switches from Ni-centred to Fe-centred remains to be determined. It also cannot be ascertained from these data alone whether a regime exists in which both metals are responsible for charge accumulation, as reported by others.^{273,275,298} A degree of synergism between metal centres is probable, considering the improved charge accumulation found in the FeOOHNiOOH sample over the FeOOH sample. More experiments are necessary in order to answer the remaining questions for these materials.

Interestingly, the rate law analysis given in Figure 6.18 reveals the same reaction order for each electrocatalyst, independent of the active metal centre in the accumulated MOOH(++) species. This strongly suggests a similar mechanism in each case, as shown in Figure 6.20. For each electrocatalyst, the (0/+) process takes place before catalysis, corresponding to the oxidation of defect sites in FeOOH (most likely associated with oxygen vacancies) and to the oxidation of Ni(OH)₂ to NiOOH in FeOOHNiOOH and Ni(Fe)OOH. After this first (0/+) oxidation process, the second oxidation (+/++) takes place, which is correlated with the onset of electrocatalytic water oxidation. As illustrated in Figure 6.20, the generated MOOH(++) states can be considered in equilibrium with much shorter-lived reactive intermediates (not directly detected in this study), with four such (++) species required to overcome the RDS. This 4th order behaviour is consistent with published DFT work suggesting that the RDS corresponds to the extraction of the 4th electron by an already oxidised neighbouring species.²⁸⁰ This high order of reaction would also agree with reports suggesting that the RDS is related to oxygen release,²⁷⁰ and the observation of accumulated oxidised species in XAS experiments prior to O-O bond formation.²⁹⁹ It is perhaps this equilibrium that affords the similar reaction order between catalysts, despite the different (++) species: these charge accumulation centres may not correspond to those that perform the final bond making and breaking steps in the oxygen evolution reactions. Regardless, it is clear that the potential onset of charge accumulation in these catalysts, whether electrodeposited or sputtered, is a major determinant in the final JV performance, equally as important as the rate at which these species are used in water oxidation catalysis.

6.4 Conclusion

This study demonstrates that the atomic nature of the states accumulated during the steady-state of water oxidation catalysis on Ni-Fe oxyhydroxides can change depending on the amount and method of Fe incorporation into NiOOH. I find that FeOOHNiOOH, which exhibits large islands of FeOOH phase, favours a catalytic process driven by Fe-centred oxidised states, most probably due to the easier accumulation of FeOOH(++) species at the interface between NiOOH and FeOOH phases. On the other hand, when the Fe is spontaneously incorporated in low amounts into NiOOH, it seems that charge accumulation has greater Ni character, resulting in the accumulation of fewer oxidised intermediates driving the oxygen evolution reaction, balanced by faster water oxidation kinetics. These results could thus help to reconcile the seemingly discordant experimental conclusions found in the literature, highlighting the need for comparable experimental procedures in order to study these types of electrocatalysts.

Chapter 7



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7 Concluding remarks

The objective of this thesis was to contribute towards an enhanced understanding of the kinetics and loss mechanisms of common transition metal oxides for water oxidation catalysis – the rate-limiting reaction in solar-driven water splitting. To this end, two different metal oxide materials were examined: WO_3 as a photoanode, and Ni/FeOOH as an electrocatalyst. Focus was placed on the use of transient optical spectroscopy and other time-resolved techniques to elucidate the kinetic differences between recombination and reaction processes and to attempt to reconcile the disputes within the scientific community regarding the complex role of defects and dopants in these processes.

7.1 WO₃

WO₃ has remained amongst the primary studied transition metal oxides for PEC water splitting since first conceptualisation, arguably earning a place in the top four alongside TiO₂, BiVO₄ and α -Fe₂O₃. The reason for this largely stems from the favourable attributes that WO₃ shares with these other popular oxides – it is fairly robust under water oxidation conditions and can be readily synthesised in a research laboratory from materials suitable for scale-up. However, despite years of research, much has remained elusive about the charge carrier dynamics in this oxide. In Chapter 4, the kinetics of water oxidation were determined on nanostructured WO₃ for the first time, revealing faster reaction half-times than any of the other common oxides – an order of magnitude faster than decay times on nanostructured TiO₂ under comparable conditions. This was not the only surprise uncovered on WO₃ kinetics. Electron extraction was found to be remarkably slow, much slower than water oxidation which is so frequently referred to as ‘sluggish’. Bias dependence studies and simple material modifications to the WO₃ samples together led to the conclusion that ionised oxygen vacancy states above the Fermi level trap electrons and thereby slow their extraction. As WO₃ generally has a higher doping density than TiO₂ and other oxides, it thus follows that electron transport kinetics in this interesting oxide may occur more slowly than in any other. This was found to be the case, further strengthening the evidence for defect-mediated transport.

These conclusions were expanded upon in the work presented in Chapter 5, which sought to better understand the role of oxygen vacancies in charge carrier dynamics. WO₃ films of different defect concentrations were examined by transient optical spectroscopy on both ultrafast and millisecond-to-second timescales. The results confirmed the trapping-detrapping nature of electron transport proposed in Chapter 4, but also revealed the existence of a delicate balance between temporary trapping and carrier loss through trap-mediated recombination. The sample with ~2% oxygen vacancies was found to best balance these opposing trends, whereas samples with fewer defects showed fast extraction but poor yields, and too heavily-doped samples suffered slow charge transport and larger recombination losses. Interestingly, charge transport was not the only material property affected by variation in oxygen vacancy density. The ultrafast studies revealed that rapid trapping into ionised vacancy states, when temporary (i.e. not too deep), can aid charge separation at very early times. This effect had never previously been reported in any common metal oxide for water oxidation but is likely to be relevant for many material in various light-driven applications.

The bias dependence of early-time processes such as charge separation were also examined in this chapter, evidencing the positive correlation between space-charge layer (SCL) formation and charge carrier lifetimes. Although this correlation was to some extent predicted (though seldom determined experimentally), the main novelty of this work was in the early observations (< 10 ps) of separated charges: localised electrons in oxygen vacancy states and holes in the SCL at the electrode surface. The rather tragic realisation to stem from these observations was that only holes that localise within the SCL in the first few picoseconds are likely to participate in water oxidation catalysis at later times, as bi-molecular recombination and a subsequent loss of hole population was dominant across the entire remaining measurement window. I concluded in this chapter that the bias-dependent amplitudes observed on the millisecond-to-second timescale in Chapter 4 were almost entirely the consequence of improved charge separation (greater band-bending) under higher biases on picosecond timescales. The importance of the SCL was further established by measurements without applied bias but using different electrolytes to vary the degree of band-bending, thereby highlighting the relevance of these findings to other research areas including photocatalysis.

Most notably, WO₃ was well-suited to these studies owing to this oxide's large intrinsic dopant concentration and the ability for this concentration to be manipulated without affecting the structural integrity or altering other material properties significantly. While an ideal concentration of oxygen vacancies was determined, this could be better optimised in future work by establishing tighter defect control. Furthermore, it is not apparent from these studies alone how well the values reported herein will translate to other oxides with different metal centres, polaron states, and electronic band structures. Nevertheless, this work has revealed the key role that defects may play in photoanode performance and highlights their importance as a parameter to consider when optimising and comparing new electrodes. What is more, it is now clear that the effects of these dopants cannot be treated in isolation – both the SCL width and charge carrier transport are determined by the dopant concentration and as such the ideal defect density may need fine adjustment to obtain the optimum performance.

7.2 Ni/FeOOH

While, in some respects, the concept of PV-electrolysis is thought to consist of mature technologies, the research into coupling solar cells and electrocatalysts has, in some ways, only just begun. For the most part, this comes down to economies of scale. The electrolyzers currently in use are based on precious metals such as platinum and palladium,⁴⁰ incurring costs which partially inhibit scale-up. Work on cheap, abundant alternatives has exploded in the last five years and nickel and iron based oxide systems have risen to the top. Since 2015, there have been more than 7000 publications that include the terms 'NiOOH' and 'water oxidation' according to Google Scholar, and more than 17000 when replacing NiOOH with 'FeOOH' (though this also includes some photoelectrochemical studies). The hype about these materials has also been justified considering that they show the highest catalytic activity for water oxidation in basic media of any reported material and also function as co-catalysts in conjunction with photoanodes. Intriguingly, it is well known that oxyhydroxide electrodes consisting of both nickel and iron perform better than either metal oxyhydroxide does alone, but, despite the large number of publications on the topic, the origin of this synergistic effect has remained unclear. Attempts to provide clarity have resulted in two camps: those who believe they have evidence that Ni is the active metal in catalysis, and those who believe the same for Fe. In Chapter 6, I aimed to address this rift by adding kinetic analyses of mixed Ni/Fe oxyhydroxides to the discussion using techniques only previously applied to photoelectrode materials.

By examining the optical difference spectra of mixed Ni/FeOOH samples containing 0%, 5%, ~80% and 100% Fe, two species could be determined in each case. The first was found to be pre-catalytic in nature, primarily assigned to the oxidation of any Ni(OH)_2 to NiOOH. Thickness dependence studies revealed that this oxidation occurs throughout the entirety of the electrocatalyst film owing to the electrolyte-permissive porosity of such electrodes. The second species was observed under higher applied potentials and the accumulation of this species was found to correlate with the onset for water oxidation catalysis. Interestingly, this species only accumulated at the surface of the electrode, was localised, and was different in nature depending on the quantity of iron in the sample. It was determined that the oxidised species accumulating during catalysis are Fe-based when the Fe concentration is adequately high, but Ni-based at low iron concentrations. In all cases, the intermediates accumulated were more molecular than metallic in nature, revealing the drawbacks of some more traditional analyses. To determine the ratio of iron to nickel that poses the critical threshold between the two regimes, or to discover if there exists an additional regime in which both metals equal accumulate charge, would require further measurements of more tightly controlled samples (as mentioned in the case for $\text{WO}_3 V_O$). Thus,

while this work has enhanced understanding of these materials, it has not adequately answered the question of which metal is ‘active’ in catalysis, for which more experiments are needed.

That being so, the kinetic conclusions reached in Chapter 6 are worthy of note. While the Ni(Fe)OOH sample formed Ni-centred intermediates and FeOOHNiOOH formed Fe-centred species, the performance of these samples in terms of current-voltage response was markedly similar. And yet the origins of their high photocurrents and early onset potentials were found to result from directly contrasting trends – FeOOHNiOOH accumulates far more oxidised intermediates than NiOOH, but has comparably slow reaction kinetics compared to those of NiOOH. These results highlight the need to consider relative ease of charge accumulation as well as rate of catalysis when examining potential candidates for water oxidation. In all of the samples examined in this work, the order of reaction with respect to the accumulated species concentration was found to be four, suggesting that the rate limiting step involved the accumulation of four such intermediates for each material, independent of accumulation site. It is therefore likely that the final bond breaking and making steps involved in oxygen evolution are very similar between each of these materials, though these final steps could not be observed in this work.

7.3 The challenge ahead

This work, as true of most academic research, was exploratory in nature and therefore has raised almost as many questions as it sought to answer. I began my PhD studies with the optimism all too common to the naive, believing that the research I was doing might provide the important answers necessary to bring solar fuels closer to reality. As I take a step back now at the end, humbled by science in all her mystery, I feel both hope and dread for the challenge ahead.

As discussed at length in Chapter 1, the threats of climate change are both very real and highly imminent, and thus there is no room for delay if solar fuels are to mitigate the crisis. Metal oxides are the best studied materials to fulfil the role of photoanodes in PEC water splitting, and the research presented in Chapters 4 and 5 has demonstrated that WO_3 is as good as any for this job. However, it is not clear that this performance is good enough. The maximum solar-to-hydrogen (STH) efficiencies achieved to date for PEC water splitting devices without external bias are 10–15%, less than half the predicted theoretical efficiency.^{300–302} With fundamental research on kinetics, dopants and mechanisms fed into the next generation of materials, I believe this percentage will continue to increase – but will we get there fast enough? Techno-economic analyses show that PEC water splitting is currently not economically viable to really challenge the fossil fuels industry (and steam-reformed H_2) due to limitations in both efficiency and stability of current devices. In order for direct solar-to-hydrogen conversion to become an affordable technology, it will be essential to discover new oxide materials with better suited band-gaps for absorbing sunlight, longer lived charge carriers, and stabilities in the range of 5–10 years.³⁰² The answer may lie in ternary and quaternary oxides which are more susceptible to changes in doping concentrations. Regardless, it is clear that the field needs to move away from the commonly studied oxides, and do so quickly.

In the meantime, hope may be sought in PV-electrolysis systems, as both photovoltaics and electrolyzers are far closer to achieving their theoretical limits, with STH efficiencies between 22–30% reported.^{301,302} Efficiency increases coupled with dramatically falling costs for PV technologies make this ‘less direct’ route to solar hydrogen more readily attainable.³⁰³ But we still are not there yet. Mismatches between functioning voltages of solar cells and electrolyzers introduce additional limitations, as well as the cost and availability of precious metal catalysts.^{40, 136, 304} As such, the development of highly active electrocatalysts/electrolyzers such as Ni/FeOOH is essential to lower material costs. Several research groups are exploring the addition of other abundant metals, for example zinc, manganese and cobalt, which have already shown some promise.^{129, 305–307} Moving forward, it will be important to couple these catalysts with the photovoltaics to determine their real world applicability. This will require international scientific collaborations beyond the

scale observed at present. I hope the community will rise to the challenge.

At the end of the day, the largest restrictions in the realisation of renewable solar hydrogen fuel may be beyond academic research altogether. Table 7.1 gives a breakdown of the typical contributing factors which delay the production of innovative technologies in chemical industry. These numbers were taken from a 1982 publication predicting solar-to-hydrogen systems for the year 2000, then a distant future by which time solar hydrogen production systems were predicted to have been commercialised.³⁰⁸

Factor	Contribution
No market or need	37.5%
Potential not recognised by management	29.2%
Undeveloped technology	8.3%
Resistance to new ideas	4.2%
Poor cooperation or communication	4.2%
Other	16.6%

Table 7.1 – Factors contributing to the delay of technology implementation in industry.

It would be nice to consider that, in the 21st century, the weight of these contributions is no longer the same as it was in the 1970s and 1980s. Certainly there is now a market for hydrogen fuel – predicted to grow to a substantial \$200 billion USD per annum by 2026³⁰⁹ – and an urgent need of it. However, large scale commercialised solar hydrogen was anticipated to be a reality by the turn of the century and yet we have still not achieved this two decades later. During my doctoral studies, the president of the world’s most powerful nation announced the withdrawal of the USA from the 2015 Paris Agreement, in which 195 nations agreed to keep global warming below a 2°C increase over pre-industrial times. The lack of recognition of crisis by those in places of power (‘management’ in the table above) and the ‘resistance to new ideas’ demonstrated for fear of a change in lifestyle have been factors equally as inhibiting on the road to solar fuels as the limitations in technological advancement, if not more so. As a result, scientists must work doubly hard, fighting on both a technological and educational front, so that resistance may be overcome with the inconvenient truth and humanity given the best chance of repairing the environmental damage we have caused.

In 1967, my academic grandfather, Nobel laureate Lord George Porter, famously said: *“I have no doubt that we will be successful in harnessing the sun’s energy. If sunbeams were weapons of war, we would have had solar energy centuries ago”*. In 2019, I stress that sunbeams can be considered weapons of war, only for war of a radically different kind. A battle not against armies but against climate change, against political denial, Big Oil, consumerism – human nature itself. By treating the climate change crisis with the seriousness and urgency of war, storage of solar energy may be

Chapter 7. Concluding remarks

realised more swiftly. Ignorance may buy temporary bliss, but burying our heads in the tar-sands won't save us from what is to come. Between the us, the scientific community, we have most of the pieces of the puzzle – it is just a matter of putting them together to build the final picture, before it is too late.

A Appendix: Additional experiment details

A.1 Other common metal oxides

In Chapter 4, Section 4.2.7, the kinetics of water oxidation on nanostructured WO_3 were compared to TiO_2 , BiVO_4 and $\alpha\text{-Fe}_2\text{O}_3$ samples. The TiO_2 ($\sim 3\ \mu\text{m}$ needles and 350 nm dense films on FTO) were synthesised by Dr Andreas Kafizas and collaborators by AA-CVD.^{118, 194} BiVO_4 (350 nm on FTO) was synthesised by Ms Shababa Selim by solgel spin coating, as previously described and analysed.⁷⁹ $\alpha\text{-Fe}_2\text{O}_3$ samples ($\sim 450\ \text{nm}$) were provided by the group of Prof Dunwei Wang and synthesised according to their published regrowth procedure.³¹⁰

A.2 Global analysis

In order to distinguish the hole signal from the electron signal in Chapter 5, Figure 5.1, a global analysis fitting based on a genetic algorithm was used. This analysis was performed by Ms Yifan Dong at Imperial College London. The TA spectrum at early times (0.6 ps) was selected as the reference, as this showed a clear signal at only one of the two spectral regions in question, with a maximum around 700-750 nm and no absorption at 500 nm. From our previous work on WO_3 and our spectroelectrochemical analysis, we assigned the feature at 700 nm to electrons (as discussed in the text). We then used this early-time spectrum as a reference for the genetic algorithm to read the spectral data at later times and search for possible outputs, the randomness added to each species output. We tested the potential for multiple components and two components gave the best fit, regenerating the electron spectrum and a second spectrum, shown in Figure 5.1, which we assign to holes. The best fitting solution was yielded through the optimisation.³¹¹

A.3 WO₃ post-deposition treatments

Four different WO₃ sample types were used in Chapter 5 and referred to as ‘very high’, ‘high’, ‘medium’ and ‘low’ in accordance with the oxygen vacancy concentration in each. Samples with ‘very high’ vacancy concentrations were the product of the deposition method itself, and thus no further treatment was required (i.e. the films were not annealed). The high defectiveness of these films can be readily observed by XPS which reveals a high W⁵⁺:W⁶⁺ ratio of 0.35, i.e. more than a third of the tungsten atoms probed were in a reduced state due to neighbouring oxygen vacancies. Samples reported herein as ‘high’ in [V_O] were attained by annealing the as-deposited material for 2 hours at 500°C in air before exposing to acid (0.1 M H₂SO₄). The films were allowed to dry at room temperature and were then annealed again for 1 hour under otherwise comparable conditions. This procedure, uncovered accidentally, consistently produced tungsten oxide films with higher oxygen vacancy concentrations (14% W⁵⁺) than regular annealing, possibly due to co-adsorbed hydrogen from the acid, though hydrogen could not be detected.²²¹ Samples with lower concentrations of defect states were obtained by altering the annealing time. WO₃ films with ‘medium’ [V_O] were annealed for 2 hours, as those studied in Chapter 4,²²⁷ whereas films with almost perfect stoichiometric ratios of oxygen to tungsten (3% W⁵⁺), herein named ‘low’, were the product of a 12 hour anneal to allow oxygen to permeate deep into the lattice structure.

The external quantum yields for these samples were calculated using the transient charge presented in Figure 5.22 as exemplified below for the ‘medium’ doped sample:

$$\text{Pulse intensity} = 0.25 \text{ mJ/cm}^2$$

$$\text{Pulse wavelength} = 355 \text{ nm}$$

$$\text{Pulse energy} \rightarrow E = \frac{hc}{\lambda} = 5.6 \times 10^{-19} \text{ J} \quad (\text{A.1})$$

$$\text{no. photons} \rightarrow \frac{\text{intensity}}{\text{energy}} = 4.47 \times 10^{14} \text{ photons/cm}^2 \quad (\text{A.2})$$

$$\text{no. electrons} = \text{no. photons} = 4.47 \times 10^{14} \text{ photogenerated electrons/cm}^2$$

$$\text{Theoretical charge} \rightarrow \text{no. electrons} \times \text{electron charge} = 7.1 \times 10^{-5} = 71 \mu\text{C/cm}^2 \quad (\text{A.3})$$

Extracted charge ('medium' [V_O]) = 6.7 $\mu\text{C}/\text{cm}^2$ (see Figure 5.22)

$$\text{EQE} = \frac{\text{extracted}}{\text{theoretical}} \times 100 = 9.4\% \quad (\text{A.4})$$

A.4 Additional synthetic details of electrocatalysts

The three electrocatalysts studied in Chapter 6 (FeOOH, Ni(Fe)OOH, and FeOOHNiOOH) were anodically electrodeposited on fluorine-doped tin oxide (FTO) (Hartford Glass) substrates. An undivided three-electrode cell consisting of a FTO working electrode (WE), a Ag/AgCl (4 M KCl) reference electrode (RE), and a platinum counter electrode (CE) were used for electrodeposition. The platinum CE was prepared by sputter coating 100 nm of platinum on top of a 20 nm titanium adhesion layer on a clean glass slide. A VMP2 multichannel potentiostat (Princeton Applied Research) was used to perform the electrodeposition. All aqueous solutions used in this study were prepared using DI water further purified by a 3-module water purification system (Barnstead E-pure water purification systems). The resistivity of the output water was $\geq 18 \text{ M}\omega\cdot\text{cm}$.

The anodic deposition of FeOOH was carried out in a 10 mM FeSO₄·7H₂O (Sigma-Aldrich, 99%) aqueous solution (40 mL) (pH $\sim$ 4.8 as prepared) at 70 °C after purging the solution with N₂ for 30 minutes. The deposition was performed at 1.2 V versus the Ag/AgCl RE with gentle stirring immediately after FeSO₄·7H₂O was fully dissolved. The total charge passed was 23 mC/cm². This resulted in a $\sim$ 80 nm thick FeOOH film (Figure 6.1). The lateral dimensions of the FeOOH film (and all other electrocatalyst films prepared in this study) were 1 cm $\times$ 1.2 cm. The as-prepared light-orange FeOOH film was rinsed with DI water and dried with a gentle stream of air. Then, the film was air-dried overnight before either NiOOH electrodeposition or spectroelectrochemical measurements were performed.

NiOOH was anodically deposited from a 100 mM NiSO₄·6H₂O (Sigma Aldrich, 98%) aqueous solution (40 mL) at 70 °C. The pH was adjusted to 6.8–7.0 using a 0.070 M NaOH (Sigma Aldrich, 97%) aqueous solution prior to raising the temperature. The deposition was carried out at 1.2 V versus the Ag/AgCl RE with gentle stirring. The as-prepared NiOOH film was rinsed with DI water and dried with a gentle stream of air. Then, the film was air-dried overnight before electrochemical measurements were performed. The as-deposited NiOOH was black but it gradually became transparent due to the conversion of NiOOH to Ni(OH)₂. The total charge passed to deposit a NiOOH film with a thickness comparable to that of the FeOOH film was 150 mC/cm². When the FeOOH and NiOOH films were prepared with comparable thicknesses, inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin Elmer Optima 2000) results showed

that the amount of Ni present in the NiOOH film was approximately 1/5 the amount of Fe present in the FeOOH film (Table A.1). This is because NiOOH is composed of vertically oriented, loosely packed, larger sheets while FeOOH is composed of more densely packed smaller plates (Figure 6.1). Since the plating solution used for the NiOOH deposition contained Fe impurities from the Ni source ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 98%), the as-prepared NiOOH contained 1 at. % Fe (Table A.1). Also, since the electrolyte used to investigate the oxygen evolution properties of NiOOH (0.1 M NaOH) contained Fe impurities from NaOH (Aldrich, and purity 98%), additional Fe was incorporated into NiOOH (5 at. % Fe) during the investigation (Table A.1). Therefore, NiOOH used in this study is denoted as Ni(Fe)OOH.

To investigate NiOOH without any Fe impurities, samples were prepared in the same manner as Ni(Fe)OOH but with two modifications. First, a higher purity $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, 99.998%) was used to make a plating solution. (Low purity Ni sources can contain Fe as an impurity.) Second, the pH of the plating solution was not further adjusted because NaOH added to adjust the pH can also contain Fe impurities. The pH of the as-prepared 100 mM $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ aqueous solution was 6.10. The absence of Fe in the NiOOH film prepared from this plating solution was confirmed by ICP-OES. All the subsequent electrochemical analyses of the Fe-free NiOOH samples were performed in purified electrolyte, in accordance with a procedure reported by Trotochaud et al.¹⁴⁵ to maintain the pure NiOOH.

Finally, the FeOOHNiOOH film was prepared by sequential deposition of FeOOH and NiOOH layers using the methods described above (23 mC/cm² was passed to deposit FeOOH and 150 mC/cm² was passed to deposit NiOOH). Although the same charge was passed to deposit NiOOH in both Ni(Fe)OOH and FeOOHNiOOH samples, the amount of Ni present in FeOOHNiOOH was slightly greater than that in Ni(Fe)OOH because the deposition of NiOOH on FeOOH is easier than that on FTO (Table A.1). The resulting FeOOHNiOOH film was ~120 nm thick (Figure 2), which is less than the sum of the FeOOH and NiOOH layers prepared separately. Also, when NiOOH was deposited on FeOOH, the change in surface morphology and film thickness was not significant until two thirds (100 mC/cm²) of the total charge was passed (Figure 6.2). This suggests that a considerable amount of NiOOH was deposited to fill the voids in the FeOOH layer and significant mixing of Ni and Fe was achieved in FeOOHNiOOH. The as-prepared FeOOHNiOOH was rinsed with DI water and dried with a gentle stream of air. Then, the film was air-dried overnight before electrochemical measurements were performed. The atomic ratio of Fe:Ni in FeOOHNiOOH was 79:21 (Table A.1). The Fe content in FeOOHNiOOH also increased during the electrochemical investigation of this film in 0.1 M NaOH. However, the relative amount of Fe incorporated into FeOOHNiOOH was negligible compared with the original amount of Fe present. Therefore, the

A.4. Additional synthetic details of electrocatalysts

atomic ratio of Fe:Ni was unaffected during electrochemical investigation.

The elemental analyses of the electrocatalysts, both as prepared and after electrochemical tests, were carried out by dissolving the electrocatalyst films in 10 mL of 10 wt. % nitric acid (Fisher Chemical, TraceMetal Grade) and quantifying the amount of Fe and Ni in the resulting solutions ICP-OES. All disposable pipette tips, polypropylene tubes, and beakers were pre-rinsed with ~5 wt. % nitric acid, followed by rinsing with DI water and drying in air prior to use to remove any residual Fe. ICP standard solutions of Fe and Ni with various concentrations (10, 50, 100, 300, and 500 ppb) were used for calibration and 100 ppb yttrium was used as an internal standard to compensate for the signal drift among samples (Sigma Aldrich 43149 (Fe), 28944 (Ni), and 01357 (Y)). The atomic % of Fe in Ni(Fe)OOH and FeOOHNiOOH samples was determined using E. The ICP-OES data is summarised in Table A.1.

Sample	Fe content (10^{-8} mol/cm ²)	Ni content (10^{-8} mol/cm ²)	Fe at. %
FeOOH (fresh)	23.50	0.10	100
Ni(Fe)OOH (fresh)	0.05	4.63	1
Ni(Fe)OOH (used)	0.25	4.38	5
FeOOHNiOOH (fresh)	23.55	6.22	79
FeOOHNiOOH (used)	23.76	6.24	79

Table A.1 – Summary of metal content from ICP-OES analysis

A.5 Electrocatalyst activation process

Anodic electrodeposition was used to produce the FeOOH and NiOOH films examined in Chapter 6. While FeOOH is stable in air, black NiOOH gradually changes to transparent Ni(OH)₂ when it is not anodically protected. Therefore, Ni(Fe)OOH, FeOOHNiOOH and NiOOH samples were activated before optical and electrochemical experiments. This activation consisted of oxidising the Ni^{II}(OH)₂ present in each of these samples to the higher valence NiOOH, resulting in the appearance of a strong absorption signal assigned to a metal-to-oxygen charge transfer. For each sample, the potential was swept five times from the open circuit potential (OCP) to 2.0 V_{RHE} (scan rate = 10 mV/s). The conversion of Ni(OH)₂ to NiOOH could be confirmed visually by the return of the black colour. The change in absorption of the films is shown in Figure A.1.

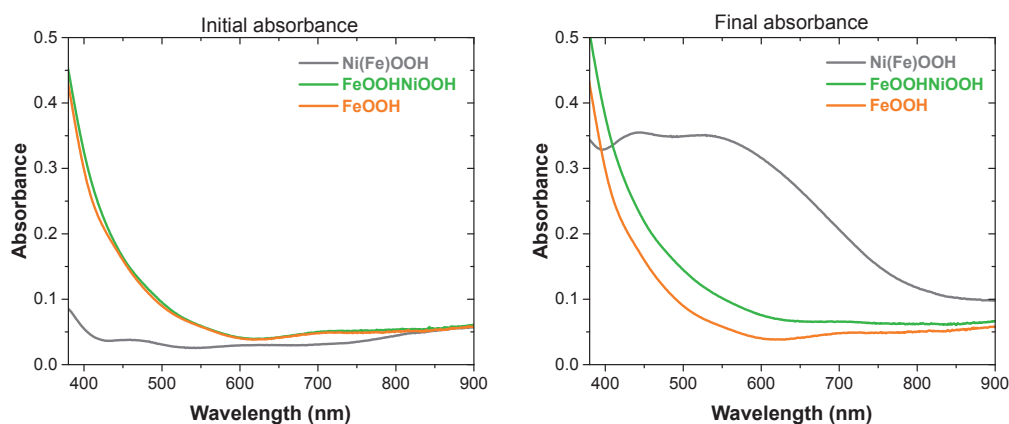


Figure A.1 – UV-Vis absorbance spectra for FeOOH (orange), Ni(Fe)OOH (grey) and FeOOHNiOOH (green) (*left*): before activation and (*right*): after activation.

A.6 Calculation of extinction coefficients (ϵ)

Estimation of the extinction coefficients (ϵ) was necessary to provide concentrations of (+) and accumulated (++) species, as discussed in Chapter 6. Two different approaches were used for the two species.

(+) species

The extinction coefficient for Ni(Fe)OOH(+) was estimated using the Beer-Lambert law, combining linear sweep voltammetry experiments and optical measurements. We integrated the current under the redox wave of the first LSV, corresponding to the conversion of Ni(OH)₂ to NiOOH to estimate the number of electrons involved in this process (Figure A.2). The absorbance value was taken at 528 nm from the UV-Vis spectrum presented in Figure A.1 (*right*).

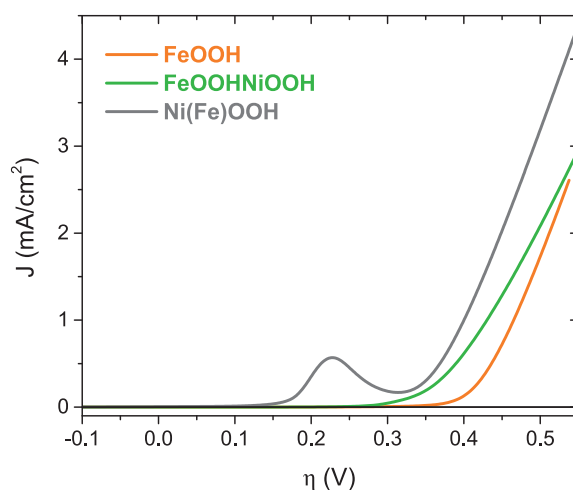


Figure A.2 – The linear sweep voltammograms (LSVs) of FeOOH (orange), Ni(Fe)OOH (grey) and FeOOHNiOOH (green) recorded during the first potential sweep of the activation process in 0.1 M NaOH (scan rate = 10 mV/s).

Appendix A. Appendix: Additional experiment details

From the Beer-Lambert law,

$$A = \epsilon \times c \quad (\text{A.5})$$

where A is absorbance at a defined wavelength, ϵ is the extinction coefficient, and c is the concentration of electrons per cm^2 .

From Figure A.1, $A (\lambda=528 \text{ nm}) = 0.324$

From Figure A.2, $c = 2.362 \times 10^{16} \text{ electrons/cm}^2$

$$\epsilon = \frac{0.324}{2.362 \times 10^{16}} = 1.37 \times 10^{-17} \frac{\text{cm}^2}{\text{number of } e^-} \quad (\text{A.6})$$

which can be converted into the common units as follows:

$$\epsilon = 1.37 \times 10^{-17} \frac{\text{cm}^2}{\text{no } e^-} \times \frac{\text{cm}}{\text{cm}} \times \frac{6.022 \times 10^{23} \text{ no } e^-}{1 \text{ mol } e^-} \times \frac{1 \text{ dm}^3}{1000 \text{ cm}^3} = 8250 \text{ M}^{-1} \text{cm}^{-1} \quad (\text{A.7})$$

(++) species

The extinction coefficient of the second oxidised (++) species was estimated for each sample using the SPAS technique detailed in Chapter 3, Section 3.3.3. We monitored the change in absorbance when a voltage step was applied. The recorded optical data is proportional to the population of oxidised states generated at that applied potential, exemplified in each case in Figures A.3, A.4 and A.5 (*upper left*). The current generated simultaneously is also measured, increasing with applied potential and revealing a reductive spike as soon as the potential is stepped down again (Figures A.3, A.4, A.5, *upper right*). This spike corresponds to the reduction of the oxidised states accumulated under greater potentials. The integration of these reductive currents (Figures A.3, A.4, A.5, *upper right, inset*) allow us to quantify the electrons used to reduce the oxidised states. Using the Beer-Lambert law (Equation A.5) we can estimate the corresponding extinction coefficients by plotting $\Delta\text{O.D.}$ against the electrons extracted (Figures A.3, A.4, A.5, *lower left*). The slope of the corresponding graphs yields the extinction coefficient (ϵ) in cm^2 per number of e^- , which can be transformed to $\text{M}^{-1} \text{cm}^{-1}$ as shown in Equation A.7.

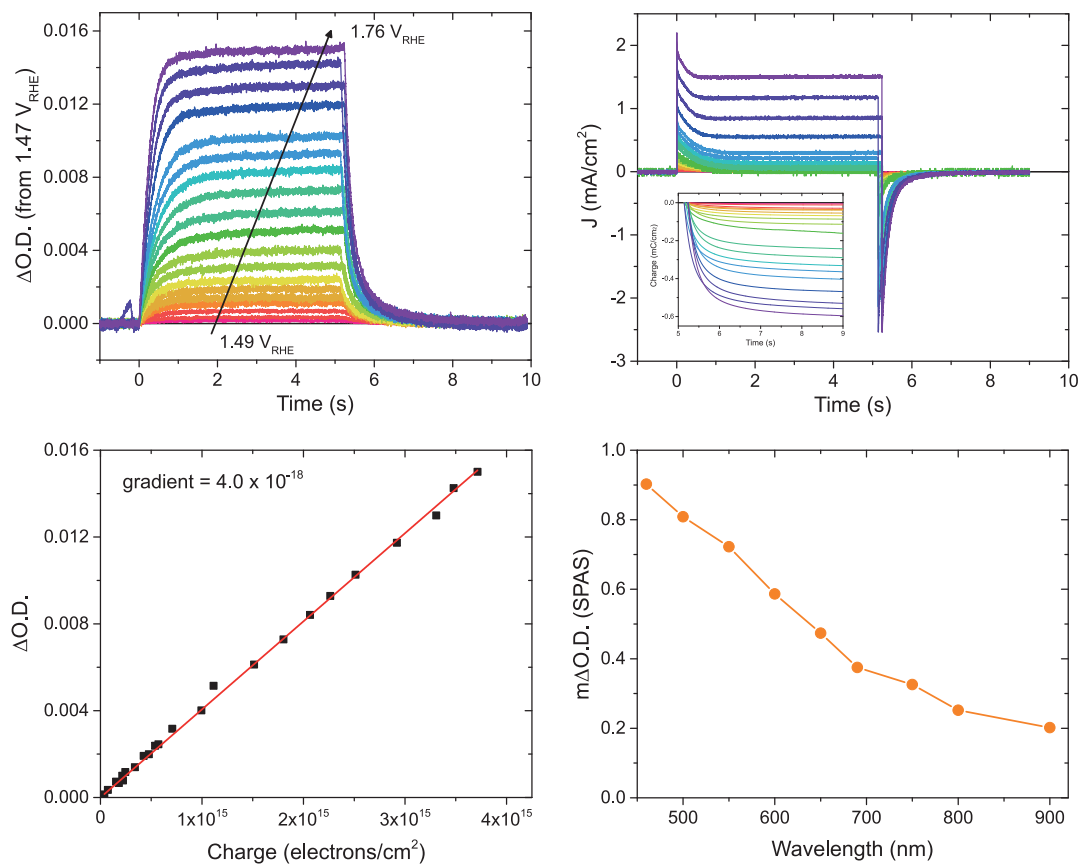


Figure A.3 – SVAS data for FeOOH from 0.24 V overpotential ($1.47 \text{ V}_{\text{RHE}}$) to $1.7 \text{ V}_{\text{RHE}}$. *upper left*: Optical data at 500 nm; *upper right*: current density with charge used to reduce the accumulated oxidised species shown in inset; *lower left*: $\Delta O.D.$ versus charge with the gradient of the linear fit giving the extinction coefficient; *lower right*: spectra of the species generated at 0.5 V of overpotential using SVAS.

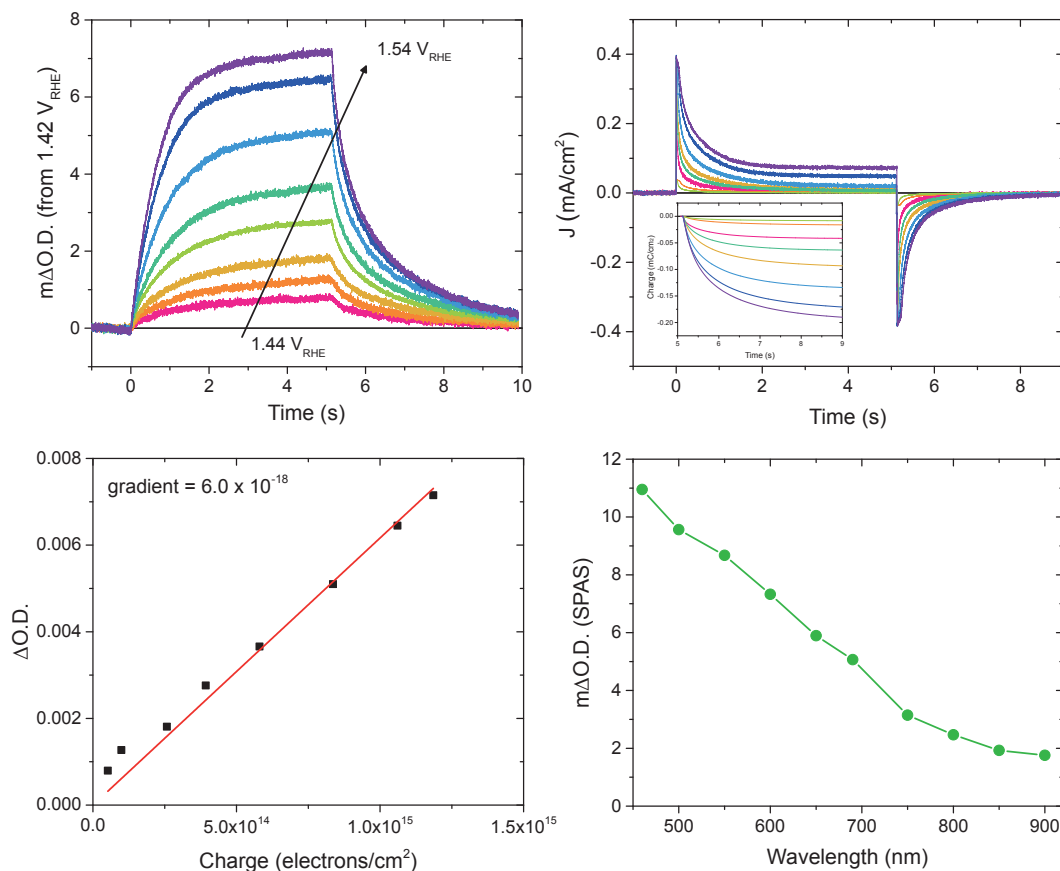


Figure A.4 – SVAS data for FeOOH/NiOOH from 0.20 V overpotential (1.43 V_{RHE}) to 1.7 V_{RHE}. *upper left*: Optical data at 550 nm; *upper right*: current density with charge used to reduce the accumulated oxidised species shown in inset; *lower left*: ΔO.D. versus charge with the gradient of the linear fit giving the extinction coefficient; *lower right*: spectra of the species generated at 0.5 V of overpotential using SVAS.

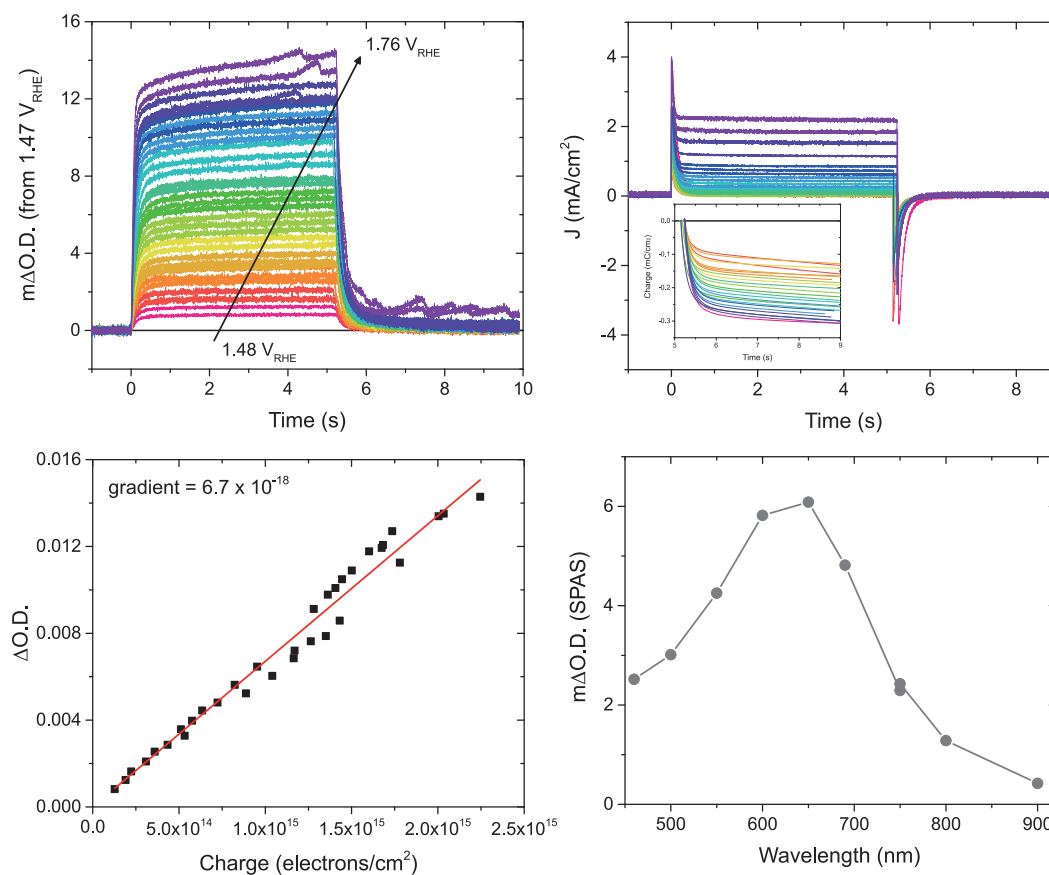


Figure A.5 – SVAS data for Ni(Fe)OOH from 0.24 V overpotential (1.47 V_{RHE}) to 1.7 V_{RHE}. *upper left*: Optical data at 650 nm; *upper right*: current density with charge used to reduce the accumulated oxidised species shown in inset; *lower left*: $\Delta O.D.$ versus charge with the gradient of the linear fit giving the extinction coefficient; *lower right*: spectra of the species generated at 0.5 V of overpotential using SVAS.

A.7 Percentage (+) and (++) species per M-centre

The quantity of (+) and (++) species can be calculated as a percentage of the total number of metal centres using the data in Figure 6.7 and the ICP-OES analysis given in Table A.1. The results are summarised in Chapter 6, Table 6.1.

(+) species

$$\% \text{FeOOH}(+) = \frac{\text{mol of Fe}(+) \text{ (SEC, Figure 6.7)}}{\text{mol of Fe (ICP, Table A.1)}} = \frac{1.4 \times 10^{-9}}{2.4 \times 10^{-7}} = 0.005 = 0.5\% \quad (\text{A.8})$$

$$\% \text{FeOOHNiOOH}(+) = \frac{\text{mol of Ni}(+) \text{ (SEC, Figure 6.7)}}{\text{mol of Ni (ICP, Table A.1)}} = \frac{5.7 \times 10^{-9}}{6.2 \times 10^{-8}} = 0.09 = 9\% \quad (\text{A.9})$$

$$\% \text{Ni(Fe)OOH}(+) = \frac{\text{mol of Ni}(+) \text{ (SEC, Figure 6.7)}}{\text{mol of Ni (ICP, Table A.1)}} = \frac{3.9 \times 10^{-8}}{4.6 \times 10^{-8}} = 0.85 = 85\% \quad (\text{A.10})$$

(++) species

$$\% \text{FeOOH}(++) = \frac{\text{mol of Fe}(++) \text{ (SEC, Figure 6.7)}}{\text{mol of Fe (ICP, Table A.1)}} = \frac{9.8 \times 10^{-9}}{2.4 \times 10^{-7}} = 0.04 = 4\% \quad (\text{A.11})$$

$$\% \text{FeOOHNiOOH}(++) = \frac{\text{mol of Fe}(++) \text{ (SEC, Figure 6.7)}}{\text{mol of Fe (ICP, Table A.1)}} = \frac{2.2 \times 10^{-8}}{2.4 \times 10^{-7}} = 0.09 = 9\% \quad (\text{A.12})$$

$$\% \text{Ni(Fe)OOH}(++) = \frac{\text{mol of Ni}(++) \text{ (SEC, Figure 6.7)}}{\text{mol of Ni (ICP, Table A.1)}} = \frac{5.3 \times 10^{-9}}{4.6 \times 10^{-8}} = 0.12 = 12\% \quad (\text{A.13})$$

A.8 NiO_x sample characterisation for thickness dependence study

Additional characterisation of the samples used in the thickness dependence study of NiO_x in Chapter 6, Section 6.2.3 are given below.

The data in Figure A.6 and Figure A.7 were obtained using a Field Emission Scanning Electron Microscopy (SEM) with a JSM-7000F JEOL FEG-SEM system (Tokyo, Japan) equipped with an INCA 400 Oxford electron diffraction x-ray spectrometer (EDX) (Oxford, U.K.) operating at 15 kV. Data were obtained and analysed by Dr Miguel Garcia-Tecedor.

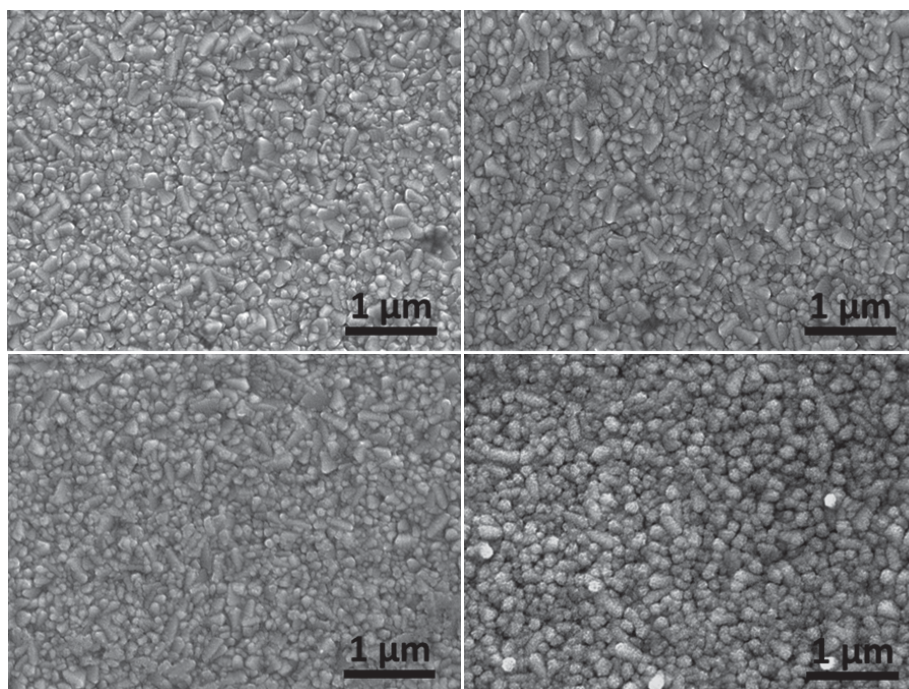


Figure A.6 – Top down SEM images of the as-synthesised sputtered NiO_x samples of (*upper left*): 5 nm, (*upper right*): 10 nm, (*lower left*): 20 nm, and (*lower right*): 100 nm thickness.

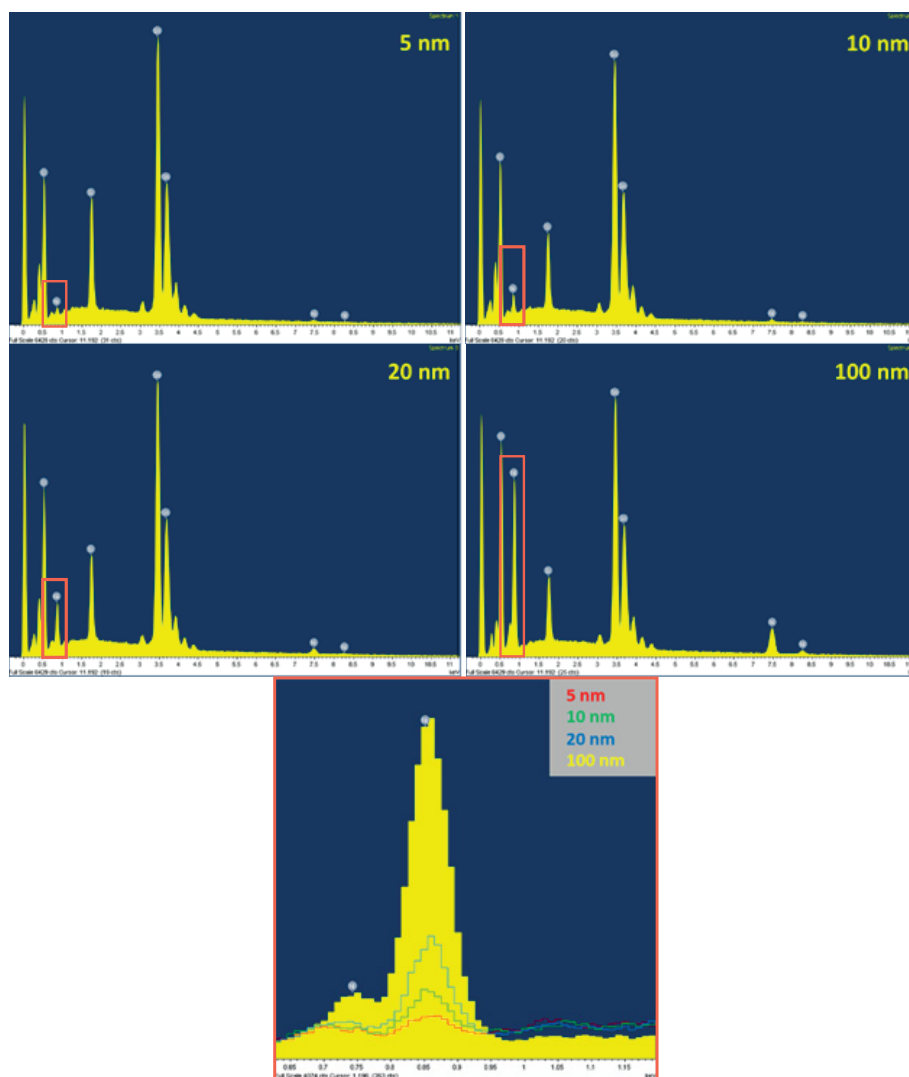


Figure A.7 – EDX spectra of the as-synthesised sputtered NiO_x samples of (*upper left*): 5 nm, (*upper right*): 10 nm, (*mid left*): 20 nm, and (*mid right*): 100 nm thickness. The Ni L_α peak is highlighted in the red box and shown magnified (*lower*). This line should be proportional with the amount of Ni in the films and thus gives indication of film thickness.

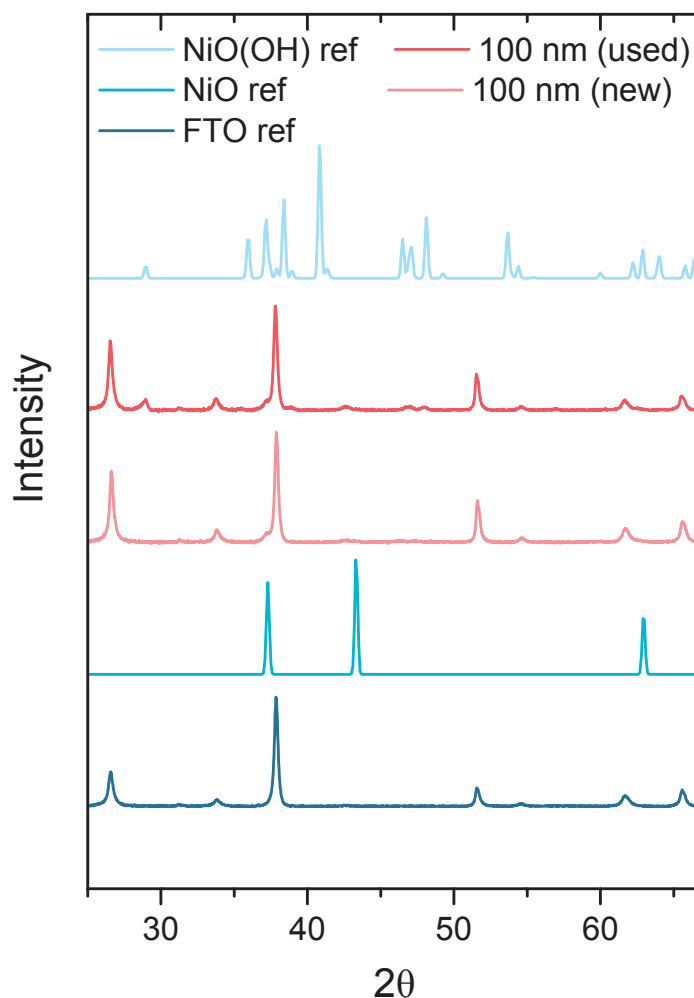


Figure A.8 – XRD characterisation of 100 nm NiO_x films, before (pink) and after (red) electrochemical activation in 0.1 M NaOH. References for FTO, NiO (bunsenite) and NiO(OH) are given in blue. There are small difference in the NiO_x film following activation, with new peaks corresponding to NiOOH present. However, the bulk of the film, after drying for 1 day, can be expected to be largely similar to the bunsenite shown before use. The 5, 10 and 20 nm films were below the resolution limit for the experiment.

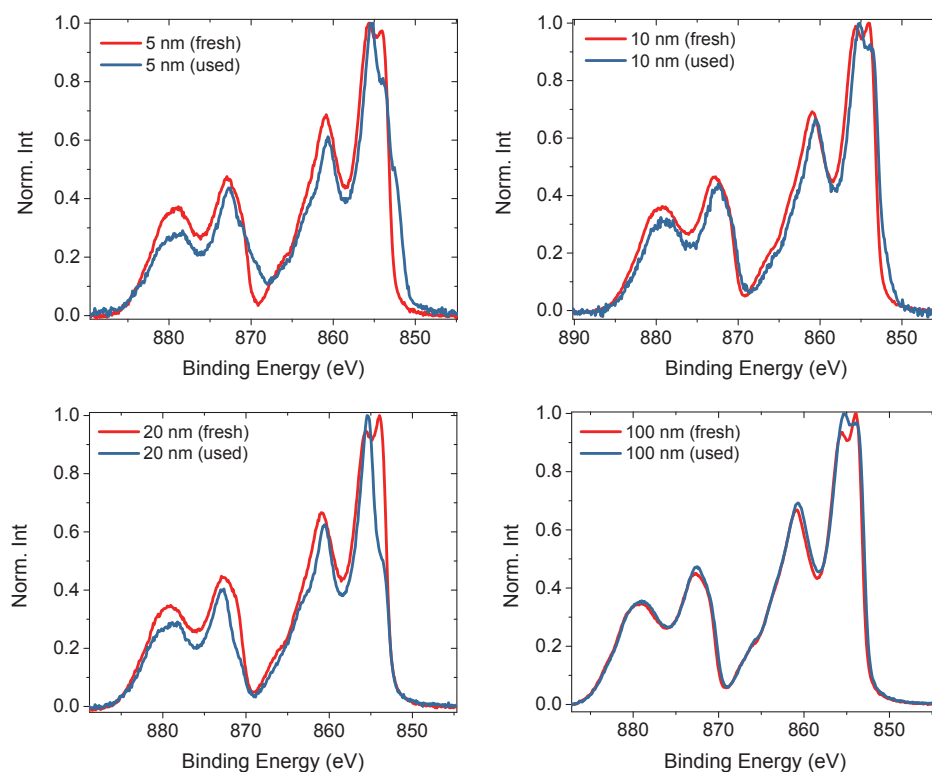


Figure A.9 – XPS characterisation of the Ni 2p peak for each film thickness; (*upper left*): 5 nm, (*upper right*): 10 nm, (*lower left*): 20 nm, (*lower right*): 100 nm, before (fresh, red) and after (used, blue) electrochemical activation in 0.1 M NaOH. Small changes in the peak shapes can be observed after usage, most notable in the thinner films and becoming less striking with thickness. We tentatively assign these peak shifts to the long lasting oxidation of some Ni centres in the film, as NiOx is converted to NiOOH by activation. Obtained with the assistance of Mr Benjamin Moss.

A.8. NiO_x sample characterisation for thickness dependence study

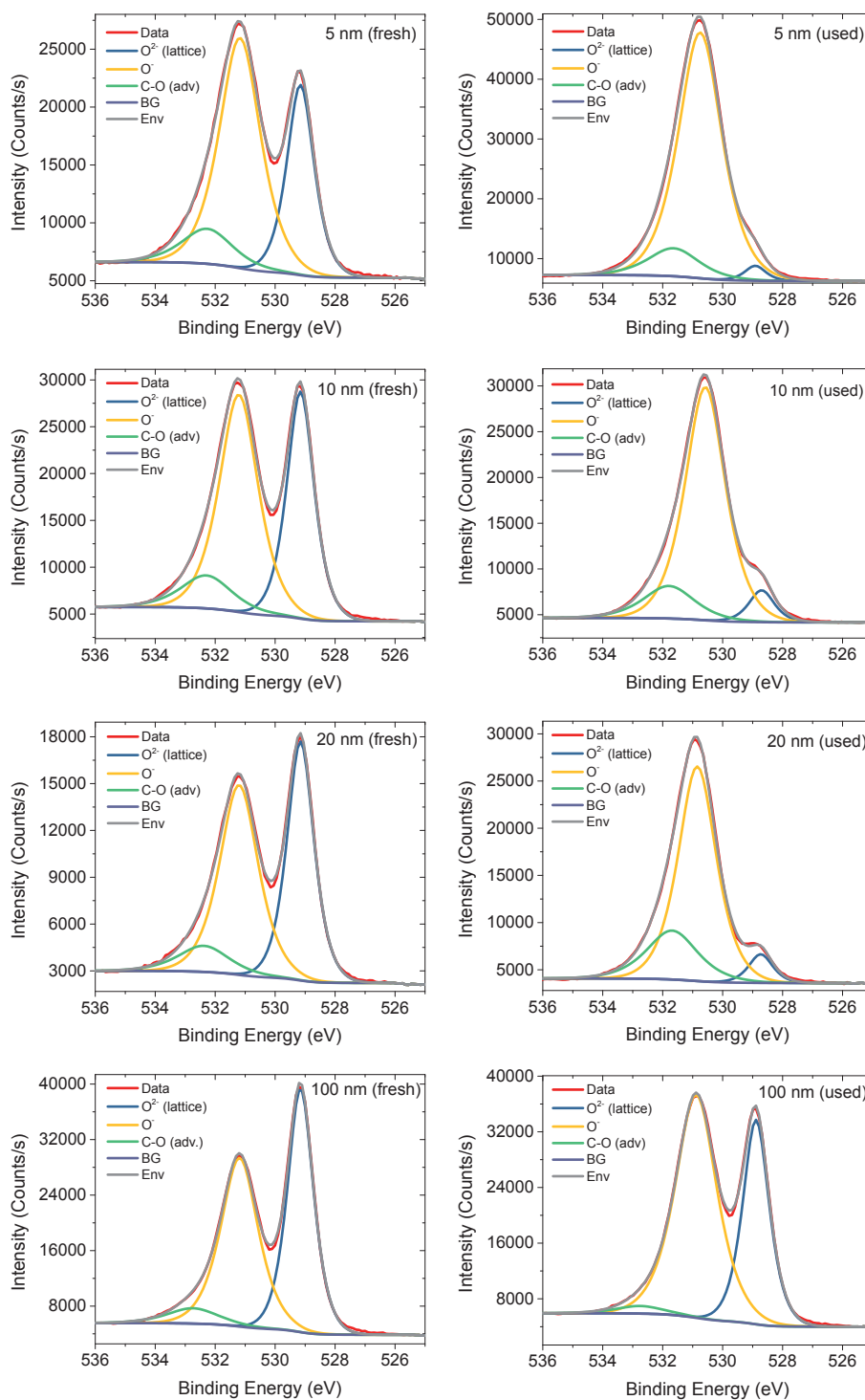


Figure A.10 – XPS characterisation of the O 1s peak for each film thickness (*left*): before and (*right*): after use. (*uppermost*): 5 nm, (*mid-upper*): 10 nm, (*mid-lower*): 20 nm, and (*lowermost*): 100 nm. Reduction of the peak at 529 eV after use is most prevalent in the thinner films, in line with the greater oxidation of Ni (see Figure A.9). Credit: Mr Benjamin Moss.

A.9 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was used in the thickness dependence study of NiO_x (Chapter 6, Section 6.2.3) in order to under the capacitive effects of these films. EIS measurements were performed and analysed by Dr Miguel Garcia-Tecedor in Spain. Frequencies between 0.1 Hz and 1 MHz were examined with a 20 mV amplitude perturbation and a step potential of 50 mV in the anodic direction. The EIS data were analysed with ZView software (Scribner associates). With the extracted capacitance values from EIS, Mott-Schottky analysis was carried out using the expression:

$$\frac{1}{C_{SC}^2} = \frac{2}{\epsilon_0 \epsilon_r e N_A A^2} \left(\phi_{SC} - \frac{kT}{e} \right) \quad (\text{A.14})$$

where C_{SC} represents space charge capacitance, e is the elementary charge, ϵ_0 is the permittivity in vacuum, ϵ_r is the relative permittivity of NiO_x , (taken as 9.1³¹²) k is the Boltzmann constant and T is the absolute temperature, taken as 298 K. From this analysis, the values of the flatband potential (V_{FB}) and the acceptor or donor density (N_D) can be extracted. The depletion layer width was calculated using the following equation equation:

$$w = \sqrt{\frac{2\epsilon_0 \epsilon_r}{e N_D} \left(\phi_{SC} - \frac{kT}{e} \right)}, \text{ where } \phi_{SC} = V - V_{FB} \quad (\text{A.15})$$

The circuit model used for our analyses in Chapter 6 is given below.

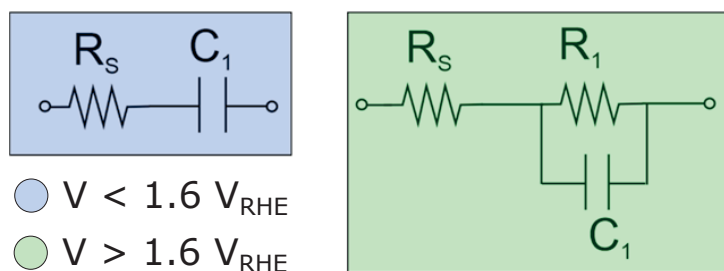


Figure A.11 – The circuit models used to fit the Nyquist plots to obtain capacitance values from electrochemical impedance data. *left*: This model was used at low anodic potentials ($V < 1.6 V_{\text{RHE}}$) when transfer at the interface is negligible and the films show pure capacitive behaviour. *right*: This model was employed at high anodic potentials ($V > 1.6 V_{\text{RHE}}$) when charge transfer becomes measurable.

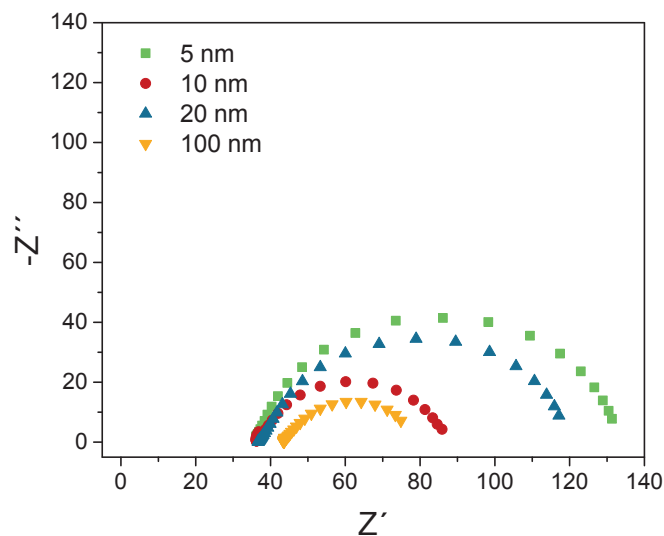


Figure A.12 – The Nyquist plots generated for each thickness of NiO_x from electrochemical impedance data using the models in Figure A.11.

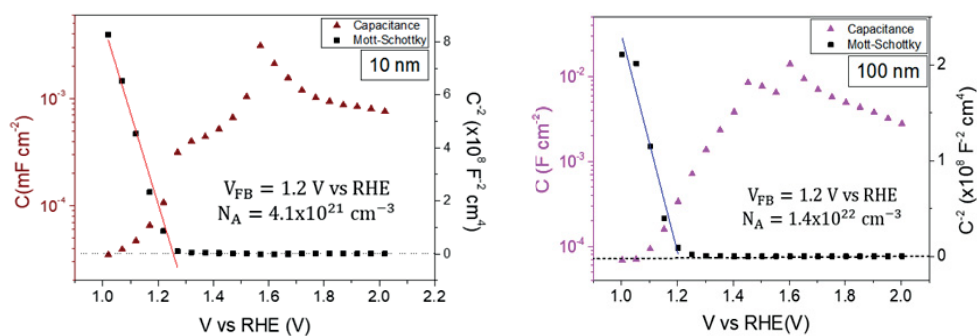


Figure A.13 – The Mott-Schottky plots showing the p-type nature of the as-deposited NiO_x samples, where (left): 10 nm, (right): 100 nm. The doping density (N_A) was calculated to be $\sim 10^{21} \text{ cm}^{-3}$ for both samples, determined using Equation A.14.

A.10 Calculation of τ and TOF

In order to calculate the τ (s) for each of the electrodeposited electrocatalysts, the concentration of accumulated MOOH(++) (cm^{-2}) was determined from the optical signal, $\Delta\text{O.D.}$, at the relevant potentials using the extinction coefficient (calculated in Appendix A.6). The current data from the same experiment was converted into charge (electrons per second) using the elemental charge (1.6×10^{-19} C). The τ value could then be calculated as shown in Equation A.16:

$$\tau(s) = \frac{[++]}{\text{number of electrons} \times s^{-1}} \quad (\text{A.16})$$

The turnover frequency (TOF) per MOOH(++) species is the inverse of the calculated τ . However, the TOF per MOOH(++) species per O_2 molecule must account for the requirement of 4 electrons as shown:

$$TOF(s^{-1}) = \frac{\text{number of electrons} \times s^{-1}}{4[++] } \quad (\text{A.17})$$

A.11 Performance comparison for purified NiOOH

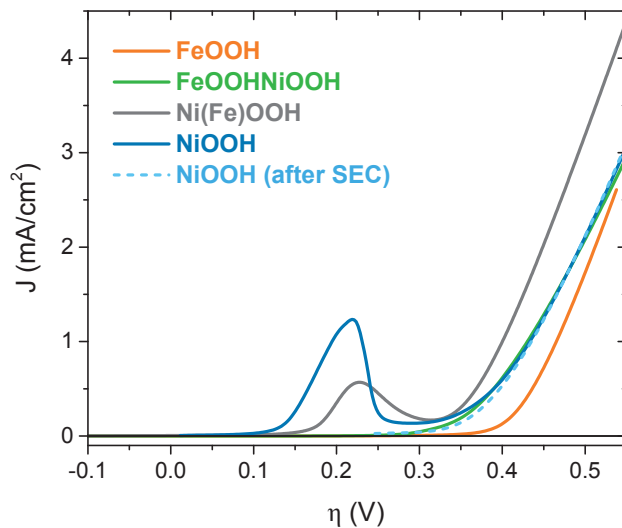


Figure A.14 – The first linear sweep (LSV) of pure NiOOH (dark blue) compared against the original electrocatalysts (Ni(Fe)OOH (grey), FeOOHNiOOH (green) and FeOOH (orange)) in 0.1 M NaOH. Despite the larger redox wave for the pure sample, suggesting the conversion of more $\text{Ni}(\text{OH})_2$ to NiOOH, the catalytic current at 0.5 V overpotential is much worse than for Ni(Fe)OOH. The LSV after this sample was used for SEC is also provided (light blue) showing no change in performance, and thus confirming no Fe incorporation.

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