INVESTIGATING CHARGE CARRIER DYNAMICS IN METAL OXIDE PHOTOANODES FOR SOLAR WATER SPLITTING

Jonathan Nip
BSc, University of Amsterdam, 2011

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Dr. Ian D. Sharp
Prof. Dr. Tom Gregorkiewicz
Prof. Dr. Rienk van Grondelle

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2 Abstract

This work investigates charge carrier dynamics in photoanodes for solar water splitting, also known as artificial photosynthesis. We investigate Fe$_2$O$_3$ nanowires with varying dopants and BiVO$_4$ using a wide array of experimental techniques including cyclic voltammetry, chronoamperometry, Mott-Schottky analysis, scanning electron microscopy, X-ray photoelectron spectroscopy, and two transient absorption spectroscopy setups in various media. We successfully developed a transient absorption spectroscopy system for long time delays (from microseconds up to seconds). Analysis of kinetic traces from Fe$_2$O$_3$ nanowire samples obtained using this system led to the development of a basic kinetic model describing charge recombination and water oxidation. We also present the most complete set of ultrafast transient absorption spectra of BiVO$_4$ to date ranging from 380 nm to 1600 nm at time delays from picoseconds to 170 nanoseconds. We take the first steps in identifying the components present in the spectra and find evidence for phonon wavepackets and Auger recombination.
3 Popular summary

3.1 English

This work aims to contribute to finding solutions to the current global energy crisis, caused by an increasing world population and increasing demand in energy. In 2010, almost 90% of our energy was produced from oil, coal, gas and nuclear energy sources. It is estimated that both the energy consumption and CO$_2$ emission will increase with approximately 50% by 2040. The growing energy demand, dwindling resources for traditional energy production and concerns for climate change, pollution and safety, ask for alternative sources of energy production.

Plants have the ability to convert sunlight, water and CO$_2$ into usable forms of energy through photosynthesis. Here, we contribute to the development of artificial photosynthesis to store sunlight in hydrogen fuel and ultimately use CO$_2$ for the creation of liquid carbohydrate fuels as clean sources of energy. The research specifically focuses on how we can effectively absorb sunlight using novel nanostructured semiconducting materials.

3.2 Dutch

Dit onderzoek tracht bij te dragen aan het vinden van oplossingen voor de huidige wereldwijde energie crisis, veroorzaakt door een toenemende wereldbevolking en een toename in de vraag naar energie. In 2010 werd bijna 90% van onze energie geproduceerd uit olie, kolen, gas en nucleaire energie. Geschat wordt dat zowel de vraag naar energie als de CO$_2$ emissie met ongeveer 50% zal toenemen tot 2040. De groeiende vraag, afnemende grondstoffoorraden voor traditionele energieproductie en zorgen over klimaatverandering, vervuiling en veiligheid, vragen om alternatieve bronnen voor energie productie.

Planten kunnen zonlicht, water en CO$_2$ omzetten in bruikbare vormen van energie via fotosynthese. In dit werk dragen we bij aan de ontwikkeling van kunstmatige fotosynthese door zonne-energie op te slaan in waterstof en uiteindelijk CO$_2$ te gebruiken voor de productie van vloeibare koolwaterstoffen als duurzame energie bronnen. Het onderzoek focust specifiek op het efficiënt absorberen van zonlicht door middel van nieuwe halfgeleider materialen.
4 Acknowledgements

First of all my gratitude goes towards my advisor Prof. Dr. Rienk van Grondelle (VU University Amsterdam), for bringing me into contact with Prof. Dr. Graham R. Fleming at UC Berkeley. It was the beginning of an incredible journey, which allowed me to not only discover California and its people, but also to be exposed to an incredible amount of cutting edge science and to receive training from highly talented researchers at one of the most renowned academic institutions of the world.

Prof. Dr. Fleming brought me into contact with Dr. Heinz Frei and Dr. Ian D. Sharp of the Joint Center for Artificial Photosynthesis at the Lawrence Berkeley National Laboratory. Especially I am grateful to Ian, for hosting me at JCAP, his support during the entire project and for reading and correcting this manuscript. I am still in awe of his seemingly infinite knowledge on virtually any topic. Of course I also want to thank Dr. Jason Cooper for his relentless efforts of problem solving and pushing me to greater understanding of the science.

Collectively, I would like to thank Dr. Yongjing Lin, Dr. Francesca Toma, Dr. Le Chen, Dr. Gary Moore, Dr. Michal Bajdich, Dr. Julien Panetier, Pepa Cotanda, Mark Hettick, Kurt Van Allsberg, Soren Scott and John Stevens for providing samples, guidance and companionship during this amazing year. Also, my gratitude goes to Prof. Dr. Tom Gregorkiewicz for providing feedback during the project and commenting on the final manuscript. I want to thank the Amsterdam University Fund, the Schuurman Schimmel – van Otteren foundation and Fundatie van de Vrijvrouwe van Renswoude foundation for indispensable financial support.

As the field of artificial photosynthesis is located at the intersection of physics and chemistry, I often found myself on unfamiliar territory. It only made this project more interesting, especially as this work contributes to new energy technologies – one of my passions. Finally, mom and dad, without your help, both financially and emotionally, this project would have been utterly impossible.

This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993.
5 Poem

“If you say that getting the money is the most important thing, you’ll spend your life completely wasting your time. You’ll be doing things you don’t like doing in order to go on living, that is to go on doing things you don’t like doing, which is stupid.”

- Alan Watts
6 Introduction

There exists a global energy problem with rising population and dwindling resources. This study aims to contribute to developing new technologies to confront that problem. In the current age, many approaches to reach this goal are being undertaken, such as solar, wind, water, tidal, geothermal, and even fusion power. This work contributes to the field of artificial photosynthesis - using the Sun to produce fuels instead of electricity, inspired by a technology that has been used for billions of years: natural photosynthesis. The history of hydrogen and its application in energy production is rich and dates back to the first fuel cell to produce electricity by Sir William Grove in 1839. The Germans further developed his ideas in the 19th century, culminating in an address by renowned German chemist Friedrich Ostwald. Well ahead of his time, Ostwald foresaw problems with pollution caused by energy production based on the combustion of coal that was also developed at the time. He proposed direct conversion to electricity by using fuel cells, thereby saving energy and reducing pollution. History took a different course.\(^1\)

6.1 Energy crisis

In 2010, global energy consumption was \(5.5 \times 10^{20}\) J or 17.5 TW, of which 89% originated from oil, coal, gas and nuclear energy sources. The remainder came from sustainable sources. The total energy consumption, as well as the global energy-related CO\(_2\) emission is projected to increase by 56% and 46% respectively, by 2040.\(^2\) Hypothetically, sufficient solar energy is available to power the needs of the most advanced human society. However, due to diurnal and seasonal solar cycles, there is a necessity for cheap energy storage. A variety of energy storage technologies exist, but cost efficiency and reliability issues remain.\(^3\) The role of chemical bonds is believed to be crucial to effectively converting and storing the Sun’s energy.\(^4\)

One solution could be hydrogen production on a massive scale as envisioned by John Bockris in the hydrogen economy.\(^5\) In order to consider such an approach, cheap and clean hydrogen production is necessary. Traditionally, hydrogen is produced using steam reforming.\(^6\) Alternatives are coal gasification, biomass and natural gas. However, these technologies result in the emission of CO\(_2\). Before the hydrogen economy based on renewable hydrogen can become economically realistic, renewable hydrogen production must become more efficient. In 2013, the U.S. Department of Energy (DOE) has set the goal for direct solar-to-hydrogen (STH) production at less than or equal to $5 per gallon of gasoline equivalent at centralized plants by 2017.\(^7\) This is a very ambitious goal. The costs of producing a kilogram of hydrogen using traditional methods lay around $1 - $2 per kg. Note that a kilogram of hydrogen is roughly the energy equivalent of a gallon of gasoline. Water oxidation using a cobalt
catalyst could costs as little as approximately $6.5 per kg, as estimated by its discoverer Daniel Nocera of MIT.\textsuperscript{8–10} Stability issues have presumably been ignored when making that estimation.

Natural photosynthesis in plants, responsible for producing the fossil fuels we use today, captures and converts solar energy to biomass at an efficiency of approximately 1%\textsuperscript{11}. In order to make a meaningful contribution to solving our energy problem, the STH efficiency needs to exceed at least 10\%\textsuperscript{12} and be based on a technology that is scalable, meaning with the use of earth abundant materials deposited using inexpensive methods. This again clarifies the magnitude of the challenge in front of us. Many current solar water splitting designs, using earth abundant materials, reach at most 5\% (see for example Abdi et al.\textsuperscript{13}), with stability being a major issue.

### 6.2 The field of solar water oxidation

One of the first accounts of the interaction between electrons and light was published in 1839, when Becquerel discovered the photovoltaic effect.\textsuperscript{14} Photocatalysis goes back as far as the start\textsuperscript{15} of the 20\(^{th}\) century. Water oxidation using TiO\(_2\) was first discovered in 1968 by P. Boddy.\textsuperscript{17} A complete PEC device (also using titania) was presented in the seminal work by Fujishima and Honda in 1972.\textsuperscript{18} Since that publication, the PEC field has received much wider attention. One way of gauging the interest is solar water splitting is by looking at the number of citations of the 1972 paper by Fujishima and Honda, which has been growing exponentially since the early 2000s.\textsuperscript{16} Review articles in this field, tracking the progress of solar water splitting, continue to emerge.\textsuperscript{19–22}

Some of the highlights of the last few decades include the multilayered PEC designs by Khaselev and Turner in 1998\textsuperscript{14} and 2001\textsuperscript{23}. Figure 6.1a shows this approach using doped GaAs and GaInP\(_2\), which does not need additional biasing for overall water splitting. The reports note STH efficiencies of 12.4 to 16\%, higher than the required threshold efficiency of 10\% as set by the DOE. Unfortunately, the complicated design, the use of rare earth materials and lack of long-term stability likely make this approach unsuitable for large scale production of inexpensive hydrogen.

\textsuperscript{8} For a detailed overview see for example Fujishima et al.\textsuperscript{16}
\textsuperscript{\dag} The design approach JCAP is currently working on is a tandem configuration.
Figure 6.1: This figure contains notable water splitting cell designs, indicating different strategies for effective solar water splitting. (a) Tandem cell approach employing several semiconductor layers to absorb a large portion of the solar spectrum. Adopted from Khaselev and Turner.\textsuperscript{24} (b) Wireless water splitting design using a cobalt catalyst for water oxidation and a NiMoZn catalyst for proton reduction on top of a triple junction amorphous silicon solar cell. Adopted from Reece et al.\textsuperscript{10} (c) Dye sensitized solar cell (yellow, grey) in a tandem configuration with Fe\textsubscript{2}O\textsubscript{3} (orange) metal oxide semiconductor. Adopted from Brillet et al.\textsuperscript{25}

Another notable design is shown in Figure 6.1b by Reece et al.\textsuperscript{10} which was mentioned above. It employs cobalt as the oxygen evolving catalyst on top of a triple junction amorphous silicon solar cell reaching projected efficiencies of 4.7%. After 24 hours, maximum efficiency decreased to 80% of the starting value, so stability remains problematic. However, as opposed to the work by Khaselev and Turner, all materials used are considered earth abundant and inexpensive to deposit, making the design potentially scalable if stability issues can be resolved. Figure 6.1c also shows a tandem approach like the work from Khaselev and Turner, but with much cheaper and more available materials. Here, metal oxides and dye sensitized solar cells (DSC) are used in tandem\textsuperscript{1} for light absorption. Fe\textsubscript{2}O\textsubscript{3} is used as the oxygen evolving agent and platinum as the hydrogen evolving catalyst. This design yields an unbiased STH efficiency of 1.2% with Fe\textsubscript{2}O\textsubscript{3} and up to 3.1% with WO\textsubscript{3}.\textsuperscript{25}

An important aspect of the field of solar water oxidation is the application to not just hydrogen production, but also CO\textsubscript{2} reduction. In this case, the anodic reaction of water oxidation is likely to be necessary in the process of creating carbon based liquid fuels, such as methanol, with water providing an abundant source of protons and electrons required for fuel forming reactions. An interesting review on CO\textsubscript{2} reduction is by Kumar et al.\textsuperscript{26}.

6.3 Joint Center for Artificial Photosynthesis

The work presented in this thesis has been conducted at the northern branch of the Joint Center for Artificial Photosynthesis

\textsuperscript{1} The design approach JCAP is currently working on is a tandem configuration.
6.4 Research goals and thesis overview

The goal of the research in this thesis is to improve the understanding of fundamental charge carrier dynamics in semiconductor photoanodes by identifying energy transitions, charge recombination pathways and water oxidation mechanisms and how this evolves in time. We do this by examining established photoanode materials (nanostructured hematite) and novel materials (bismuth vanadate) using transient absorption spectroscopy as the main experimental technique.

In order to obtain a multifaceted perspective on the materials that we investigate, we employ a broad spectrum of experimental techniques, which we will discuss in Chapter 7 (p. 21). An ultrafast transient absorption spectroscopy system was operational at JCAP, however, a system for long time delays (microseconds to seconds) was not, and was developed during this work (Chapter 8, p. 21). Before presenting experimental results, we provide the theoretical background for this type of research and an overview of the scientific literature of the field of photoanodes for solar water splitting (Chapter 9, p. 39). The experimental results follow in Chapter 10 (p. 63) covering first hematite nanowires and subsequently bismuth vanadate photoanodes. We conclude with a summary of our findings in Chapter 11 (p. 96).
7 Methods

This chapter describes the main experimental methods used during the research for this thesis. These techniques were used to gauge photo-electrochemical properties, determine the constituents of the semiconductor photoanodes, and understand the role of chemistry and structure on carrier dynamics within the materials we are investigating.

7.1 Electrochemical experiments

7.1.1 Potentiostat

The potentiostat is an important electrochemical instrument we use for many experiments in this report, such as cyclic voltammetry and chronoamperometry. For this study, we used a Biologic potentiostat, model SP-300. The potentiostat is connected to a three-electrode cell, containing a working, counter and reference electrode. Its role is to set and control a potential over the working electrode.

![Basic circuit of potentiostat](image)

Figure 7.1: Basic circuit of potentiostat with a source of potential $e_i$, an amplifier, a counter electrode (ctr), reference electrode (ref) and working electrode (wk). See text for further explanation. Adopted from Bard and Faulkner.  

Schematically, a potentiostat looks like Figure 7.1. The amplifier controls the current that flows through the counter electrode such that the reference electrode is at $-e_i$. Maintaining this potential even if resistances change during experiments is the main function of the potentiostat. Because the working electrode is grounded, the potential at the working electrode is $e_i$ with respect to the reference electrode.

In n-type semiconductors, the majority carriers are electrons and the minority carriers are holes, and in p-type vice versa. In this thesis we consider n-type photoanodes in which the minority carrier holes are required at the surface of the working electrode for oxygen evolution. As we will discuss in further detail in Section 9.1.3.2 on band energetics in photo-electrochemical cells, illumination of semiconductors drives the minority carriers towards the electrolyte. This is why n-type semiconductors are used as the photoanode.
In the dark, semiconductors have a minimum amount of minority carriers. In an experimental setup where the working electrode consists of a semiconducting material, minimal current will flow between the working and counter electrode when an n-type (p-type) semiconductor is anodically (cathodically) biased due to minimal minority carrier concentration available for charge transfer into the electrolyte. However, when the semiconductor is illuminated with photons of sufficient energy, minority carrier charge can flow through the semiconductor and the solution to the counter electrode due to the creation of minority carriers. This causes the resistance over the semiconductor to drop, and thus the current over the circuit to increase.

To the careful reader we note that, as represented in the circuit diagram of Figure 7.1, the current would flow in the wrong direction for a photoanode driving water oxidation. We can solve this, of course, by changing the sign of the applied potential.

### 7.1.2 Electrode preparation

For in situ measurements, the samples were constructed into electrodes such that only the semiconductor and the glass substrate is in contact with the electrolyte, and only the conducting fluorine doped tin oxide (FTO) layer is in contact with the wires. The FTO / hematite substrate is connected to a potentiostat as the working electrode in a three electrode cell. A platinum counter-electrode and Ag/AgCl reference electrode are also connected. The semiconductor is in ohmic contact with the FTO layer, as is the FTO and the wire (using conducting silver based epoxy), so minimal series resistance losses should occur. This design is shown in Figure 7.2.

![Figure 7.2: Electrodes for in situ characterization of semiconductor materials, using methods such as cyclic voltammetry, Mott Schottky analysis and TAS. (a) From left to right: glass or quartz (light blue), FTO (light pink), semiconductor sample (light red) and a conducting wire (grey). (b) Insulating epoxy resin (blue), semiconductor (light red), wire (grey). Note that on the back of the electrode on the right,](image-url)
the glass is left free of epoxy, in order for light to transmit through the constructed electrode.

The potentiostat can maintain the semiconductor at a fixed potential. The application of an anodic (positive) potential enhances the extraction of electrons from the semiconductor and is measured as a current in (for example) CV scans. This current is a result of electron-hole separation after the creation of electron-hole pairs through light absorption within the semiconductor. The holes travel to the semiconductor liquid junction (SCLJ) where they are in contact, through the electrolyte, with the counter-electrode. The electrons are extracted from the sample and travel through the FTO and the wire to the counter-electrode (depicted in Figure 7.1).

7.1.3 CV and CA diagrams

Cyclic voltammetry (CV) is a standard measurement to gauge the performance of photoanodes. By applying a bias over the sample and measuring the current while in the dark and illuminated, one obtains a measure of the photoactivity of the sample. The sample electrode should not produce significant current in the dark, otherwise the conducting layer of the sample might be in contact with the electrolyte. The measured photocurrent is normalized to the sample active area (A) giving a diagram containing J (current density, A cm\(^{-2}\)) versus E (applied potential, V). We obtained A of the electrodes by measuring the area in a digital photograph of a sample using a graphics editing program.

Chronoamperometry (CA) is used to measure the current as a function of time while applying a fixed potential to the sample. This allows us to apply biases during in situ transient absorption spectroscopy measurements and continuously monitor the current through the sample to check for sample degradation as well as the level of photo-activity.

7.1.4 Mott-Schottky diagrams

To assess the effect of doping on the electron density and flatband potential we perform electrochemical impedance spectroscopy using a potentiostat. To determine these quantities we use the Mott-Schottky equation:\(^{31-33}\)

\[
\frac{1}{C^2} = \frac{2}{\epsilon_0 \epsilon N_d} \times \left( E - E_{FB} - \frac{kT}{e} \right)
\]  

(1)

With C the specific capacitance (F cm\(^{-2}\)), \(e_0\) the electron charge (1.602 \(\times 10^{-19}\) C), \(\epsilon\) the dielectric constant of hematite (80, according to Cesar et al.\(^{34}\) and Ling et al.\(^{33}\)), \(\epsilon_0\) the permittivity of vacuum (8.85 \(\times 10^{-12}\) F m\(^{-1}\)), \(N_d\) the electron density, E the applied potential, \(E_{FB}\) flatband potential, k the Boltzmann constant (1.38 \(\times 10^{-23}\) J K\(^{-1}\)) and T, the temperature in Kelvin.
Using the potentiostat, we measure the imaginary component of the impedance \((Z)\) as a function of applied potential. Using (2), we obtain the capacitance per cm\(^2\) of the samples:

\[
C = \frac{1}{\left|Z\right| 2\pi f A}
\]  

(2)

Where \(Z\) is the imaginary component of the impedance, \(f\) the frequency at which the impedance was measured (10 kHz), and \(A\) the area of the electrode. The plot of \(C^2\) versus applied potential contains the quantities we are looking for. When we extrapolate a linear fit of the data points, we find the \(E_{\text{flatband}}\) where the fit intersects with the \(x\)-axis. The electron density is related to the slope of the fit as:

\[
N_d = \frac{2}{\varepsilon_0 \varepsilon_r} \sqrt{\frac{d(C^{-2})}{dv}}^{-1}
\]  

(3)

This relation only holds when the \(C^2\) vs. \(E\) plot is linear.

### 7.2 Scanning electron microscopy

Scanning electron microscopy (SEM) is a widely used technique for surface morphology characterization.\(^{35}\) A sample is raster scanned by a beam of electrons creating a highly detailed nanoscale image of the surface of the sample under high vacuum conditions. For this thesis a Quanta FEG 250 from FEI was used with a reported maximum magnification of 1,000,000 times.\(^{36}\)

SEM is based on illuminating a sample with a narrow electron beam on the order of a few nanometers depending on the electron acceleration. The Quanta FEG 250 accelerates electrons with voltages ranging from 0.2 kV to 30 kV. The electron beam is emitted from a field emission electron gun (primary beam) and focused by a series of lenses. The primary beam can be steered in the \(x\)- and \(y\)-direction by scanning coils allowing for raster scanning of the electrons over the sample. Depending on the type of sample, the electrons penetrate the surface up to a few \(\mu\)m and electrons exiting the sample are used for imaging. The two main types are elastically scattered primary electrons with energies up to the energy of the primary beam, and inelastically scattered secondary electrons with energies of a few eV. Secondary electrons give the best resolution, as the penetration depth of these low energetic electrons is short (a few nm).\(^{37}\)

### 7.3 X-ray photoelectron spectroscopy

XPS is a widely used surface sensitive spectroscopic technique that measures the kinetic or binding energy of electrons that are ejected out of a material by X-ray photons. The penetration depth is between 0 to 10 nm. XPS often requires an ultrahigh vacuum and can be used to detect elements and their oxidation state.\(^{38}\) At JCAP we use an AXIS Ultra DLD XPS from Kratos Analytical.
Figure 7.3: X-ray photoelectron spectroscopy (XPS) mechanism. (a) An atom emits a photoelectron after being illuminated with an X-ray photon. (b) A core level electron is emitted and its binding energy (BE) is obtained through measuring the electron’s kinetic energy (KE). $\Phi$ is the work function of the photoelectron spectrometer. See Equation (4).

In Figure 7.3 we see schematically how XPS works. X-rays are produced from a magnesium Kα (1,253.6 eV) or aluminium Kα (1,486.7 eV) source. After a core level electron is emitted by X-ray photons, its kinetic energy is measured in a photoelectron spectrometer. The X-ray photon transfers its energy to the electron, which has to overcome the binding energy and the work function (Φ). The remaining energy is converted into kinetic energy. Solving for the binding energy then gives:

$$BE \, (eV) = h\nu - KE - \Phi_{det}$$

(4)

$\Phi_{det}$ is the work function of the detector. It is instrument dependent and is found through calibration. As said, XPS is surface and chemically sensitive. This is due to neighboring atoms affecting the binding energy of core level electrons so that for example, a change in the oxidation state leads to a change in the kinetic energy. Because the emitted electrons have a short inelastic mean free path only the photoelectrons from the surface emerge without inelastic scattering. This causes 95% of detected electrons to originate from a depth of:

$$d = 3\lambda$$

(5)

As X-rays have a wavelength in the order of nanometers, the probing depth of XPS is also in the order of nanometers.39,40

7.4 Transient absorption spectroscopy

In transient absorption spectroscopy (TAS) one looks at the change in absorption of a sample after being excited with a laser pulse. The absorption change is a measure of the presence of charge carriers in the sample and can be used to probe the carrier lifetimes. At JCAP we use two TAS systems, for short (fs - μs), and long timescales (ns - s). First we discuss the principle of TAS, then our ultrafast TAS (ufTAS) system, while in Chapter 8 we discuss
extensively the development of the millisecond to second TAS (msTAS) setup for longer timescales.

Figure 7.4: Basic TAS setup. An intense pump laser pulse excites a sample which is followed by a much weaker probe beam at a later time. The probe light is analyzed using a detector at the output of a spectrometer to monitor the change of absorption of the light as a function of wavelength and time delay between probe and pump. This figure shows a probe consisting of white light. One difference between the ufTAS system and the msTAS system is that the latter uses continuous monochromatic light, while the ufTAS system uses pulsed white light as a probe. Details will be discussed in the sections dedicated to each setup. Figure adopted from Berera et al. 41

In Figure 7.4 we see a pump beam of energy larger than the bandgap exciting the sample and a probe beam. After passing through the sample the pump beam is dumped, while the change of the absorbance of the probe light is measured. To be more precise, TAS measures the difference of the absorbance between when the sample has just been excited by the pump and the absorbance when the sample was not excited by the pump and is in the ground state. For solid state systems, absorbance is defined as the natural logarithm of the ratio between the incoming light, $I_0$, and $I_1$, the light that has passed through the sample. 41 Mathematically, this can be simplified as follows:

$$\Delta A = A_{\text{excited state}} - A_{\text{ground state}} = \ln \left( \frac{I_{0,\text{excited}}}{I_{1,\text{excited}}} \right) - \ln \left( \frac{I_{0,\text{ground}}}{I_{1,\text{ground}}} \right) =$$

$$\ln(I_{0,\text{excited}}) - \ln(I_{1,\text{excited}}) - \ln(I_{0,\text{ground}}) + \ln(I_{1,\text{ground}}) \quad (6)$$

With the subscripts ground and excited representing the cases in which the sample is in the ground, or excited state. Because the incoming light $I_0$ remains the same whether the sample was excited by the pump beam or not, this reduces to:
\[ \Delta A = \ln \left( \frac{I_{\text{ground}}}{I_{\text{excited}}} \right) \] (7)

\( \Delta A \) is also dependent on the time delay between the pump and probe beam, as well as the wavelength of the probe. These three quantities combined give a three dimensional relation between change in absorbance, probe wavelength \( \lambda \) and delay time \( t \) between pump and probe, or \( \Delta A(\lambda, t) \).

Examining Equation (7), we can deduct the meaning of a positive or negative signal. A positive signal is produced when the transmitted light intensity is larger in the ground state, than in the excited state. This means that due to the pump beam, the sample absorbs more photons. This case occurs when, for example, carriers excited into conduction band by the pump, absorb photons to higher energy levels. The opposite case is also possible, where the ratio between the light intensity in the ground state to the intensity in the excited state is smaller than 1, leading to a negative \( \Delta A \) signal. This can occur when the pump beam partially depopulates the valence band from electrons. These electrons are now unavailable to absorb photons, which decreases absorption in the excited state. This is referred to as a bleach of the ground state.

TAS can be performed in air as well as in solution. For PEC applications, measurements in situ are more valuable since they mimic the actual PEC environment. Also, the effect of applying potentials (using a potentiostat) and different electrolyte environments on the carrier dynamics of the materials can be studied.

7.4.1 Ultrafast transient absorption spectroscopy setup

The ultrafast TAS setup uses a titanium:sapphire-based regenerative amplified laser (Libra, Coherent). This laser operates at a repetition rate of 1 kHz, a pulse width of 100 fs, 4 W output and a center wavelength of 800 nm. 50% of the primary laser output is used to pump an OPA (OPera Solo) to generate a pump beam that can be adjusted to emit from near-infrared to ultra-violet wavelengths. The pump beam passes through a chopper to periodically block the beam. While the beam is blocked the systems obtains measurements \( I_{\text{ground}} \) and \( I_{\text{excited}} \) is obtained when the pump is present. See Figure 7.5 for a schematic of the system. For the experiments in this paper the OPA was set to 310 nm, with an intensity of 3 mW or 3 \( \mu \)J per pulse, and the spot size of the pump beam was measured to be 7.8\( \times \)10\(^{-4} \) cm\(^2\). For some measurements, the pump intensity was varied in order to determine the impact on the sample response. The setup has two TAS spectrometers incorporated in the overall design, namely the HELIOS and EOS systems (both designed by Ultrafast Systems). Both these systems use the same pump beam as produced by the OPA described above.
HELIOS is used for short time delays from sub ps up to 8 ns, using an optical delay stage. For probe generation it uses fraction of the remaining 50% of the 800 nm fundamental laser. This is used to pump crystals in order to generate the white light (WL), which serves as a probe beam from infrared to ultra-violet wavelengths. Crystals include sapphire (450 - 900 nm), calcium fluoride (350 - 700 nm) and a thick sapphire crystal (800 - 1800 nm). Prior to the sample, the probe beam is split - a portion is transmitted through the sample as the probe and the remainder of is used as a reference beam to compensate for intensity fluctuations during the measurement, thereby yielding a better signal to noise ratio.

The EOS mode of the setup uses a probe generated by a supercontinuum laser (Leukos fiber laser, Leukos Systems), ranging from UV to the near IR (350 - 1600 nm) with a pulse width of 1 ns. The probe is electronically triggered, meaning it generates probe pulses at randomized time delays from the pump, which over time averages out to a full temporal spectrum. This allows for time delays up to hundreds of microseconds with a temporal resolution of 1 ns. As with HELIOS, the probe is split in two before passing through the sample to create a reference beam to improve signal to noise.

Finally, the probe beam spectrum is detected by two, two component spectrographs: two 2D Si CMOS detector (UV-Vis range) and two InGaAs detector arrays to detect near-infrared photons. These two double spectrographs are used to analyze the probe beam and the reference beam as shown in Figure 7.5. The dA spectrum is calculated using Equation (7).

7.5 Sample preparation

7.5.1 Fe₂O₃ nanowires

The hematite nanowires are made according to the procedure of Ling et al. The nanowires are grown on top of FTO covered glass. First, through a hydrothermal method, a layer of iron oxyhydroxide (FeOOH, yellow) nanowires was synthesized on the FTO by heating it in 20 mL pH 1 precursor solution containing 0.15 M FeCl₃ and 1M NaNO₃ at 95 °C for 4 hr. Subsequent sintering of these substrates in
air at 550 °C for 2 hr resulted in α-Fe₂O₃ (hematite) nanowire films, now with the characteristic red hematite color. Ling et al. have shown using XRD\(^\text{§}\) that all the FeOOH is converted into α-Fe₂O₃. Then either a SnCl₂ or TiCl₄ ethanol solution was dropped on the FeOOH film surface to introduce dopants into some samples. After that, all samples were annealed in the CVD system at 800 °C for 10 min. The morphology of the wires did not change during the 800 °C annealing although Ling et al. report that the thickness of the wires increased slightly. Note that Sn diffuses from the FTO substrate into the wires during this high temperature annealing process. The report shows using XPS that Sn is also present in the undoped samples, implying it must be present in the Ti doped sample too, through diffusion from the FTO substrate.

For the measurements we used three different batches (A, B and C) of hematite, deposited according to the methods mentioned above. Each batch contains undoped and doped versions of the sample and thus ideally, we would compare results within one batch of samples, because differences in, for example, sample thickness should be minimized. This was not possible, but in order to distinguish between samples we use the following nomenclature:

- Batch A: Fe₂O₃-A, Sn:Fe₂O₃-A
- Batch B: Fe₂O₃-B, Ti:Fe₂O₃-B
- Batch C: Fe₂O₃-C, Sn:Fe₂O₃-C, Ti:Fe₂O₃-C

7.5.2 BiVO₄

The bismuth vanadate samples were prepared using the drop-cast method (see Luo et al.\(^\text{42}\)). Bi(NO₃)₃·5H₂O was dissolved in glacial acetic acid (0.2 M, 0.9 mL) and vanadyl acetylacetone (0.03 M, 5.82 mL) was dissolved in acetylacetone. Both solutions were mixed in a 1:1 mol ratio of Bi : V. The final solution was obtained after 20 min of sonication and was dropped onto an FTO substrate. The sample was then dried at 150 °C to evaporate the solvents and then calcined at 470 °C. This created one layer of BiVO₄. A finished sample was made with a total of four layers.

\(^\text{§}\) X-ray diffraction spectroscopy
8 Developing millisecond TA setup

Through the course of this work, an experimental setup for millisecond to second TAS (msTAS) was developed at JCAP. This chapter covers the details of the development process, the components of the system and how it operates.

8.1 Millisecond TAS setup description

A schematic representation of the msTAS system is shown below in Figure 8.1. The following sections will discuss all aspects of the setup.

![Schematic diagram of the msTAS system](image)

**Figure 8.1: Millisecond TAS setup at JCAP. See following sections for description.**

8.1.1 Pump generation and triggering

The pump laser is a Continuum Minilite II,\textsuperscript{43,44} which can provide laser pulses at frequencies between 1 and 15 Hz. This repetition rate is too high for longer time delay measurements. Using a delay generator (Stanford Research Systems DG535), we manually control (trigger) the repetition rate of the laser. Figure 8.2 shows how we manually trigger the pump to lower firing rates. The Minilite II provides a trigger signal to the oscilloscope from the Q-SWITCH SYNC OUT (see Figure 8.2). The Q-SWITCH SYNC OUT is 60 ns ahead of the pump pulse due to a buildup time necessary to produce the pulse. This trigger is necessary to display a stable waveform of the probe signal on the Tektronics DPO 4054 oscilloscope. The oscilloscope then obtains an average of up to 500 pump-probe cycles to minimize noise in the data.

The laser generation is based on a flashlamp that optically pumps a Nd:YAG (Nd:Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}) rod (gain medium) enclosed by two mirrors at the ends. This causes spontaneous emission (laser generation) in the Nd:YAG rod as soon as the flashlamp pumps the material,
resulting in a high energy but low peak power due to the broadness of the pulse. The introduction of a Q-switch delays spontaneous emission and increases the energy stored in the lasing medium by introducing an additional loss pathway for photons. This helps to prevent stimulated emission and thus builds up more electronically excited electrons in the gain medium. The Q-switch consists of a quarter wave plate (linearly polarized light is converted into circularly polarized light and the other way around), horizontal polarizer and a crystal and is placed in the laser cavity containing the Nd:YAG rod. Vertically polarized light exiting the rod is now blocked by the horizontal polarizer and cannot reenter the rod. In contrast, horizontally polarized light can pass through the horizontal polarizer, is rotated 45° when exiting the rod by the quarter wave plate, and again rotated 45° when attempting to reenter to the rod. Now vertically polarized, the horizontal polarizer prevents the light from reentering the rod. After approximately 150 µs the energy stored is maximized and a high voltage is applied over the crystal of the Q-switch causing light to rotate 180°. Horizontally polarized light can reenter the rod, oscillate between the mirrors and cause the energy in the excited electrons to release. This results in a short, powerful and monochromatic (1064 nm) laser pulse of approximately 5 ns.44

Figure 8.2: Triggering the Minilite II pump laser. Both the flashlamp and the Q-switch are externally triggered with two TTL signals (0 to +5 V DC and 15 µs wide). The Q-switch is triggered ≈150 µs after the flashlamp for maximum energy buildup producing a pulse with ≈5 ns duration. The Q-switch sync out triggers the oscilloscope. Adopted from the Minilite manual.44
The 1064 nm fundamental laser pulse can be frequency doubled, tripled and quadrupled through non-linear processes in certain crystals. In the crystal, two photons can combine into one photon under specific conditions (such as the conservation of energy), creating harmonics of the 1064 nm fundamental laser. Combining one 1064 nm photon and one 532 nm photon (produced by two 1064 nm photons), we obtain through frequency summation \((1/532 + 1/1064 = 1/355)\), a pump wavelength of 355 nm. This is shown schematically in Figure 8.3.

![Figure 8.3: Generating harmonics of the fundamental 1064 nm laser.](image)

8.1.2 Probe light

The probe light is generated using a halogen lamp connected to a monochromator. After passing through the sample, the light is collected in a spectrometer (see below for details). Both the monochromator and spectrometer are based on the principle of a diffraction grating dispersing light, so that specific wavelengths can be filtered out and others selected. So the combination of the monochromator and spectrometer is used for selecting individual wavelengths for analysis, while ensuring all other wavelengths are excluded. In principle, measurements could be performed with only the monochromator or only the spectrometer. However, both are used for achieving the sensitivity required for this measurement. Using a monochromator, rather than full spectrum probe light, ensures that, while the overall probe intensity is low, the probe intensity at the desired wavelength is well matched to the dynamic range of the detector. The spectrometer ensures unwanted scattered light from the environment and the pump laser is effectively excluded.
The setup shown in Figure 8.1 uses a Newport QTH Lamp Housing (model 67009), with an output between 10-250 W and f-number 2.2. This lamp housing is equipped with a halogen lamp that provides the Newport Oriel Cornerstone 260 1/4 m monochromator with light, which results in the probe beam. The monochromator uses an asymmetric in-plane Czerny-Turner configuration (see Figure 8.5) with input f-number of 3.9. A Cornerstone 260 dual grating (Newport model 74163, 1200 grooves / mm, 350 nm blaze wavelength) is used in this monochromator.

On the entrance and exit ports are mounted two micrometer driven variable slits (model 74001, Newport). These slits control the amount and angle of light entering and exiting the monochromator. This affects the spectral resolution of the monochromator. Ideally, the monochromator output consists of one single wavelength. In practice however, the output consists of a band around a single frequency (see Figure 8.4). We chose to set the slits to 2.5 mm for the experiments presented in this thesis, meaning a resolution of 25 nm (full width at half maximum).

As indicated above, the resolution of the measurement is actually defined by the settings of the spectrometer. However, as the spectrometer filters out a single wavelength, the total intensity output of the spectrometer is reduced. We found that by opening up the slits of the spectrometer completely, the decrease in spectral resolution was balanced by the increase in intensity of the probe. This means that the spectral resolution of the setup is effectively determined by the monochromator resolution shown in Figure 8.4.

![Figure 8.4: Resolution of light exiting the monochromator measured by the full width at half maximum (FWHM) versus the slit widths of the monochromator. First a spectrum (intensity vs. wavelength) of the output of the monochromator was obtained with a calibrated spectrometer. Then the FWHM of the peak was measured. The black line shows a linear fit to the data points, showing that the resolution is reduced with increasing slit width, which is a disadvantage. The](image-url)
The advantage of a larger slit width is that it transmits more light, resulting in a higher S/N ratio.

As future steps in the development of the setup involve effective filtering of the monochromator output with the spectrometer, next we discuss the spectrometer properties. We use a Newport Oriel MS257 1/4 m Monochromator and Imaging Spectrograph, which the probe light enters after passing through the sample. The spectrograph also uses an asymmetric in-plane Czerny-Turner configuration (see Figure 8.5) to select wavelengths from an incoming light source. The f-number of the incoming lens is 3.9, with different focal lengths for the entrance (220.0 mm) and exit (257.4 mm) of the spectrograph. The spectrograph is equipped with the same slits as the monochromator. Four different gratings can be used:

<table>
<thead>
<tr>
<th>grating</th>
<th>blaze (nm)</th>
<th>groove (grooves / mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>grating 1</td>
<td>350</td>
<td>1200</td>
</tr>
<tr>
<td>grating 2</td>
<td>400</td>
<td>600</td>
</tr>
<tr>
<td>grating 3</td>
<td>500</td>
<td>300</td>
</tr>
<tr>
<td>grating 4</td>
<td>800</td>
<td>150</td>
</tr>
</tbody>
</table>

Table 1: Grating options for the spectrometer.

Figure 8.5: Monochromator (a) and spectrometer (b) Czerny-Turner configuration. For the monochromator we use the axial exit, while for the spectrometer we use the lateral exit. Adopted from instrument manuals.

The spectrograph exit is equipped with a photodiode that converts the probe light into a voltage. The next section covers this instrument, as well as the pre-amplifier and its function to reduce noise.

8.1.3 Signal, noise and change in absorbance

The spectrograph is connected to a Thorlabs 110A2 avalanche photodiode (APD) that converts the probe photons into voltage. The output voltage noise of the detector is 1.65 mV_RMS. The bandwidth of the detector is DC – 50 MHz, signals above this threshold are attenuated. The detector consists of Si, which is normally not
By applying a large bias (100-200V) over the Si, the photons that create electrons through the photoelectric effect cause an avalanche breakdown thereby multiplying the signal. The current created in the silicon is converted to a voltage by a transimpedance amplifier. Due to Ohm’s law, increasing current causes a voltage drop over the resistor in the transimpedance amplifier. Thus the detector output voltage is proportional to the resistor \( V_{out}/I_{in}=R \). Summarizing, increasing light intensity, increases the current, and leads to an increase in the voltage. For this photodiode, the gain \( G \) related to the resistance \( R \), is 100,000 V/A. Other factors also contribute for conversion of light intensity (P) to \( V_{out} \), such as the M-factor, related to the temperature of the detector \( (M = 50 \) at room temperature) and the spectral responsivity \( R(\lambda) \), shown in Figure 8.6. This can be summarized in Equation (8):\(^\text{45}\)

\[
V_{out} = P \cdot R(\lambda) \cdot M \cdot G 
\]

(8)

Figure 8.6: APD110A2 photodiode responsivity at \( M = 1 \). Adopted from instrument manual.\(^\text{45}\)

In every experimental setup one has to manage noise either picked up by the detector or at other stages of data collection. First let us look at possible sources of noise, after which we will take a close look at the pre-amplifier, used to minimize the influence of noise. There are two general types of noise in experiments, intrinsic and non-essential noise sources. Intrinsic noise is due to, for example, fluctuations in electron density or resistance in a resistor, as well as noise due to recombination in semiconductors. These noise sources are incoherent. To find the total noise, ones takes the square root of the sum of the squares of each noise component. The second type is non-essential noise that can, in principle, be avoided in the laboratory. See Figure 8.7 for typical examples. Other examples include capacitative coupling (voltage of nearby instrument couples to the detector through stray capacitance), inductive coupling (a nearby changing current creates a magnetic field that induces a voltage in the detector) and ground loops (noise voltage due to currents in an apparatus with a common connection). Strategies to minimize these noise sources include turning off or removing the noise source, using
of capacitative or magnetic shielding (include detector in a metal box) and connecting all instruments to the same physical ground.  

46  

Figure 8.7: Typical noise spectrum in the laboratory. Adopted from the SR560 pre-amplifier manual.  

$V_{\text{out}}$ from the APD is amplified and filtered using a Stanford Research Systems SR560 pre-amplifier. The data readout is performed with the oscilloscope and a computer. The pre-amp has two important functions. First of all, it can be used to create low or high pass filters. We set low pass filters at a cut-off frequency just above the frequency of the signal we are interested in. This filters all high frequency noise from the measurement. Low frequency noise is not filtered out and will negatively affect the longer time scales of the measurement. To solve this, we use low pass filters of a lower frequency to collect the longer time scale measurements of a photoanode sample. See Section 8.2.6 on ‘gain and filters’ for a visual explanation of how we apply different low pass filters to one sample measurement.

The second function of the pre-amp is crucial to this TAS setup. Because we are interested in the change in absorption, and not the absolute value of the transmitted light, we set the pre-amplifier to AC mode, which introduces a capacitor in series. This removes any DC offset from the signal and only records changes in the intensity of the transmitted light. This is necessary because the changes in absorption are very small compared to the average transmitted light through the sample. In order to effectively register the absorbance changes we need to amplify the change in signal, not the entire signal. Amplifying the entire signal, including the DC offset, would limit the magnitude of amplification because the large DC offset would quickly overload the maximum capacity of the pre-amplifier and oscilloscope.

Finally, the filtered and amplified signal exiting the pre-amp is fed into the oscilloscope to improve S/N (through averaging the signal, see section 8.1.1) and for data readout. An important setting on the oscilloscope is whether to use AC or DC coupling of the pre-amp signal. Since the signal is AC coupled to the pre-amp, one might think that the oscilloscope could also be set to AC coupling. This is incorrect because the capacitor responsible for the DC component
removal also introduces a high pass filter. For the pre-amp, this amounts to 0.033 Hz, which does not interfere with measurements on the timescales we are interested in (up to a few seconds). However, this is different for the oscilloscope as it inserts a 100 Hz high pass filter, which is detrimental to our measurements as it introduces a transient feature masking the low frequency responses that we are also interested in.

Finally, the pre-amplifier slows the overall instrument response function (IRF) of the system (see Figure 8.8). Because the time window of our TAS measurements starts at 10 μs, this is not a concern.

![IRF graph](image)

Figure 8.8: Instrument response function (IRF) of the msTAS system obtained through recording the pump laser with the photodiode. The laser pulse is 5 ns long but is increased to approximately 1 μs due to the response time of the pre-amplifier.

8.1.4 Summarizing

The experiment is set up in the following way. The pump laser, typically at 0.33 Hz, passes through two dichroic mirrors. These mirrors only reflect a narrow band of wavelengths around 355 nm, which is the wavelength we require. We use these to remove any lower harmonics still present after laser generation, which could interfere with the observed signal. After exciting the sample, the pump beam is dumped. The probe light exiting the monochromator passes through the sample and then through a 400 nm long-pass filter. This filter is necessary because glass from the sample and sample holder fluoresces under the pump beam. The probe beam then passes through the spectrometer, which provides additional wavelength selectivity. The APD is mounted to the output port of the spectrometer. After the APD converts the photons into a voltage, the signal passes through a pre-amplifier. Because we are interested in the change in absorption, and not the absolute value of the transmitted light, we set the pre-amplifier to AC mode. Let us think about what information this signal now contains. The AC mode of the pre-amp only registers the change of light intensity after the
pump excites the sample. It does not register a signal before the pump, as the sample is in the ground state and the light transmission constant. Therefore, it sees the changing light intensity while the sample is excited compared to when the sample is in the ground state.

This signal is thus exactly the ratio \( \frac{I_{\text{ground}}}{I_{\text{excited}}} \) from Equation (7). As explained in Section 7.4, taking the natural logarithm of this ratio means that when the intensity in the excited state is larger than the intensity in the ground state, a negative signal is obtained, and vice versa. The second function of the pre-amp is to filter this signal to improve S/N. Using the potentiostat, we can examine the effect of bias by applying a potential over the sample in the electrolyte and record electrical current. The filtered and amplified signal of the change in absorption is averaged by the oscilloscope to further improve S/N and is finally sent to a computer.

In the following paragraphs we will discuss in more detail how we verified the principles from this section and also how exactly we obtain \( \Delta A \) corrected for changing light intensities as we change samples and probe wavelengths.

### 8.2 Developing the setup

This section provides insight into the considerations that led to the final setup design as outlined in the previous section. Through continuous testing and implementing improvements we finally obtained high quality transient absorption data. We go deeper into this process here because developing the setup required considerable research time and it resulted in a new experimental setup at JCAP.

#### 8.2.1 Finding a transient signal and reducing noise

One of the first difficulties we encountered was the interference of the pump laser. Initial experiments were attempted with a Continuum Powerlite DLS Nd:YAG laser. However, electromagnetic radiation from the flash lamps penetrated the casing of the laser introduced significant noise into the measured signal. We solved this issue by using the much smaller, although powerful, Continuum Minilite II Nd:YAG laser. There was also a persistent low frequency noise in the data of approximately 60 Hz. The obvious explanation was that it had to originate from the 60 Hz AC power supply. This problem was solved after connecting all units onto an uninterruptable power supply resulting in a filtered ground relative to the laser table ground which contained noise from the laser.

Next we set out to find a TAS signal. We noticed a large, short-lived negative feature right after the pump pulse at \( t = 0 \) s. To determine the source of the feature we experimented with switching the pump and probe beam on and off. Figure 8.9 shows the results.
Figure 8.9: Measuring a hematite test sample in air while only varying the presence of the pump and probe. Note that the vertical axis is in volts, as we have not yet converted the raw data to $\Delta A$. The pump wavelength is set to 532 nm, with a probe wavelength of 650 nm.

From Figure 8.9 we conclude that the negative peak is visible only in cases where the pump is on (Figure 8.9c and d), while the probe beam is off in Figure 8.9c in one of those instances. This implies that the negative peak is a result of the pump laser, and thus considered an artifact. As discussed above, we are using a spectrometer before the APD detector to only allow specific wavelengths into the APD detector, so we did not expect such an artifact. However, in practice we found that the spectrometer also caused the light intensity to drop significantly, thus we chose to open up the spectrometer slits resulting in higher intensity, but also lower resolution. Also, the photodiode is very sensitive so that even a small amount of stray light that might travel through the detector leads to a significant signal. In the next set of measurements we try to eliminate this peak.

Figure 8.10: In order to eliminate the artifact from detection of the pump laser, we placed a 550 nm long pass filter in front of the spectrometer entrance slit.

In Figure 8.10 we see that the addition of a 550 nm long pass filter blocks stray light of the pump laser wavelength of 532 nm. Later, when we set the pump wavelength to 355 nm we used a 400 nm long pass filter, which proved effective as well. While the
introduction of a cutoff filter was effective in reducing the magnitude of the feature originating from the pump beam, it was not entirely eliminated. After much searching, we discovered that the source of this feature was from the Nd:YAG fundamental output at 1064 nm. To solve this issue, we installed two dichroic mirrors immediately after the Minilite (see Figure 8.1) to filter out the fundamental mode of the laser (and the second harmonic at 532 nm for the case of 355 nm excitation), which caused this artifact. A final note (to the careful reader) is that the traces in Figure 8.9 and Figure 8.10 do not start at zero on the vertical scale; these measurements were performed at an early stage with non-optimal elimination of the DC offset. In the next measurements, these issues are resolved.

Now that the main signal artifacts have been eliminated we search for a proper transient signal caused by a hematite test sample.

Figure 8.11: We compare measurements of a sample with bare FTO and a hematite sample while varying the pump intensity. Measurements performed in air, at a probe wavelength of 650 nm. We note that the small oscillations most prominent in (d) are due to a non-optimal configuration at an early stage of the setup development and are eliminated in the final design.

Figure 8.11a – d show the emergence of a transient absorption peak when we switch between a bare FTO sample and FTO with hematite on the surface. This positive transient feature is consistent with literature at 650 nm. Note that we also see the return of a short-lived negative feature when we pump at high intensity in case of the FTO. This negative signal is obscured by the large positive feature in Figure 8.11d. We discuss this more detail in Section 8.2.5.

8.2.2 Verification of oscilloscope calibration

In order to ensure that the calculated absorbance changes are independent of the oscilloscope setting, it was necessary to check that all voltage and time scales were calibrated with one another.
In Figure 8.12 we find that the oscilloscope functions correctly, nearly all traces obtained at different scales lie on top of each other. However, it is important to note that when the scaling was set to low V / div values (Figure 8.12a), the signal could extend outside the detection window and the measured data was clipped. For all measurements, the scale was carefully selected to ensure that the data were not clipped and, at the same time, the range was well matched to the magnitude of the signal to ensure the best signal to noise.

8.2.3 Effect of pump and probe intensity

The pump beam with super bandgap energy creates excited states in the sample that can be measured by the probe beam. Ideally, one would use a pump at 1 sun intensity, in order to simulate the real life effects of solar excitation. Figure 8.13 shows the effect of pump intensities on the TAS signal. Comparing these intensities with 1 sun illumination can be done when one calculates the intensity of 1 sun (100 mW/cm²) during a pulse with the same width as our pump beam (5 ns). This corresponds to 5x10⁻⁷ mW/cm², much lower than the pump intensity we use. Figure 8.13 shows the advantage of high pump power, namely a better S/N ratio.
hematite, no non-linear effects were found after normalizing the traces to the peak voltage.

However, higher intensity can give rise to non-linear effects (such as Auger recombination). Also, it will degrade a sample more quickly. Sample degradation can be seen visually, by looking at the sample and observing discoloration. A more quantitative method is shown in Figure 8.14: with time, the photocurrent produced by a spin coated BiVO$_4$ sample decreases substantially during a TAS experiment. Although not shown in the figure, this process would continue until virtually no photocurrent was present. Note that pump intensity is not solely responsible for sample degradation, factors such as electrolyte or applied bias also have this effect. Finding a balance between intensity and quality of signal is desired. The Fe$_2$O$_3$ nanowire samples we used show a high level of stability, and we chose to use high pump power to obtain a high level of S/N. During the work for this thesis, significant progress was made improving the S/N ratio and it must be the goal of future experiments to lower the pump intensity to mimic real solar conditions.

Figure 8.14: Linear sweep voltammetry (LSV) of spin coated BiVO$_4$ samples, while being periodically illuminated, resulting in a photocurrent during illumination. The three measurements were done before, during and after a 1.5 hr long TAS experiment in solution.

Figure 8.15 shows the effect of the probe intensity. Higher probe intensity should lead to a higher signal to noise ratio but not affect the magnitude of the transient absorption signal or the decay kinetics. However, the raw data show a strong dependence of the measured signal on the probe power and it is important to provide an accurate conversion from the amplified detector output to the change of the absorbance in optical density.
8.2.4 Calculating $\Delta A$

TAS measurements are dependent on the sample and the medium it is in, the pump and probe wavelength, and the pump intensity. Increasing the probe intensity leads to a higher signal because the amount of light incident on the detector becomes larger. However, the probe intensity often differs with changing probe wavelength, due to the spectral output of the lamp, and sample, due to changes of thickness or absorption coefficient. Thus, we must convert the amplified detector response, in V, to the change of absorption, in optical density (OD). Recalling Equation (7):

$$\Delta A = \ln \left( \frac{I_{\text{ground}}}{I_{\text{excited}}} \right)$$

Although this relation is quite simple, there are a number of additional factors present in the experiment that must be considered for calculation of the TAS response. In order to eliminate any remnant artifacts, a background signal was collected by turning off the probe and subtracting this signal from the $\Delta A$ signal. Another factor to take into account is the effect of the pre-amplifier. By amplifying the signal we can improve the signal to noise ratio, but this gain factor needs to be compensated to obtain the true $\Delta A$ value. Considering these factors, $\Delta A$ calculation is performed as follows:

$$\Delta A = \log \left( \frac{V_D - V_{\text{background}}}{V_p - V_{\text{signal}} \cdot \text{gain}} \right)$$

(9)

With $V_D$ the average DC output of the APD as measured by a multimeter, $V_{\text{signal}}$ is the voltage measured on the oscilloscope and recorded with the PC, gain the multiplication factor from the pre-amp, and $V_{\text{background}}$ the background signal. $V_D$ is equal to the transmitted light intensity when the sample is in the ground state, because the changes in absorption are so small compared to the absolute signal. We inverted the signal using the oscilloscope so that when light is absorbed we obtain a positive value. Then, by subtracting $V_{\text{signal}}$ from $V_D$ one obtains the intensity after the sample was excited. Using (9) we find that $\Delta A$ values are independent of probe intensity (see Figure 8.16).

Figure 8.15: Hematite test sample measurements in air, with 650 nm probe, 500x gain while varying the probe intensity.
Figure 8.16: TAS of hematite test sample in air at 650 nm and different probe intensities. We only see an increase in the signal to noise ratio with increasing probe intensity, not an increase in signal amplitude.

8.2.5 Fluorescence

While measuring some samples, we found a negative feature lasting a few microseconds. The feature occurred with the probe beam blocked and only using the pump laser to illuminate the sample. Figure 8.17 shows the wavelength dependence of the feature.

Figure 8.17: Measurements of a hematite test sample with the probe beam blocked at different probe wavelengths. We observe a strong negative signal from the APD (in Volts) within a few microseconds after pumping the sample for wavelengths between 550 and 650 nm.

Figure 8.18: The amplitude of the signal from Figure 8.17 at 1.16 µs after pump excitation. The feature is only present at shorter wavelengths.
Because the feature is only present at shorter wavelengths, only with the pump beam active, and with filters and dichroics carefully installed to prevent stray pump laser light, we believe this feature is due to fluorescence of glass. The samples are prepared on a glass substrate and also the electrochemical cell, containing the sample and the electrolyte for in situ measurements, is made out of glass. The shape of the feature in Figure 8.18 resembles fluorescence measurements from literature.\textsuperscript{17} Currently it is not possible to eliminate the fluorescence, apart from subtracting it from the signal (which in turn creates other issues). A quartz electrochemical cell was designed and constructed to eliminate the effect. However, it was not complete in time for use in the present work. In the future, quartz sample substrates will also be utilized. Nevertheless, the fluorescence decayed at times shorter than $1 \times 10^{-5}$ s, so this artifact did not adversely affect the msTAS measurements described in this work. We note that the fluorescence likely decays much faster than the observed few microsecond transient. However, the decay time is due to the slower ISF with the pre-amp installed, as shown in Figure 8.8.

8.2.6 Application of gain and filters

Noise in the system does not allow us to record a time trace from the shortest time delays out to the longest timescales simultaneously. It is necessary to break the time scales up, and apply different electronic filters to each time window. For example, we would use high frequency low pass filters for short time delays, typically in the range of $10^5$ Hz. The low pass frequency was decreased with increased time scale in order to filter out as much high frequency noise from each time scale of interest (see Figure 8.19). The filter can be set to be either of first or second order referring to how strong the filter attenuates the signal frequency above the cut-off frequency. We use a second order filter, or 12 dB/oct, meaning the amplitude of the signal is divided by four every time the frequency doubles. This filter attenuates the amplitude of the signal twice as strong as the other option on the pre-amp, of 6 dB/oct.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure819.png}
\caption{TAS of hematite test sample in air at 650 nm, using different low-pass filters. Decreasing the frequency results in a roll-off} \end{figure}
of the higher frequencies in the signal but also reduced noise in the applicable, longer time window.

In order to find the right balance between preserving as much data in the time domain and obtaining a good signal to noise ratio we experimented with different filters for different time windows, as shown in Figure 8.20.

Figure 8.20: TAS of a hematite test sample in air at 650 nm at different time scales and different low-pass filter settings. We see that traces overlap, until the filter causes a roll-off of the signal at shorter times. This plot was very useful in finding combinations of time scales and filters that would minimize the number of measurements per sample, while maximizing the signal to noise ratio. Using a log-log plot is in this case useful also because it helps to see where the signal has decayed to zero (around 10 ms).

8.2.7 Other comments and considerations

In the previous sections we provided a somewhat chronological view of the developmental stages of the millisecond TAS setup. Now we discuss a number of insights that were not mentioned before but were critical to successful operation of the setup. Generally we found that it is easy to observe noise, but much harder to locate the source. In one instance, we suspected that the fan of the halogen lamp was causing temperature fluctuations in the lamp and thus changes in light intensity. By inserting a long tube between the fan and the housing, we sought to randomize the air stream behind the fan, and thus remove any variation in the cooling of the lamp. It turned out not to have any effect on the noise. As discussed in Section 8.1.2, we found this noise to be caused by a 60 Hz signal being transmitted through the common grounding. We solved this issue by connecting all instruments to an uninterruptable power supply that filtered out the 60 Hz ground noise relative to the table.
Another important aspect to keep in mind is how to connect the different detection units such as the APD, pre-amplifier and the oscilloscope. We lost precious time after receiving erroneous information from Stanford Research Systems on whether to run the pre-amplifier in AC or DC mode. After solving this issue, we made the mistake of using the oscilloscope in AC mode, which significantly distorts the signal due to the 100 Hz high pass filter imposed by the oscilloscope's capacitor in AC mode.

Another key consideration is the impedance of the input and output ports of devices. Getting it wrong can result in very different signal read-outs. In the case of the APD, it can also result in damage. The APD consists of a highly biased piece of silicon, which becomes conductive as the photons cause an avalanche breakdown through the photoelectric effect. The electrons that were created by photons are converted to a potential through a transimpedance amplifier. To protect the detector from damage, there is a maximum $V_{\text{out}}$ determined by the load connected to the detector. For high impedance that is 3.6 V, for low impedance (50 Ω) this is 1.8 V (divide by 2). The pre-amplifier and multimeter connected to the detector have high impedance inputs, thus the maximum output voltage on the detector is 3.6 V. In the case of connecting the pre-amp to the oscilloscope, it is necessary to match the impedance of the input and output. The output impedance of the pre-amp was 50 Ω, while the oscilloscope was set to a high impedance input (1 MΩ). Connecting a 50 Ω terminator to the oscilloscope or multimeter input channel is necessary to correctly impedance match the system.

During the in situ, biased, measurements we also encountered a recurring issue. The TAS data showed distinct peaks or plateaus that were non-physical and were not present when the sample was not connected to the potentiostat. While these features were not present in all traces, we observed that the time vs. current graphs obtained during in situ measurement exhibited large peaks of current. These features were also accompanied by overloading of the potentiostat. The origin of this issue was that the pump laser induces a sudden spike in current through the sample. The maximum current range on the potentiostat, to protect against high currents, was set to ‘auto’, but the response time was too slow to adapt to the pulsed laser excitation. Changing this to fixed value well above the current spike resolved the problem and removed the artifacts from the TAS data. As the experimental system is improved and measurements at lower pump powers becomes possible, this problem should become less critical.

Finally, making sure all optics are properly aligned (and remain aligned) is an important condition for high quality data.

** DC mode involved manually applying an offset bias to the pre-amp using a Keithley 2400 Sourcemeter.
9 Theory and literature overview

Photoanodes play a crucial role in many design strategies for solar water splitting: absorbing light, separating charge and oxidizing water. This chapter will provide a concise overview of the status of the photoanode research in general and specifically we discuss TiO$_2$, Fe$_2$O$_3$ and BiVO$_4$.

9.1 Theory

While much of the background of transient absorption spectroscopy lies within the realm of solid-state physics, the research field where the photoanodes will be used, namely artificial photosynthesis crosses into the realm of electrochemistry or physical chemistry. The aim of this chapter is to go into the main topics that apply to charge carrier dynamics in semiconductors in aqueous environments and the application in photo-electrochemical cells for solar water splitting.

9.1.1 Light absorption in semiconductors

The bulk of a semiconductor contains many energy states, though not all are accessible. The lowest energy bands, such as the 1s states, are highly localized and always occupied. These states do not contribute to charge carrier dynamics in the present systems. Neither do the highest energy levels, as electrons are unable to attain energies high enough to occupy them. We are left with the bands surrounding the Fermi level ($E_F$)$^{\dagger\dagger}$, see Figure 9.1.

Figure 9.1: (a): Energy ($E$) vs. momentum ($k$) energy band diagram, and (b): energy ($E$) vs. density of states (DOS) diagram for typical semiconductor, see text for a description.

$^{\dagger\dagger}$The Fermi level is the level where theoretically the chance of finding an electron is 1/2. Even though, in the case of semiconductors, the Fermi level is located in the bandgap, where no allowed states exist.
Figure 9.1a shows an E-k diagram for a typical semiconductor referring to the energy (E) and momentum (k) of carriers in the band. The lowest band is the spin orbit band (I), which lies below the valence band made up of the heavy-hole (II) and light-hole (III) bands. 'Heavy' and 'light' refers to the effective mass of the carriers, which is inversely proportional to the second derivative of E vs. k. Above the valence band lies the conduction band (IV). Due to conservation of momentum, a photoexcited carrier can only move vertically (1) in the diagram, or diagonally (2) if the carrier can gain or lose momentum through interaction with its environment (e.g. absorbing or emitting a phonon wavepacket). The energy required to move between bands can be supplied by the absorption or emission of photons.

Figure 9.1b shows an energy vs. the density of states diagram of a typical semiconductor. The solid blue area indicates that the states in that valence band (VB) are occupied, while the conduction band (CB) is mostly empty. The fact that there is a gap between these two bands (bandgap) makes the material a semiconductor, and the E_F is situated in between the two bands. When E_F is closer to the conduction band, the semiconductor is of n-type, when it is closer to the valence band it is p-type. For n-type materials, the majority carrier is an electron, and the minority carriers are holes (vice versa for p-type), as indicated in Section 7.1.1.

Quantitatively, the emergence of energy bands can be understood through the Kronig-Penney model representing an electron in a one-dimensional crystal lattice with a periodic potential U_0. The Block theorem states that all solutions for the Schrödinger equation for a periodic potential have the generalized form:

$$\psi_k(x) = u_k(x) \exp(ikx)$$

With \(\psi\) the wavefunction of the electron, \(k\) the wave vector and with potential \(u_k(x) = u_k(x + c)\) indicating the periodicity of the lattice. It is possible (but tedious) to find an analytic solution to this boundary condition problem. One then finds that the energy of an electron in a periodic lattice is confined to a set of allowed values which is the cause of the energy bands in crystal lattices.

The concept of energy bands can be explained qualitatively by saying that the wave functions of the molecular orbits that make up the valence and conduction band are delocalized compared to the lower energy levels. The wave functions of atoms in the crystal overlap significantly. When in a solid the number of molecules becomes very large, the wave functions of the highest occupied and lowest unoccupied become indistinguishable and become continuous throughout the solid, creating bands.

Figure 9.2 shows charge carriers in semiconductors and typical photon absorption transitions. For simplicity sake, we portray the bands as flat (only showing the energy dependence of the transitions), while keeping in mind that momentum has to be conserved for any
transition to occur. It is not uncommon for semiconductors to have gap states, known as trap or defect states, to which electrons and holes can transition to or from. A final remark, holes act as quasi particles and can also absorb light, see Figure 9.2 (V).  

Figure 9.2: Typical absorption mechanisms in semiconductors, showing transitions of electrons (solid dots) and holes (circles) between energy bands, trap states and energy levels surrounding the VB and CB. For simplicity, the bands are displayed as being flat. (I) An electron is excited from the valence band into a trap state under absorption of a photon \( (h\nu) \), leaving a hole (blue circle) on the valence band, (II) an electron in the trap state transitions to a higher energy level, (III) a VB electron absorbs a photon of energy higher than the bandgap and transitions to the CB, (IV) a CB electron is excited to a higher energy state, (V) a hole absorbs a photon and transitions to a lower level. Not all possible transitions are shown, as it is also possible, for example, for electrons to move from the trap state to the CB, or from the VB to the higher states above the CB.

9.1.2 Electron-hole recombination

Let us now look at different mechanisms through which charge carriers can recombine. Six different categories of charge recombination are indicated in Figure 9.3. Bulk recombination consists of either direct band-to-band recombination or trap-assisted recombination. In the latter case, gap states exist, which lie within the forbidden bandgap, and are present due to crystal impurities (such as doping, vacancies, anti-sites, etc.). Gap states close to either the conduction or the valence band can act as efficient recombination centers. This is because charge carriers first need to occupy the trap state, before recombination can occur, and this is easier close to the band edges. Gap states far away from the band edges, also known as deep levels, are highly localized in real space, but delocalized in k-space. Therefore, they can enable recombination of electrons and holes at different k-values (i.e. across an indirect gap). Another recombination pathway is across the bandgap in the depletion layer. At the semiconductor liquid junction (SCLJ), electronic defect states, often referred to as surface states, exist. They are caused by the abrupt termination of the crystal and can act as recombination centers. It is also possible for electrons to tunnel through the potential
barrier caused by the band bending and recombine with surface-accumulated holes. Finally, electrons with sufficient thermal energy can overcome the potential and transfer across the interface into the electrolyte. In principle, all recombination mechanisms can be suppressed, except bulk recombination. In practice, all recombination mechanisms contribute to efficiency losses in parallel and passivation methods, as well as carrier selective blocking layers, are actively developed to reduce their impact on device performance.\textsuperscript{49}

![Image](image.png)

**Figure 9.3**: Recombination pathways for electrons and holes at a SCLJ for an $n$-type semiconductor following photoexcitation. The figure also includes the creation and subsequent band edge relaxation of excitons ($J_{ex}$). With $J_{br}$ bulk recombination, $J_{dr}$ depletion region, $J_{ss}$ surface states, $J_t$ tunneling and $J_{et}$ electron transfer across the surface. We see oxygen evolution occurring from the valence band. Note that the surface states might both facilitate recombination and oxygen evolution, this is part of an ongoing debate in the literature. Indicated are the typical time scales at which these processes occur. The solid arrows represent the hole absorption by the electrolyte and electron extraction by the back contact, which contribute positively to device performance. Adopted from Lewis\textsuperscript{49}.

All processes have different characteristic kinetics that lead to different decay times. This can aid in determining the physical origin of decay traces in transient absorption spectroscopy (TAS), as we attempt to do in this thesis.
9.1.3 Water oxidation kinetics in PEC

The light absorbing properties of semiconductors can be utilized not only for generating electricity, but also for storage in the form of hydrogen. Water oxidation in photo-electrochemical cells (PEC) is a complicated multistep process involving four electrons and four protons. By some it is called ‘one of science’s grand challenges’.\(^{50}\)

9.1.3.1 Water oxidation

We will discuss water splitting for a PEC design involving a separate n-type photoanode and a cathode in a conductive electrolyte, connected through a wire (see Figure 9.4).\(^{20}\)

![Figure 9.4: Photo-electrochemical cell for solar water splitting. See text for description. Adopted from Bak et al.\(^{51}\)](image)

Photons create excitons, or electron-hole pairs, in the photoanode. The holes will travel to the surface of the photoanode where they oxidize water in the electrolyte and generate protons:

\[
2 \mathrm{H}^+ + \mathrm{H}_2\mathrm{O} (l) \rightarrow \frac{1}{2} \mathrm{O}_2 (g) + 2 \mathrm{H}^+ \tag{11}
\]

The electrons move to the cathode through the circuit (see section 7.1.1 on the potentiostat) and the protons move to the cathode through the electrolyte, where protons are reduced to \(\mathrm{H}_2\):

\[
2 \mathrm{H}^+ + 2 \mathrm{e}^- \rightarrow \mathrm{H}_2 (g) \tag{12}
\]

Overall, including the two photons required to produce two electron-hole pairs, the solar water splitting reaction is:

\[
2\mathrm{hv} + \mathrm{H}_2\mathrm{O} (l) \rightarrow \frac{1}{2} \mathrm{O}_2 (g) + \mathrm{H}_2 (g) \tag{13}
\]

According to the Nernst equation

\[
E = \frac{\Delta \gamma F}{2N_A} \tag{14}
\]

the Gibbs free energy required to split one mole of \(\mathrm{H}_2\mathrm{O}\) is 247.14 kJ mol\(^{-1}\), and \(N_A\) is Avogadro’s number. This gives us a minimum photon energy of 1.23 eV (or photon wavelength of approximately
1000 nm) required to drive reaction (13). The electrons in the system now create a potential of 1.23 V (also called electromotive force, EMF) over the system. However, this only holds in a case were no losses occur in the PEC. For example, even large bandgap materials such as TiO_2 only produce photo voltages of maximally ≈ 0.9 V.\textsuperscript{51} An externally applied bias or tandem configuration with two or more light absorbers is therefore required to provide the overpotential required to drive the water splitting reaction in a PEC. We will discuss this is more detail in the next section.

9.1.3.2 Band energetics in PECs

We now discuss the band energetics that allow for solar water splitting in PEC systems, step by step, from Figure 9.5 to Figure 9.9. In the first scenario we find an n-type semiconductor and metal cathode (often Pt) submerged in a conducting electrolyte, in the dark. We see the valence band (E\textsubscript{V}), conduction band (E\textsubscript{C}) and bandgap (E\textsubscript{g}) of the semiconductor. The Fermi levels (E\textsubscript{F1}, E\textsubscript{F2}) and work functions (\Phi\textsubscript{1}, \Phi\textsubscript{2}) of both materials are shown, as well as the potentials for the redox couples (H\textsuperscript{+}/H\textsubscript{2}; O\textsubscript{2}/H\textsubscript{2}O). This is before equilibration of the Fermi levels, and no band bending has yet occurred.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{Energy diagram for an n-type semiconductor (left) and metal (right) with no illumination of the setup and no contact between the n-type semiconductor and the metal cathode. See text for description. Adopted from Bak et al.\textsuperscript{51}}
\end{figure}

When we connect the photoanode to the cathode, charge flows between both electrodes until the Fermi levels equilibrate, charge will flow mostly from the material with higher work function, the anode in this case, see Figure 9.6.
As the Fermi level drops, so does the valence band and upward band bending occurs (with $eV_B$). This is also shown in Figure 9.7, explained from a different perspective. Figure 9.7a, shows the case before equilibrium, then, the charge in the semiconductor equilibrates with the electrolyte and band bending occurs. The direction of band bending (upwards or downwards) depends on the relative position of the Fermi energy and the electrochemical potential, which, in turn, affects the flatband potential of the semiconductor. Ideally, the flatband potential is equal to this difference. However, other factors, including the presence of surface defects, can lead this value to deviate from the ideal. The value can be determined through Mott-Schottky analysis. In Figure 9.7b we see an excess negative charge build-up on the electrolyte side of the SCLJ. A Schottky-type contact is formed on the SCLJ, and free electrons from the bulk are trapped at states on the semiconductor surface. Overall charge neutrality exists by the balance of ionized atoms in the bulk and this negative layer of electrons. The near-surface region of the semiconductor, in which these ionized atoms are located, is known as the space charge layer (due to the presence of ionized fixed charge, in this case cations) or, equivalently, as the depletion layer (due to the depletion of free charge carriers, in this case electrons). Due to this space charge layer, an electric field is present in the semiconductor. It is this field that can enable photogenerated electron-hole pairs to be physically separated, with extraction of electrons in the direction of the bulk, and holes in the direction of the interface. Thus, because of the difference between the electrochemical potential, the Fermi level of the photoanode and the Fermi level of the cathode, there naturally occurs charge separation of the electron-hole pairs created by light.\textsuperscript{52}
Figure 9.7: Energy band diagrams at an (n-type) semiconductor liquid junction. With \( E_c \) the conduction band, \( E_f \) the Fermi level, \( E_V \) the valence band, \( E_{\text{redox}} \) the redox potential of the electrolyte, + positive charge carriers, - negative charge carriers, \( \Theta \) conduction band electrons. Adopted from Grätzel.\(^{53}\)

When we illuminate the photoanode (Figure 9.8), with photons of energy greater than \( E_g \), holes are created in the \( V_B \) and electrons in the \( C_B \). This changes the surface potential of the photoanode, as well as the band edge positions relative to the \( \text{H}^+/\text{H}_2 \) potential, by an amount equivalent to the photovoltage \( V_{\text{ph}} \), as shown in Figure 9.8. However, for the case given, \( E_f \) of the metal is still below the hydrogen reduction potential and overall water splitting cannot occur.

Figure 9.8: Illumination of the n-type semiconductor. See text for description. Adopted from Bak et al.\(^{51}\)

The solution is to apply a bias to the circuit, as shown in Figure 9.9. The bias increases the Fermi level of the cathode with \( E_B \), and is now above the \( \text{H}_2 \) reduction potential with \( U_a \). The valence band is below the \( \text{H}_2\text{O} \) oxidation potential with \( U_a \). The extra energies \( U_c \) and \( U_a \) are the overpotentials needed to account for losses in the system and drive reactions at the catalysts in the desired direction.\(^{51}\)
Another class of PEC designs is the so-called ‘wireless’ approach, which does not require an externally applied bias. This approach is pursued by JCAP. Figure 9.10a shows a single bandgap design involving an n-type photoanode in ohmic contact with a metal cathode, but is also possible with a p-type photocathode and metal anode. Charge is separated at the SCLJ of the semiconductor which pushes the minority carriers to oxidize water, while the majority carriers recombine at the semiconductor / metal interface which drives the other half of the redox reaction. While simple (and thus generally cheap), the single bandgap design often does not produce enough photovoltage to drive the reaction and requires semiconductors with wide bandgaps that are not well matched to the solar spectrum (see below). Instead of using a metal cathode, a p-type photocathode can be used to provide additional driving force (Figure 9.10b). Another way to increase the photovoltage is to include a p-n junction photovoltaic cell in between an n-type photoanode for water oxidation and a metal cathode for hydrogen reduction (Figure 9.10 c). In Figure 9.10d, only metal anode and cathode are used with two p-n PV cells, referred to as a ‘buried junction’, as no SCLJ exists. Figure 9.10b – d are examples of dual bandgap configurations designed to utilize a larger part of the solar spectrum.\textsuperscript{20}
Photoanodes are required to perform multiple functions simultaneously while not dissolving or otherwise degrading in often corrosive environments. As mentioned before, the efficient oxidation of water is necessary to provide protons and electrons both for hydrogen production and for CO\textsubscript{2} reduction. This underlines the importance of photo-anodes for solar fuel production in general. One of the crucial properties of photo-anodes is the size of the bandgap because it provides an upper limit for the PEC efficiency. We consider the case of a single bandgap PEC device, in the absence of bias. The maximum solar-to-hydrogen efficiency, $\eta_{\text{STH}}$, is calculated using:\cite{footnote23}

$$\eta_{\text{STH}} = \frac{j_{\text{photo}}V_{\text{redox}}}{P_{\text{light}}}$$  \hspace{1cm} (15)

With $P_{\text{light}}$ equal to 100 mW/cm\textsuperscript{2} (AM1.5 one sun intensity) and $V_{\text{redox}}$ (1.23 V) the potential required to drive the water splitting redox reaction. The quantity $j_{\text{photo}}$ is calculated by integrating the solar spectrum above the bandgap energy, assuming all photons above the bandgap are absorbed and that all absorbed photons lead to a photocurrent that is available for water splitting.\cite{footnote23} Note that by combining materials with different bandgaps, the theoretical maximum efficiency can be increased.\cite{footnote23} Because of the stability requirement for photoanodes, metal oxide semiconducting materials

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\footnote{This adds to the complexity of the device, which often implies greater losses.}
have been the focus of much research and also the focus of this thesis. The bandgap energies and maximum theoretical efficiencies of commonly used metal oxide photoanodes are listed in Table 2.

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>Bandgap (eV)</th>
<th>η_{STH} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Fe₂O₃</td>
<td>2.1</td>
<td>15.3</td>
</tr>
<tr>
<td>WO₃</td>
<td>2.5</td>
<td>7.5</td>
</tr>
<tr>
<td>BiVO₄</td>
<td>2.4</td>
<td>9.2</td>
</tr>
<tr>
<td>TaON</td>
<td>2.4</td>
<td>9.2</td>
</tr>
<tr>
<td>TiO₂ (anastase)</td>
<td>3.26</td>
<td>1.1</td>
</tr>
<tr>
<td>TiO₂ (rutile)</td>
<td>3.05</td>
<td>2.0</td>
</tr>
</tbody>
</table>

*Table 2: Bandgap values and solar-to-hydrogen efficiencies of commonly used metal oxide photoanodes, adopted from Schoonman and Van De Krolo.*

In the traditional case of a single bandgap PEC design, where a photoanode is connected to a metal cathode through a wire (previous Section 9.1.3.2), a Schottky junction is formed at the SCLJ. When the photoanode is illuminated, the Fermi level is split into quasi-Fermi levels for the electrons and holes in the semiconductor. The electron quasi-Fermi level equilibrates with the reduction potential of the electrolyte and the Fermi level of the metal cathode. The potential difference between the quasi-Fermi levels constitutes the maximum energy that can be extracted from the semiconductor. If the potential difference is higher than 1.23 V plus an overpotential, the water splitting reaction can take place in the PEC. Generally, the larger the band gap, the larger the achievable quasi Fermi-level splitting. We now find a fundamental dilemma of solar water splitting. The bandgap needs to be large enough to provide sufficient energy for the redox reaction, but small enough to absorb enough sunlight. These problems can be solved by using multi bandgap designs, although that implies higher complexity.

9.1.3.4 Catalysts

Often catalysts are used in order to improve the water splitting kinetics and decrease the necessary overpotential. This results in better photocurrents at lower potentials (see Figure 9.11).
Figure 9.11: (a) Qualitative representation of the effect of catalysts. The onset potential, the potential at which a photocurrent is present, is shifted to the left for both the light and dark reactions. Adopted from Walter et al.\textsuperscript{20} (b) Actual photocurrent measurements of hematite photoanodes with electrodeposited cobalt phosphate (Co-Pi) catalyst on the surface. A beneficial anodic onset potential is observed. Adopted from Zhong et al.\textsuperscript{55}.

On the bare surface of semiconductors hydride species\textsuperscript{88} often form that constitute a barrier for hydrogen production. Effective catalysts are capable of facilitating the required reaction as fast as the light absorber can supply electrons or holes and remain stable. Catalysts are generally thin films or particles on the semiconductor surface. This is to prevent blocking of the photons that need to be absorbed by the semiconductor. When metallic catalysts are present on the semiconductor surface, minority carriers\textsuperscript{***} must be injected from the semiconductor into the catalyst and, from there, to the redox couple. The catalyst can form a Schottky contact with the semiconductor, where the Fermi level of the catalyst equalizes with the Fermi level of the semiconductor. For a continuous thin film catalyst, this can result in a loss in the voltage provided by the junction. For effective catalysis, the associated energy loss must be smaller than the gain in the redox reaction rate. Alternatively, porous catalysts or particles can be used so that the SCLJ is retained but catalytic activity is improved. In these ways, the catalyst proves to be beneficial to the overall PEC performance.\textsuperscript{20}

Many examples of catalysts are found in the literature. The designs with record breaking solar-to-hydrogen (STH) efficiencies discussed in the introduction use platinum and RuO\textsubscript{2} catalysts.\textsuperscript{23,56} Other frequently used catalysts are based on cobalt, as in the reports by Nocera.\textsuperscript{9,10} Figure 9.11 shows the effect of the cobalt phosphate (Co-Pi) catalyst on hematite. The Co-Pi catalyst has also been used during the research for this thesis.

\textsuperscript{88} Hydride species are binary compounds (containing only two elements) of which one elements is hydrogen.

\textsuperscript{***} Charge carriers that react with the redox couple are always the minority carriers due to the direction of the band bending. In n-type semiconductors these are the holes.
There is debate on the role of the Co-Pi catalyst.\textsuperscript{57} The notion that the catalyst is responsible for enhancing reaction rates even though it forms a barrier for carriers between the semiconductor and electrolyte might not be correct. Barroso et al.\textsuperscript{58} argue that the enhanced hole lifetime they observe through TAS is caused by the Schottky barrier itself, not by accelerating the reaction rate at the catalyst / liquid junction. Due to observed similarity in decay traces for biased hematite without catalyst and unbiased hematite with catalyst the study concludes that this must be due to enhanced charge separation in the semiconductor.

Finally, an interesting article was published on so-called adaptive semiconductor / electrocatalyst junctions.\textsuperscript{59} The study discovered that ion-permeable catalysts can form a Schottky interface with the semiconductor where the energy barrier changes in situ with the oxidation state of the catalyst film. The oxidation state of the catalyst changes as it evolves oxygen (from Ni\textsuperscript{2+} to Ni\textsuperscript{3+/4+}, in this study). The extra positive charge is compensated by ions from the bulk of the electrolyte that can move through the catalyst layer. This causes the Fermi level of the catalyst to change and thus the difference with the conduction band of the semiconductor which constitutes the energy barrier. This is as opposed to ion-impermeable catalysts that have a buried junction and thus a fixed barrier height. As the barrier height increases, so does the open circuit voltage which determines the maximum amount of energy to be extracted from the semiconductor.

\section*{9.2 Literature review of selected photoanodes}

We have arrived at the core subject of this thesis. Photoanodes play a crucial role in design strategies for solar water splitting: absorbing light, separating charge, and oxidizing water. Due to stability requirements, one major focus of the field of photoanodes is on metal oxides and specifically to find ways of reducing the overpotential necessary to drive the water splitting reaction. The application of nanostructured and mesostructured surfaces has greatly increased photocurrents in materials that exhibit poor charge transport properties by allowing charge carriers created more deeply absorbed photons to be extracted to a nearby surface.\textsuperscript{60}

Furthermore, finding the balance between the following two quantities is key. Firstly, in order to efficiently extract minority carriers from the semiconductor, the carrier mobility is an important property related to the material quality. Secondly, by increasing the bulk conductivity through introducing dopants, voltage drops in the material can be minimized. However, increased majority carrier concentration decreases the width of the space charge layer, which facilitates charge separation. In the case we are considering, the minority carriers are holes and the majority carriers are the electrons.
To make intelligent choices for designing efficient photoanodes, it is essential to properly understand the charge carrier dynamics inside these materials. In the next sections we discuss the interplay of crystal structure, light absorption and charge recombination pathways for three metal oxides. This chapter will provide a concise overview of the status of photoanode research in general. In addition, details of progress in research related to TiO$_2$, Fe$_2$O$_3$ and BiVO$_4$ will be presented.

9.2.1 Fe$_2$O$_3$ photoanode

Hematite, α-Fe$_2$O$_3$, is a well-characterized phase of iron oxide that was first used as a photoanode in 1976.\textsuperscript{61} It is the most common crystalline form of iron oxide. The Fe$^{3+}$ and the O$^{2-}$ are arranged in the corundum structure. The anions surround the cations hexagonally, as shown in Figure 9.12.\textsuperscript{62}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.12.png}
\caption{(a) Unit cell of hematite. (b) Detail of the unit cell. The electrostatic repulsion of the cations causes two different Fe-O bond lengths, as indicated by the light grey (long) and dark gray (short) rods. Adopted from Sivula et al.\textsuperscript{63}}
\end{figure}

Hematite shows weak infrared absorption (α ≈ 10$^3$ cm$^{-1}$), caused by d-d transitions of Fe$^{3+}$, which does not lead to a photocurrent.\textsuperscript{64,65} The absorption coefficient remains fairly low until and after the bandgap energy. Specifically hematite shows absorption peaks at 2.4, 3.2 and 5.8 eV, which explains the red color of rust.\textsuperscript{66,67} The bandgap size is between 1.9 and 2.2 eV (see Table 2). Although there still seems to be a debate on the nature of the bandgap, recent studies\textsuperscript{68–70} conclude that the transition is likely between O 2p (valence band) and Fe 3d (conduction band) states. Electrical conductivity is low (10$^{-14}$Ω$^{-1}$cm$^{-1}$).\textsuperscript{71} Studies\textsuperscript{72,73} have modeled charge carrier transport as carrier ‘hopping’ between F$^{3+}$ and Fe$^{2+}$ which can be thought of through a polaron\textsuperscript{‡‡‡} model, because of the different sizes of F$^{3+}$ and Fe$^{2+}$. Carrier transport requires an activation energy because it is phonon

\textsuperscript{‡‡‡} Also known as rust.

\textsuperscript{‡‡‡} A polaron is a lattice distortion as a result of crystal ions being attracted or repulsed by charge carriers.
assisted which would explain the higher conductivity at increased temperatures.\textsuperscript{74} To increase hematite conductivity, which is required for PEC applications, the introduction of impurities is necessary. Different dopants can create n-type (Ti\textsuperscript{4+}, Sn\textsuperscript{4+}, Zr\textsuperscript{4+}, Nb\textsuperscript{4+}) or p-type (Mg\textsuperscript{2+}, Cu\textsuperscript{2+}) hematite with increased carrier concentrations and electron mobility.\textsuperscript{72,74}

Let us summarize the mechanisms and potential solutions governing PEC performance in hematite. The bandgap of hematite is smaller than most metal oxide semiconductors and the material can potentially absorb around 40% of the solar spectrum. Also, hematite is chemically stable with maximum theoretical STH efficiencies of approximately 15%.\textsuperscript{75} Unfortunately hematite has a long optical absorption length in the visible part of the solar spectrum, poor carrier mobility and a short hole diffusion length of 2-20 nm.\textsuperscript{66,71,74,76} Water oxidation kinetics are slow.\textsuperscript{77,78} Furthermore, the position of the flat band potential is thermodynamically unfavorable,\textsuperscript{76} see Figure 9.13. These factors lead to high overpotentials to drive the redox reaction. In order to increase electron concentration and increase conductivity, dopants are introduced which decreases the width of the depletion region.\textsuperscript{79} Combining this limitation with a low absorption coefficient causes the ratio between the space charge layer and semiconductor thickness to become very low. Adding to the complexity is the very short hole diffusion length. These factors work perfectly against each other culminating in low quantum efficiencies.

![Figure 9.13: Solar water splitting using n-type semiconductor α-Fe\textsubscript{2}O\textsubscript{3}. Note that a bias potential \(V_b\) is required to drive the Fermi level up in the counter electrode (often Pt) for water oxidation to occur. Adopted from Sivula et al.\textsuperscript{67}](image)

As indicated above, the small space charge layer combined with a very short hole diffusion length provides a major drawback for hematite photoanodes. One class of solutions constitutes the use of complex PEC designs such as tandem configurations (such as in Figure 6.1c). An issue with this approach is the high cost that comes with complexity. Another would be to tune the morphology of the
hematite surface. An example of the latter is the nanowire approach, which we employ in this thesis. Nanowires on conducting FTO would minimize grain boundaries which enhances the majority carrier (electron) transport and still allows the minority carriers (holes) to travel to the SCLJ. Other possible solutions could be introducing a surface catalyst such as Co-Pi, which in some cases resulted in a 0.1 V cathodic shift in the onset potential. Yet another approach focuses on the surface traps that act as recombination centers. These surface states can be passivated using an extremely thin metal oxide overlayer, such as Al₂O₃, resulting in some cases in a 0.1 V onset potential shift.

Figure 9.14 shows the TAS spectrum of Si-doped hematite without an applied bias. The main feature in this graph is a transient absorption peak around 580 nm with a lifetime of approximately 10 ms. However, ultrafast TA studies show free charge carriers lifetimes on the order of a picoseconds – far too short for effective water oxidation. Also, the effect of hole scavengers on this decay lifetime is reported to be negligible pointing to the conclusion that the electron-hole recombination is taking place in the bulk of the material. The application of an anodic (positive bias) has a significant effect on the TAS signal of the material as shown in Figure 9.15.

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Figure 9.14: Transient absorption spectroscopy measurement of unbiased Si-doped atmospheric pressure CV α-Fe₂O₃. Measurement is performed under Ar. Pump wavelength used is 355 nm at an intensity of 200 μJ /cm² at 1 Hz repetition rate. The trace is obtained at a probe wavelength of 580 nm, while the spectrum in the inset is obtained at a delay time of 500 ns. The sample was immersed in an alkaline electrolyte and illuminated from the side of the semiconductor/electrolyte interface (front side). The decay trace was fitted with an exponential function (light blue). Adopted from Barroso et al.

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Chemical vapor deposition.
Figure 9.15: Effect of an anodic bias on the TAS spectrum of nanostructured Si-doped CVD grown hematite in 0.1 M NaOH. The sample was pumped using a 355 nm, 200 uJ cm\(^2\) laser at a repetition rate of 0.33 Hz. A 75 W Xe lamp was used in combination with a monochromator to probe the changes in absorption. Adapted from Barroso et al.\(^75\)

The emergence of a broad long-lived absorption band is shown in Figure 9.15 with an applied bias of 0.8 V vs. RHE. This feature is assigned by Barroso et al.\(^75\) to photo-generated holes. The rationale is that the bias, anodic of the flat band potential, extracts the electrons from traps and mid bandgap states in the hematite. This reduces the recombination of these electrons with holes and leads to the formation of a depletion region near the SCLJ and subsequent enhanced charge separation. They conclude that the long-lived absorption thus must be due to holes. Furthermore, the presence of the hole scavenger methanol, reduces the decay lifetime by a factor of 5. This indicates that the holes are located on the surface of the hematite and are the source of water oxidation. The latter conclusion is drawn from an observed correlation between the PEC performance and the decay time of these long-lived photogenerated holes. The 580 nm bleach feature is assigned to band filling, or the Moss-Burstein effect, based on difference steady state absorption under applied biases.\(^75\)

Recently, the mechanism through which water oxidation in hematite occurs was investigated through impedance spectroscopy.\(^85\) Figure 9.16 shows a generalized model of how recombination and water oxidation occurs. It also shows the density of states of the surface states for different pH values of the electrolyte. The surface states are mainly located below the potential for water oxidation and are thus able to oxidize water. The study shows that trap assisted water oxidation is the main route for photo-generated holes, instead of traveling from the valence band to the SCLJ.
Figure 9.16: (a) Model for recombination and water oxidation in hematite. (b) DOS calculations of hematite surface states at different pH levels. The solid lines are the DOS at pH of 6.9, the dashed lines the DOS at pH 13.3. Different illumination intensities are shown: 0.1 sun (orange triangles), 0.33 sun (yellow squares) and 1 sun (green diamonds). Adopted from Klahr et al.85

9.2.1.1 Recent developments

The solar water oxidation field is very active and new papers come out every day. Here, we discuss some promising recent work.

Li et al.86 combine hematite nanorods with plasmonic gold nanoholes. This enhances sub bandgap energies and acts as a waveguide for supra bandgap photons. The study reports a tenfold increase in photocurrent at a bias of 0.23 V vs. Ag/AgCl.

An interesting study by Warren et al.87 report a method to distinguish the effect of different nanostructures. The report identifies ‘champion’ morphologies that might exist within a single sample using an AFM. This enables them to distinguish the differences of performance resulting from different structure that naturally occur within one sample.

Figure 9.17: (a) Using a conductive AFM it is possible to measure the charge transport properties of individual nanostructures, indicated with different colors. Adopted from Warren et al.87. (b) Growth strategy using gold nanoholes and hematite nanorods to use plasmon induced resonant energy transfer to accomplish higher photocurrents. Adopted from Li et al.86.

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*Atomic force microscopy.*
Cao et al.\textsuperscript{88} found that an acid treatment that corrodes the surface of Ti\textsuperscript{4+} doped hematite causes a cathodic shift of the onset potential with as much as 100mV. The mechanism by which this occurs is thought to be by reducing the back reaction. Another study that improves the onset potential position involves an undoped hematite substrate, with Ti\textsuperscript{4+} doped hematite nanorods on top β-FeOOH ‘nanobranches’\textsuperscript{89}. The supposed role of the β-FeOOH particles on the nanorods is to decrease resistance between the semiconductor and the electrolyte.

9.2.2 BiVO\textsubscript{4} photoanode

Bismuth vanadate was first used as a photoanode in 1998 by Kudo et al.\textsuperscript{90}. BiVO\textsubscript{4} has a band gap of approximately 2.4 eV, which is larger than desired for a photoanode (see Table 2). However, the valence band is favorably positioned at 2.4 V vs. RHE, which is sufficient for water oxidation.\textsuperscript{91} Another advantage of BiVO\textsubscript{4} are the comparatively light effective masses of the charge carriers, this should lead to low carrier resistivity.\textsuperscript{92,93} These properties, combined with availability of the materials, make BiVO\textsubscript{4} a promising photoanode. On the downside of BiVO\textsubscript{4}, the conduction band is below the H\textsubscript{2} reduction potential \textsuperscript{††††} for water oxidation.\textsuperscript{91} Also, the carrier recombination rates are high, the carrier diffusion length is relatively short, and the intrinsic water oxidation kinetics are slow. Just as in hematite, a multitude of approaches exist to solve these issues, such as doping (with W or Mo), surface morphology manipulation (nanostructured materials) and hetero-structures (coupling with other metal oxides).\textsuperscript{94}

BiVO\textsubscript{4} occurs in two main crystal structures, scheelite and zircon.\textsuperscript{95} Figure 9.18 shows the differences between these structure types. The crystal structure is important for the PEC performance, and it is found that monoclinic scheelite has better photocatalytic properties than the zircon type. This is due to the smaller bandgap of scheelite BiVO\textsubscript{4}.\textsuperscript{96}

There is an ongoing debate on the nature of the bandgap, whether direct or indirect. Part of the research for this thesis was involved in studying the bandgap properties of BiVO\textsubscript{4}. It was found that BiVO\textsubscript{4} is in an indirect semiconductor, with a direct transition relatively close to the bandgap. Other studies arrived at slightly different findings. DFT calculations by Walsh et al.\textsuperscript{92} show a direct bandgap dominated by a O 2p band and a conduction band mainly consisting of V 3d. Payne et al.\textsuperscript{97} find a direct bandgap of 2.48 eV through diffuse reflectance spectroscopy and X-ray spectroscopy (see Figure 9.19), while Zhao et al.\textsuperscript{93} found BiVO\textsubscript{4} to be an indirect semiconductor.

\textsuperscript{††††} Disadvantageous in the case of single photoelectrode PEC device.
Figure 9.18: Blue: bismuth; red: vanadium; grey: oxygen. (a) tetragonal scheelite, (b) zircon, (c) tetragonal scheelite, (d) monoclinic scheelite, (e) zircon. Bond lengths are in Angstrom. Adopted from Park et al.\textsuperscript{98}

Figure 9.19: (a) Ion-projected electronic density of states from Walsh et al.\textsuperscript{92}, (b) diffuse reflectance spectroscopy and (c) XES, XAS measurements, adopted from Payne et al.\textsuperscript{97}

The main issue with the low efficiencies in BiVO\textsubscript{4} was found to be the high recombination rate due to poor charge separation.\textsuperscript{98} An interesting discovery was the effect of front versus backside illumination by Liang et al.\textsuperscript{99} In these experiments, a layer of FTO was covered with SnO\textsubscript{2} on which BiVO\textsubscript{4} was deposited using spray pyrolysis. Illuminating the backside of the sample (the side of the FTO) provided a much higher photocurrent than illuminating from the front side of the BiVO\textsubscript{4}. Figure 9.20 shows a proposed explanation. As opposed to hematite, the electron diffusion length is short, while the hole diffusion length is long. Thus, illuminating the sample from the back facilitates electron extraction due to a shorter path length for the electrons. This leads to significant higher IPCE value of 46% at 450nm and 1.63 V vs. RHE for W-doped BiVO\textsubscript{4}/FTO/SnO\textsubscript{2} (an increase of approximately a factor of 7 from BiVO\textsubscript{4} on FTO). Abdi et al.\textsuperscript{100,101} however found that over 60% of the excitons recombine before reaching the SCLJ, which means
photocurrents are still very low. Even though doping with W aids electron transport, resulting in higher photocurrents ($\approx 2.3$ mA cm$^{-2}$ at 1.23 V vs. RHE with 1% W-doped BiVO$_4$ with the Co-Pi catalyst$^{102}$), poor charge separation remains a challenge for BiVO$_4$. However, as the author of this thesis experienced first hand, stability is an even greater issue for BiVO$_4$.

![Figure 9.20: Back (a) versus front (b) illumination of BiVO$_4$ photoanodes on a FTO substrate. Due to short electron diffusion length, illumination from the back reduces recombination when compared to illumination from the front. Adopted from Liang et al.$^{99}$](image)

Another study by Abdi et al.$^{103}$ employing time-resolved microwave conductivity spectroscopy revealed the origin of the low photocurrents. The report estimates the extremely low carrier mobility at approximately $4 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ (undoped BiVO$_4$, 1 sun illumination), but with a diffusion length of 70 nm, which is relatively long. They conclude that W-doping creates carrier traps that reduce the carrier mobility, but also increases carrier density, which combined results in higher photocurrents.

One of the first studies on transient absorption on BiVO$_4$ was conducted by Aiga et al.$^{104}$ The report employs ultrafast transient absorption spectroscopy and uses electron scavengers (Fe$^{3+}$) to identify the charge carriers. The features below 700 nm are assigned to surface holes, while above 700 nm the transient absorption is attributed to charge carriers (either electrons or holes) in the bulk. Figure 9.21 shows that the presence of electron scavengers increases the amplitude of the transient signal. According to the report, this is due to a decrease in electrons, causing a decrease in surface recombination. Thus the feature at 633 nm must be assigned to surface holes. Whether this assessment is accurate is not entirely clear, as the differences between traces in Figure 9.21 are small (and normalized).
Figure 9.21: Ultrafast transient absorption spectroscopy of BiVO$_4$ in different solutions. At 850 nm no difference is measured, while at 633 nm the presence of electron scavengers causes an elongated lifetime of the transient pointing towards the presence of surface holes. Adopted from Aiga et al.

9.2.2.1 Recent developments

An interesting approach to solve the low charge separation in BiVO$_4$, though this approach is not limited to BiVO$_4$, comes again from Abdi et al. The study uses so-called gradient doping to facilitate more efficient charge separation. Like the reports we discussed above by this group, the dopant is W and a Co-Pi catalyst is used. Figure 9.22 shows the principle of gradient doping and the associated charge separation. The gradient doped BiVO$_4$ shows 80% charge separation at a bias of 2.0 V vs. RHE. Combining this photoanode with a double junction amorphous silicon solar cell, the researchers were able to achieve a maximum of 4 mA cm$^{-2}$, or 4.9% STH.

Figure 9.22: Different doping profiles, (a) 1% W: BiVO$_4$, (b) 1% W: BiVO$_4$/BiVO$_4$, (c) BiVO$_4$/1% W: BiVO$_4$, (d) starting from 0% doped BiVO$_4$ towards 1% doped BiVO$_4$ with incremental steps. Adopted from Abdi et al.
Figure 9.23: Measurements of level of charge separation of the compounds shown in Figure 9.22, with gradient doped W:BiVO$_4$ showing the best performance. Adopted from Abdi et al.$^{13}$

Other studies attempt doping using molybdenum and an iron oxyhydroxide (FeOOH) overlayer with mixed success. One study$^{105}$ concludes that Mo improves charge separation (up to 57% at 0.6 V vs. RHE) but the hole injection yield of the FeOOH overlayer is not unity. So while the catalyst enhances the water oxidation kinetics, the increased surface recombination prevents overall higher performance. Another study$^{106}$ does record higher performance using the FeOOH overlayer.

Jiang et al.$^{107}$ take a combinatorial approach to finding optimal doping combinations for BiVO$_4$. Using ink-jet printing of oxide precursors the researcher created a high-throughput combinatorial system to analyze different dopant levels. W doping showed the best result with an 18 fold increase in photocurrent. However, the bandgap increased compared to undoped BiVO$_4$.

9.2.3 TiO$_2$ photoanode

It has been over forty years since water oxidation was first demonstrated, and titanium dioxide (titania, TiO$_2$) was used as the first photoanode.$^{17,18}$ Four decades later, Fujishima shows in a review article$^{16}$ that the number of citations of the 1972 paper and the number of papers on TiO$_2$ photo-catalysis was increasing exponentially during the 2000s.

This continued interest has a number of explanations. Low cost, chemical stability, favorably positioned valence and conduction bands are named as important advantages of TiO$_2$ as photoanode.$^{108}$ However, theoretical limits of STH efficiency are low, because of the large bandgap of 3.2 eV for anatase TiO$_2$ (see Table 2). High electron-hole recombination rates (60 to 90% up to the nanosecond regime some studies show$^{109-111}$) are seen as an important limiting factor for high quantum efficiencies. The vast amount of studies conducted on TiO$_2$ might make it an excellent test case for water oxidation studies, which could explain the continued interest. Also, narrowing the bandgap could make TiO$_2$ a realistic photoanode candidate.$^{112}$ Finally,
as the author experienced during research for this thesis, TiO$_2$ is highly corrosion resistant, making it suitable as an overlayer protecting other semiconductors in a multijunction cell.

Figure 9.24 shows the identification of the charge carriers in TiO$_2$. Trapped holes peak at approximately 520 and 1200 nm, trapped electrons around 770 nm and a free electron response goes far into the IR.$^{113}$

![Figure 9.24: Solid dots: transient absorption spectrum of 2-5 um thick TiO$_2$ film in N$_2$-saturated D$_2$O, excited at 355 nm with a pump intensity of 160 $\mu$J cm$^{-2}$, the time delay is 1 $\mu$s. Solid line is obtained through the use of hole scavengers. Circles are obtained by subtracting the electron response from the total transient giving the hole response. Adopted from Yoshihara et al.$^{113}$](image)

9.2.3.1 Recent developments

Pesci et al.$^{112}$ show that hydrogen treated rutile TiO$_2$ nanowires showed an increase in oxygen vacancies just below the conduction band with XPS measurements. These nanotube arrays have resulted previously in a record 1.1% STH efficiency. It is now found that the oxygen vacancies act as electron donors. Through transient absorption it became clear that the improved efficiency was caused by incident photon to converted electron (IPCE) ratio values of over 90%, which is an important finding since poor charge separation is one of the main limitations for TiO$_2$. Similar performance improvements through hydrogen treatment have been seen in other metal oxides. Solid theoretical understanding behind this phenomenon has yet to be developed.
10 Results and Discussion

So far we have been building a theoretical and scientific basis for analyzing and interpreting experimental data. The experiments for this thesis have focused on two semiconductor compounds, namely Fe$_2$O$_3$ and BiVO$_4$, which we will examine in that order. As we have discussed in the previous chapter, many reports are available on hematite. The hematite experiments initially served for development and calibration purposes of our msTAS setup, but analyzing the effect of bias on long-lived holes proved very interesting. We conclude with bismuth vanadate. TAS data for this material is scarce in the literature and we present some first steps into interpreting the results.

10.1 Fe$_2$O$_3$ nanowires

In Section 7.5.1 we discussed the different hematite samples under investigation, namely batch A, B and C, with different dopants. We will specify the samples throughout the document, although we note in advance that hematite batch C was used only for Mott-Schottky and XPS analysis. As indicated in the previous chapter, hematite has a long optical absorption length in the visible part of the spectrum and a short hole diffusion length. The rationale behind the nanowire configuration is to increase STH efficiency by increasing the surface area and decreasing the path length for holes to reach the electrolyte.

10.1.1 Photo-activity and stability

Figure 10.1 shows current density vs. applied bias for the hematite nanowire samples. In the dark, we do not detect any current, so our electrical contacts are well insulated by the epoxy. However, when illuminated with a light source of 1 sun, a photocurrent of approximately 0.4 to 0.7 mA cm$^{-2}$ at 0.6 V vs. Ag/AgCl is observed. This demonstrates the photo-activity of the Fe$_2$O$_3$ nanowire samples.

![Figure 10.1: (a) Fe$_2$O$_3$-A and Sn:Fe$_2$O$_3$-A samples under dark and illuminated (1 sun) conditions. (b) Fe$_2$O$_3$-B and Ti:Fe$_2$O$_3$-B doped samples under dark and illuminated (1 sun) conditions. Note the differences in current density and an anodic shift in the onset potential with doping.](image-url)
When we compare the Sn:Fe$_2$O$_3$-A sample with Ling et al., who deposited these samples, we find that the photocurrent is roughly twice as low. This can be attributed to a different sample batch or sample degradation due to the pump laser and the applied bias after TAS experiments. CA and CV measurements were obtained before and after TAS measurements. As we will see below, the hematite samples are found to be stable in aqueous environments for extended periods or time, thus we conclude that the differences in photocurrent are due to a different sample batch.

The anodic onset potential shift is disadvantageous to doped hematite performance because a higher bias is required to achieve the same photocurrent density as the undoped samples. Generally, a shift can be caused by changes in band alignment (caused by dopants or overlayers), surface recombination or catalysis (see Section 9.1.3.4 for a discussion on catalysis). In Section 10.1.4, where XPS results are presented, we continue this discussion.

Chronoamperometry (CA) measurements (Figure 10.2 a – b) of the Fe$_2$O$_3$-A sample indicate the stability of these Fe$_2$O$_3$ samples. These CA diagrams were obtained during the TAS measurements. The peaks seen in the graphs correspond to the pump laser exciting the sample, creating a spike in the current. This only occurs at higher bias, at low bias, the current is effectively zero.
Figure 10.2: Chronoamperometry measurements of Fe$_2$O$_3$-A at -0.48 V (a), +0.12 V (b), +0.62 V (c) vs. Ag/AgCl. The inset shows a larger time window of the same measurement. Data obtained during in situ TAS measurement and demonstrates the stability of the hematite samples in the alkaline conditions, under pump and probe illumination and applied bias for extended time periods. CA graphs for the other Fe$_2$O$_3$ nanowire samples look similar.

Over the course of the work for this thesis, which extended far past the measurements in Figure 10.2, no degradation was observed in the hematite samples. This is in strong contrast with the BiVO$_4$ samples.

10.1.2 Mott-Schottky analysis

Mott-Schottky (MS) analysis was performed on the four hematite samples to understand the role of doping and preparation on the flatband potential.

Figure 10.3: Mott-Schottky diagrams for Fe$_2$O$_3$-A(a), Sn:Fe$_2$O$_3$-A(b), Fe$_2$O$_3$-B(c) and Ti:Fe$_2$O$_3$-B(d).
Looking at Table 3 we see that the carrier densities range from $3.6 \times 10^{21}$ to $1 \times 10^{22}$ cm$^{-3}$. These values are high. As a comparison, the Sn:Fe$_2$O$_3$ nanowires from Ling et al.\textsuperscript{33}, have a reported electron density of $5.38 \times 10^{19}$ cm$^{-3}$. Also, the reported flatband potential lies at 0.49 V vs RHE, quite different from our value of 0.61 V vs. RHE. The flatband potentials listed in Table 3 vary substantially, even between the two undoped samples, which are deposited using the same technique. It is important to note that determination of flatband potential and carrier density from Mott-Schottky plots assumes that samples are spatially homogeneous – this includes homogeneous doping throughout the wires and a well defined surface. Although this is a powerful technique, we must conclude that Mott-Schottky analysis is not suitable for this particular batch of samples.

### 10.1.3 SEM

In understanding differences in electrode performance it is important to investigate the surface morphology. Using scanning electron microscopy (SEM) we can look at magnified images of the surface. This enables us to use statistics to get a quantitative measure of the dimensions of the hematite nanowires. We measure the length and width of a large number of wires and create a histogram of size (nm) versus occurrence (N). Fitting this diagram with a Gaussian function gives us an average measure of the wire dimensions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N_d$ (cm$^{-3}$)</th>
<th>$E_{\text{flatband vs RHE}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$-A</td>
<td>$4.3 \times 10^{21}$</td>
<td>0.45</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-B</td>
<td>$3.6 \times 10^{21}$</td>
<td>0.64</td>
</tr>
<tr>
<td>Sn:Fe$_2$O$_3$-A</td>
<td>$5.0 \times 10^{21}$</td>
<td>0.61</td>
</tr>
<tr>
<td>Ti:Fe$_2$O$_3$-B</td>
<td>$1.0 \times 10^{22}$</td>
<td>0.29</td>
</tr>
</tbody>
</table>

\textit{Table 3: MS analysis results showing the calculated electron density and flatband potential.}
Figure 10.4: SEM images of Fe₂O₃-C from the top (a) and at a 45 degree angle (b), the scale bar indicates 1 µm. (c) and (d) show Gaussian plot of a histograms of the wire length and width respectively. The average length is 339 nm and average width is 77 nm.

Figure 10.5: SEM images of Sn:Fe₂O₃-C from the top (a) and at a 45 degree angle (b), the scale bar indicates 1 µm. Through fitting the histograms in (c) and (d) with a Gaussian function we obtained an average length of 181 nm and average width of 39 nm.

Figure 10.6: SEM images of Ti:Fe₂O₃-C from the top (a) and at a 45 degree angle (b), the scale bar indicates 1 µm. In (c) and (d) we obtained an average length of 132 nm and average width of 40 nm.
Table 4: Length and width of nanowires in three types of samples.

Table 4 shows that the length and width of the samples display significant variation. The doping process seems to decrease the length and width of the wires. One reason for this could be the formation of an overlayer (SnO$_2$ and/or TiO$_2$), partially covering the wires and burying the ‘roots’ of the wires, as discussed below.

10.1.4 XPS

XPS is a very useful technique to investigate the constituents of a material. The following graphs are XPS peaks of the three hematite samples from batch C. In Figure 10.7a, b and c we see two peaks centered at 724 eV$^{114}$ and 711 eV$^{115}$ corresponding to the Fe 2p$_{1/2}$ and Fe 2p$_{3/2}$ peaks respectively. Fe 2p peaks of different substances are known to overlap, for example with FeOOH which is the compound from which the hematite nanowires are grown.$^{116}$ As stated before in this work, Ling et al.$^{33}$ confirmed that all FeOOH was converted into Fe$_2$O$_3$ through XRD. The second feature is seen in Figure 10.7b, around 717 eV. This corresponds to the 3p$_{3/2}$ orbital of SnO$_2$ at 717 eV$^{117}$, as the metallic Sn 3p$_{3/2}$ peak is at 714.6 eV$^{118}$ and binding energy is well known to increase with oxidation state. This indicates that there exists a SnO$_2$ overlayer. Let us look at the Sn peaks next.

Figure 10.7: XPS Fe 2p peaks of Fe$_2$O$_3$-C (a), Sn:Fe$_2$O$_3$-C (b) and Ti:Fe$_2$O$_3$-C (c).
Figure 10.8: XPS Sn 3d peaks of Fe$_2$O$_3$-C (a), Sn:Fe$_2$O$_3$-C (b) and Ti:Fe$_2$O$_3$-C (c), showing that Sn is present in the samples even in absence of deliberate Sn doping. However, the amplitude of the peaks is much larger for Sn:Fe$_2$O$_3$-C.

We assign the peaks in Figure 10.8 to the SnO$_2$ 3d$_{3/2}$ (486 eV$^{119}$) and 3d$_{5/2}$ (495 eV$^{120}$) peaks. This means that all samples have SnO$_2$ on the surface. Notice that the 3d peaks for the Sn:Fe$_2$O$_3$ sample are approximately 5 to 10 times larger than in the other samples. Combining these results with the SnO$_2$ peak from Figure 10.7, we conclude that the Sn doped sample has by far the highest concentration of SnO$_2$.

Figure 10.9: XPS O 1s peaks of Fe$_2$O$_3$-C (a), Sn:Fe$_2$O$_3$-C (b) and Ti:Fe$_2$O$_3$-C (c) nanowires. Notice the small shoulder on the left side of the main peak.
The peak in Figure 10.9 corresponds to the O 1s peak in Fe$_2$O$_3$ at 530 eV$^{121}$. The small shoulder left of the peak is H$_2$O (at 533 eV$^{122}$) or OH adsorbed to the Fe$_2$O$_3$.

Finally, we look at the Ti peaks present in the Ti:Fe$_2$O$_3$-C sample (Figure 10.10a). The peaks 2p$_{1/2}$ and 2p$_{3/2}$ peaks of TiO$_2$ are centered at 464 eV$^{123}$ and 459 eV$^{124}$, while the 2p$_{1/2}$ and 2p$_{3/2}$ peaks of metallic Ti are located at binding energies of 454$^{125}$ and 460 eV$^{126}$. We conclude that the peaks must correspond to TiO$_2$. When we looked at the Ti 2p peaks of the Sn doped sample, we also found TiO$_2$ to be present. This is a very surprising result, as it should not have been possible for TiO$_2$ to find its way onto this sample. We did not find any TiO$_2$ peaks in the undoped sample.

Note that XPS is a surface sensitive technique, so it does not give information about the bulk doping properties. We can conclude that the samples have SnO$_2$ (Fe$_2$O$_3$-C, Sn:Fe$_2$O$_3$-C) and SnO$_2$/TiO$_2$ (Ti:Fe$_2$O$_3$-C) overlayers. We assume that these overlayers also exist in the hematite samples from batch A and B.

The valence band position relative to the Fermi level is found by looking at the onset of photoemission of electrons with the lowest binding energy.
Figure 10.11: The graphs show the valence band level of Fe$_2$O$_3$-C (a), Sn:Fe$_2$O$_3$-C (b) and Ti:Fe$_2$O$_3$-C (c). Data obtained with XPS.

<table>
<thead>
<tr>
<th>sample</th>
<th>valence band (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$-C</td>
<td>1.67</td>
</tr>
<tr>
<td>Sn:Fe$_2$O$_3$-C</td>
<td>1.69</td>
</tr>
<tr>
<td>Ti:Fe$_2$O$_3$-C</td>
<td>1.98</td>
</tr>
</tbody>
</table>

Table 5: Valence band positions relative to the Fermi level of hematite nanowire samples obtained through XPS.

Determining an explanation of the shifts in the valence band potential is difficult. SnO$_2$ is present on all samples, and TiO$_2$ appears to be present on two out of three samples, in varying concentrations. The larger bandgaps of the SnO$_2$ (3.5 eV) and TiO$_2$ (3.2 eV) overlayers compared to Fe$_2$O$_3$ presumably have an effect on the valence band. Indeed, from inspection of the shape of the VB in Figure 10.11, we can conclude, qualitatively, that the SnO$_2$ and TiO$_2$ overlayers contribute to higher binding energy emission compared to nominally bare hematite in Figure 10.11a, consistent with the core level spectroscopy presented above.

Finally, remembering the onset potential shift in the CV scans in Section 10.1.1 for the doped samples, we might shed some light on the reason behind the shifts. Although overlayers appear to be present in all samples, the onset shift only occurs for the doped samples. If we assume that the overlayers are much more pronounced in the doped samples we can explain the shift. The bandgap of the Fe$_2$O$_3$ has to equilibrate with the bandgap of the overlayer. Apparently, this process presents a barrier that can only be overcome at higher bias. It also seems that the Sn doping process leads to a higher maximum photocurrent, but the Ti doping does not.

Together, all measurements indicate that the series of doped samples are far more complex than originally thought due to the presence of overlayers in addition to the possible role of dopant incorporation.

10.1.5 msTAS

Now we turn to the results from the msTAS system that enable us to observe the charge carrier dynamics in situ. Before
quantitatively analyzing the hole dynamics associated with water oxidation, we compare our measurements at three wavelengths with literature and verify the hole-related response.

10.1.5.1 Probe wavelength and effect of hole scavengers

In section 9.2.1 we discussed the work by Durrant et al.\textsuperscript{58,75,127} who have extensively studied hematite photoanodes. Let us again look at Figure 9.15:

![Figure 9.15](image)

With increasing bias, Durrant et al. see the emergence of a negative feature (bleach) around 575 nm, and a long lived transient (positive) component (colored red in Figure 9.15) ranging from 500 out to 900 nm. The bleach and the transient are convoluted so the negative feature at 575 nm partially suppresses the positive feature peaking at 650 nm. The trace at 612.5 nm is located at roughly the transition point between the bleach and the transient at longer wavelengths. Figure 10.12 shows very similar results for our Sn:Fe$_2$O$_3$-A sample.

![Figure 10.12](image)

*Figure 10.12: Sn:Fe$_2$O$_3$-A sample at three different biases, -$0.48$ V, $+0.12$ V, $+0.62$ V vs. Ag/AgCl corresponding to $+0.5$ V, $+1.1$ V and*
+1.6 V vs. RHE in Figure 9.15 respectively. The effects of these three biases have been investigated at three wavelengths: 575 nm (a), 612.5 nm (b) and 650 nm (c). Measurements were taken in situ (0.1 M NaOH, pH 13), 355 nm pump pulse (10 mJ cm\(^{-2}\) pulse\(^{-1}\), 0.33 Hz) and 5 mW probe light.

Each trace in Figure 10.12 has been obtained at three different time scales and three different low pass filters and then stitched together for optimal signal to noise (see Section 8.2.6). In Figure 10.12 we see that at 575 nm the dA amplitude decreases significantly, although no true bleach is observed. This might be due to differences in the sample. Barroso et al.\(^{75}\) suspect that this negative signal is due to a transition between the valence band and localized states just below the conduction band. At low bias (or bias close to the flatband potential), these states are mostly filled with electrons (reduction of gap states) and can trap holes resulting in a positive dA feature. This feature then decays as electrons from the conduction band recombine with the trapped holes. However, at anodic biases, these gap states become oxidized (void of electrons) which reduces ground state absorption, resulting in a bleach. When holes recombine with these trapped electrons, the bleach decays. At 612.5 nm, this effect has disappeared, although the maximum dA amplitude is not visible until 650 nm, much in accordance with Barroso et al. The broad absorption band peaking at 650 nm is assigned to hole absorption, according to Barroso et al. Photogenerated holes at the surface are responsible for this absorption, which is a process that increases with bias. Due to the anodic potential, the electron density in gap states is lowered resulting in a space charge layer. In this region, electron-hole recombination is retarded and a build-up of holes at the surface is formed. We can confirm this with the use of hole scavengers, as shown in Figure 10.13.

![Figure 10.13: The effect of hole scavengers on TAS at 650 nm. The blue traces show the same traces as in Figure 10.12 (c). The green traces](image)
are obtained under the same conditions as above (0.1 M NaOH), only with 0.1 M Na$_2$SO$_3$ added, a known hole scavenger. The long-lived transient feature appearing at anodic biases is greatly diminished with Na$_2$SO$_3$ present. Measurements were taking with a 355 nm pump pulse (10 mJ cm$^{-2}$ pulse$^{-1}$, 0.33 Hz) and 5 mW probe light.

Na$_2$SO$_3$ is a known hole scavenger (hole acceptor). When present in the solution (see Figure 10.13), it allows for facile charge transfer of the minority carrier holes to the electrolyte. Therefore, if the presence of the hole scavenger diminishes the hole density on the surface of the photoanode, and the TAS signal at 650 nm is caused by a build-up of holes at the surface, we expect to see a more rapid decay of the transient absorption signal amplitude and decay time. Similar to what we learn from the literature, Figure 10.13 shows that in the presence of a hole scavenger, the amplitude and decay time of the long lived absorption feature is suppressed. This indicates that charge carriers responsible for absorption at 650 nm, is in fact due to a surface photohole response.

On the shorter timescales between 10 µs to approximately 1 ms, we observe a fast decaying component. We see that the decay is unaffected by the presence of the hole acceptor and that the amplitude increases with bias. The fact that the hole acceptor has no effect on the decay kinetics of the fast decay trace indicates that the holes responsible for this absorption are not located at the surface. Because the amplitude of the trace increases with bias we conclude that the holes recombine within the depletion region. As the bias extends the space charge layer further into the photoanode, thus retarding electron-hole recombination, this results in a higher amplitude of the signal at higher bias. When we compare our TAS traces at 650 nm to the work by Pendlebury et al.\textsuperscript{127}, we find very similar decay traces, see Figure 10.14. The figure also allows us to find that the origin of the steep initial decay phase, is due to a high pump intensity. Figure 10.14 shows that the fast decay component occurs at higher pump power (up to 2.2 mJ cm$^{-2}$). Our excitation beam is approximately 10 mJ cm$^{-2}$. We will further discuss the nature of this recombination feature using a fitting model (Section 10.1.5.3).
Figure 10.14: CVD grown Si:Fe$_2$O$_3$ photoanode, probed at 650 nm at pump intensities ranging from 23 μs cm$^{-2}$ (dark green) to 2.2 mJ cm$^{-2}$ (brown). The inset shows the traces normalized at 125 ms, indicating there the slow decay phase is independent of pump power. Adopted from Pendlebury et al.\textsuperscript{127}

The TAS data presented in this section verifies that our msTAS allows us to observe what has been reported in the literature. We can now proceed with the analysis of the 650 nm signal as a function of doping, as we confirmed that surface photoholes are causing the slow decay TAS feature at 650 nm. These holes are thought to be responsible for the photocurrent,\textsuperscript{127} and long-lived holes are necessary for oxygen evolution\textsuperscript{128}. We are most interested in this process in hematite.

10.1.5.2 Doping effects

The photo-electrochemical performance of Fe$_2$O$_3$ as photoanodes can be improved using dopants and we now present the results from TAS measurements on the Fe$_2$O$_3$ nanowires with different dopants.
Figure 10.15: TAS measurements at 650 nm of Fe₂O₃-A (a), Sn:Fe₂O₃-A (b), Fe₂O₃-B (c) and Ti:Fe₂O₃-B (d) under applied bias of -0.48 V, +0.12 V, +0.62 V vs. Ag/AgCl. Measurements were taking in situ (0.1 M NaOH, pH 13), 355 nm pump pulse (10 mJ cm⁻² pulse⁻¹, 0.33 Hz) and 5 mW probe light.

We find that the initial amplitude of the traces increases with increasing bias. Also, we see the emergence of a plateau shaped feature at the highest bias, with return to equilibrium lasting a few seconds. In the next section we use kinetic models and interpret these traces, in order to draw more quantitative conclusions.

10.1.5.3 TAS fitting model

In order to describe the TAS decay traces and gain insight in the carrier dynamics of the sample, we model the decay components convoluted in the TAS signal using rate equations. Rate equations are different depending on the number of reactants in a reaction, possible intermediate reactions and the number of end products. These reactions and associated equations are part of basic chemistry and can be found in chemistry books such as from Brown et al.¹²⁹

A zeroth order reaction is independent of the concentration and the reactant concentration thus evolves linearly with time. A first order reaction involves one reactant A, and its concentration [A], as follows:

\[- \frac{d[A]}{dt} = k[A]\]  (16)

Rearranging and integrating this equation gives the time evolution of [A]:

\[A = [A_0] \, e^{-k(t-t_0)}\]  (17)

Where \([A_0]\) is the initial concentration of A, k is the rate constant and \(t_0\) is the initial starting time of the reaction. The reciprocal of k gives the time constant associated with a 1/e decrease in amplitude of \([A_0]\). The order of a reaction can be extended to n-th orde for reactions composed of several reactants, which can also include non-integer n-th order reactions:

\[- \frac{d[A]}{dt} = k[A]^n\]  (18)

Although slightly more involved, finding a generalized function for the time evolution is straightforward:

\[A = \left[A_0 \, (n - 1)k(t-t_0)\right]^{1-n}\]  (19)

With n is the order of the reaction. The other parameters are similar to (10). Note that the generalized form of (19) is not valid for n = 1 (for n = 1, see (17)). For values of n larger than 1, (19) behaves similar to a power law function. Characteristic for the power law family of functions is linear appearance in a log-log plot, together with extended tails. This first property is useful to us, as the initial fast decay looks somewhat linear on a log-log plot, see below.
Figure 10.16: Log-log plot of Fe$_2$O$_x$-A TAS decay trace at +0.62 V vs. Ag/AgCl, including a linear fit to the initial fast decay phase, indicating that this component could be approximated using a power law.

We first attempt to fit the data with the least amount of parameters possible. We found that this was possible using one first order and one n-th order rate equation, or the sum of (17) and (19):

$$ dA(t) = [A_0^{1-n} + (n-1)\left(\frac{t-t_0}{\tau_1}\right)^{1-n}] + [B_0]\frac{t-t_0}{\tau_2} $$

The following graphs show fits to the data using Equation (20).
Figure 10.17: Fits of hematite nanowire TAS kinetic traces (shown in Figure 10.15) made using Equation (13), made with Igor Pro 6.3.2.3.

We summarize the fit parameters in the table below.
In Table 6, we can observe trends in the parameters of the fits to the nanowire samples. At the lowest bias, -0.48 V vs. Ag/AgCl, all traces can be well described by a single n-th order rate equation. The time constants associated with this fast component range from 2.7–21 µs, and n ranges from 2.8–3.5.

For traces at +0.12 V vs. Ag/AgCl bias, we fit the fast time component with the n-th order equation lasting between 17–29 µs, with n ranging from 3.1–3.6. However, the data cannot be described solely by an n-th order rate equation, as a slow, long-lived component emerges. This component could be fit with a first order equation with time constants ranging from 0.1–0.35 s.

The traces at the highest bias (+0.62 V vs. Ag/AgCl) are fit with a fast component lasting between 12–35 µs, and a reaction order parameter ranging between 2.5–3.1. The slow, first order component is further extended, between 0.67–1 s.

As we have just seen, the kinetics of the traces is well described by Equation (20). We use the n-th order rate equation to represent the fast decay phase caused by electron-hole recombination, present in all samples, at all biases. The value for n lies around n = 3, implying a ternary reaction (involving three components). Band-to-

<table>
<thead>
<tr>
<th>sample</th>
<th>bias</th>
<th>( A_0 )</th>
<th>( t_1 ) (s)</th>
<th>n</th>
<th>( B_0 )</th>
<th>( t_2 ) (s)</th>
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<tr>
<td>Fe(_2)O(_3)-A</td>
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<td>6 µs</td>
<td>3.2</td>
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<td>-</td>
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<td></td>
<td>+0.12</td>
<td>0.8</td>
<td>18 µs</td>
<td>3.6</td>
<td>0.07</td>
<td>0.32</td>
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<td></td>
<td>+0.62</td>
<td>0.73</td>
<td>12 µs</td>
<td>2.8</td>
<td>0.23</td>
<td>0.86</td>
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<td>0.3</td>
<td>2.7 µs</td>
<td>2.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>+0.12</td>
<td>0.62</td>
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<td>0.1</td>
<td>0.3</td>
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<td>+0.62</td>
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<td>27 µs</td>
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<td>0.26</td>
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<td>3.2</td>
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<td>-</td>
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<td>+0.12</td>
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<td>29 µs</td>
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<td>0.2</td>
<td>0.1</td>
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<tr>
<td></td>
<td>+0.62</td>
<td>0.9</td>
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<td>3.1</td>
<td>0.2</td>
<td>1</td>
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<td>3.5</td>
<td>-</td>
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<td>+0.62</td>
<td>0.85</td>
<td>35 µs</td>
<td>3</td>
<td>0.2</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Table 6: Fit parameters for the hematite nanowire fits. With \( A_0 \) the amplitude of the n-th order equation, \( t_1 \) the time constant for the n-th order equation, \( B_0 \) the amplitude of the 1-st order equation and \( t_2 \) the time constant for the 1st order equation. The fits are made with Igor Pro 6.3.2.3 and are shown below (large versions of the fits are found in the appendix).
band and deep level (defect or trap state)\textsuperscript{‡‡‡‡} recombination involves two reactants and the decay kinetics do not follow the approximately 3\textsuperscript{rd} order reaction. Auger recombination does involve three reactants (more on Auger recombination in BiVO\textsubscript{4} in Section 10.2.2), where energy emitted during electron-hole recombining is transmitted to a third electron in the conduction band or a hole in the valence band. The kinetics is dependent on the relative rates of other recombination pathways and doping levels and does follow a 3\textsuperscript{rd} order reaction. Auger recombination usually takes place at high carrier densities which often only occur at the shortest timescales. We concluded from Figure 10.13, that the fast recombination phase occurs within the depletion layer of the photoanode. We also know that there is a buildup of carriers on the surface of the photoanode, depending on the bias and thus the direction of the band bending, this can be electrons or holes. Our hypothesis is that the carrier concentration is high enough for Auger recombination to occur. An argument supporting that theory is that the fast, approximately third order decay, only emerges at very high pump intensities as determined by the comparison with the pump intensity series in Figure 10.14.

At higher biases we see the emergence of an additional first order component. This first order reaction is well explained by holes reacting at the surface of the photoanode, as is described in the literature.

Finally we note, that making comparisons between the different samples based on the fitting is challenging because the samples vary greatly in terms of morphology (length and width of wires) and composition (SnO\textsubscript{2} and TiO\textsubscript{2} overlayers).

In Figure 10.18, we show a schematic of our proposed charge carrier dynamics. Before 1 ms, recombination processes dominate and we see a steep decay that occurs relatively fast (see Figure 10.18a). Since our TAS measurements start at 10 µs, we might only see the tail of process (I). We concluded earlier that Auger recombination dominates at this short timescale (II), due to the approximately third order decay in combination with high pump intensity. The time constant for this component is short (tens of µs). At the two higher biases, we see the emergence of a first order equation, a reaction with just one reactant (see Figure 10.18b). We identify this as the process of oxygen evolution (III). We find that at -0.48 V vs. Ag/AgCl, the long-lived component is either not present or very small. This is in accordance with literature as well as our CV and CA diagrams, as there is (almost) no photocurrent present at that potential. As bias increases, the initial amplitude (initial concentration) from the long-lived component increases from zero, and the time constants increase up to 1s. Recalling that this time constant represents a 1/e decrease in amplitude, multiplying the time constant by 3, gives a rough estimate of the total lifetime of the surface states. Again, this

\textsuperscript{‡‡‡‡} Also known as Shockley-Read-Hall (SRH) recombination.
component represents the holes reacting at the surface, either directly from the valence band to the solution, and potentially assisted by surface states. Long-lived surface holes with lifetimes of the order of seconds\textsuperscript{75,76} are necessary for water splitting. Our fits indicate that this is indeed possible with hematite.

![Figure 10.18: Proposed model for recombination and water oxidation in hematite nanowires: bulk recombination (I), Auger recombination (II) and oxygen evolution (III). (a) Shows the relevant processes up to 1 ms. (b) After 1 ms, oxygen evolution dominates, provided sufficient bias has been applied. See text for further clarification.](image)

In order to compare our proposed model, we attempt an alternative fitting model. We use the sum of first order reaction components including a stretching parameter, which is a common approach in the literature:

$$dA(t) = \sum_i [A_i] e^{-\frac{t-t_0}{\tau_i}}^\alpha$$  \hspace{1cm} (21)

$[A_i]$ represents the initial concentrations of the component, $\tau_i$ the time constant of the reaction, $t_0$ the starting time of the reaction and $\alpha_i$ the stretching parameters. Stretching parameters effectively ‘stretch’ the lifetime of the component and is often used in the literature.\textsuperscript{130,131} The following graphs (Figure 10.19) show fits of Fe$_2$O$_3$-A using Equation (21). We found that the minimum amount of components required for a reasonable fit was 2.
We found that capturing the initial fast decay phase using Equation (21) was challenging, the function follows a steeper curve than the decay trace. A solution could be to increase the initial concentration $[A_0]$, but that leads to non-physical parameters, because the initial concentration of the fit then becomes higher than the initial concentration of the traces.

Also, the time constants for the traces at -0.48 V and +0.12 V vs. Ag/AgCl do not seem to accurately represent the decay time, as the decay time of the slow component seems to be longer at negative biases. During the fitting of the other samples we encountered similar issues: finding an accurate fit would result in non-physical fitting parameters (time parameters being abnormally small, or initial concentrations too large). When we increase the number of exponential decay components (Figure 10.20), the initial fast decay is captured better. This could indicate that several recombination pathways are present in parallel, but the large number of fitting parameters severely complicates finding an unambiguous fit. Also, a close inspection reveals that the fit function is still quite steep at early times, and might not be able to adequately capture a trace going out to shorter timescales.
Figure 10.20: Fit of A-Fe$_2$O$_3$ decay trace using three exponential decay components (see Equation (21)). The parameters a, b and c represent the stretching parameters. See text for explanation.

The use of stretching parameters is not undisputed. The stretching parameter causes the tail of the function to extend, thereby increasing the apparent lifetime of the function. However, this is not reflected in the values of the time constants. The misleading time constants found in the fits above, is due to this effect. A physical explanation can originate from the holes recombining through several pathways (such as band-to-band, SRH and surface state recombination). On the other hand, the stretching parameters can lead to non-unique fits and large variations in time constants and initial concentrations, indicating non-physical origins.

We make the observation that for both models, the time constants vary with bias. This indicates that different processes dominate at different biases. If the processes remained the same, but would only change in amplitude (initial concentration), the time constants would be equal. This tells us that the application of bias has an effect on the sample that surpasses simply increasing the initial concentration of the charge carrier responsible for the process.

While the work for this thesis was being finalized, a new article by Le Formal et al. was published on charge carrier dynamics in Fe$_2$O$_3$, which allows the opportunity to compare the fitting models. The TAS traces presented in the paper look very similar to the results presented in this thesis, with a fast decay phase and a plateau shaped feature emerging at approximately 1 ms at higher bias. The fact that our fast decay component is steeper, is due to the higher pump power. Le Formal et al. attribute the initial decay phase to fast electron-hole recombination and the second slow decay phase to water oxidation. Fits of the traces are performed using Equation (21), and shown below in Figure 10.21.
The conclusion of the analyses above is that our data is best described by an n-th order (approximately 3rd order) plus first order equation. A 3rd order equation might imply Auger recombination to be present at short timescales, but further investigation is required, as the physical explanation is not straightforward. Lowering the pump intensity might eliminate the n-th order dependence in the decay traces, as indicated by the fitting of hematite decay traces from Le Formal et al. Overall, there is a need for a more advanced model for charge carrier recombination and water oxidation and a well defined set of hematite samples in order to clearly distinguish the effects of doping and morphology.

10.2 Transient absorption spectroscopy of BiVO₄

BiVO₄ is viewed as a promising water splitting photoanode that remains to be thoroughly investigated using TAS. To the best of our knowledge one of the very few papers on TAS of BiVO₄ is by Aiga et al. This work covers TAS from 550 to 740 nm and up to 100 ps. Here, we present larger time windows and a broader spectrum with higher spectral resolution, ranging from below 400 up to 1580 nm with a time delay of up to 9 ns. The future goal of this research is to understand water oxidation using BiVO₄ photoanodes with the aim to improve this process. Compared to water oxidation using hematite, this process occurs on a much slower timescale and little is known about the electronic structure and charge carrier dynamics in BiVO₄. Hematite is well characterized in the ultrafast regime, therefore verifying that the TAS feature at 650 nm was due to photogenerated surface holes was sufficient. This information is not known in the case of BiVO₄, so we begin our investigation of BiVO₄ with TAS on an ultrafast timescale.
10.2.1 BiVO₄ spectrum

We begin our study with the steady state absorption spectrum of BiVO₄. The absorption spectrum in Figure 10.22 has two interesting features. First of all, we see a large absorption peak starting around 500 nm. This corresponds to absorption across the bandgap as BiVO₄ has a bandgap of approximately 2.4 eV (517 nm). The second feature is a broad IR response of increasing absorbance out to 1600 nm. As BiVO₄ is an n-type semiconductor, few holes are present in the material and we can assign the transitions in this spectral range to electron absorption.

![Absorption spectrum of BiVO₄](image1)

**Figure 10.22: Absorption spectrum of BiVO₄ (see Section 7.5.2 on sample preparation). Data obtained using a Shimadzu Solid Spec-3700 UV-VIS-NIR Spectrophotometer.**

In order to further identify the broad IR response, we first look at the complete uTAS spectrum in Figure 10.23. We show the spectrum at four different time delays (1 ps, 1 ns, 10 ns, 150 ns) ranging from 380 nm to 1580 nm.

![uTAS spectrum](image2)

**Figure 10.23: BiVO₄ spectrum from 380 nm to 1580 nm obtained through both the HELIOS and EOS modes of the uTAS setup. Measurements obtained at 3.0 mW pump power in air. Gaps in the data are due to fundamental laser interference (HELIOS, ≈ 800 nm) and due to absence of stable white light generation (EOS, ≈ 1100 nm).**
The small trough in the HELIOS data around 610 nm is an artifact of the data processing and will be ignored in the further analysis.

In both the steady state absorption and the uTAS spectra, we observe a broad and increasing response in the IR. Such a feature is characteristic of free carrier absorption (see below). Because of the similarity in the shape of the feature in both spectra and the fact that the steady state absorption spectrum is dominated by majority carrier (electron) response, we assign the IR absorption feature in both cases to free electron absorption. In general, free carrier absorption is defined as the absorption of photons without the creation of an electron hole-pair, and is thus an intraband transition within the conduction band or valence band.\textsuperscript{132} The Drude-Zener model predicts the absorption coefficient to evolve as:\textsuperscript{133}

$$\alpha = \frac{4\pi}{nc} \cdot \frac{Ne^2\tau}{m^* (1 + \omega^2\tau^2)}$$

(22)

With $\omega$ the angular frequency of the radiation, $n$ the refractive index of the material, $m^*$ the effective mass of the carriers with concentration $N$, $\tau$ the mean relaxation time of the carriers. In the limit where $\omega^2\tau^2 \gg 1$, at sufficiently long wavelengths and realizing that $\omega$ is inversely proportional to $\lambda$ this reduces to the absorption coefficient being proportional to $\lambda^2$. This holds for the absorption of photons by carriers in a metal being driven by a periodic electric field. Other dependencies of the absorption coefficient on wavelength also exist, according to Pankove\textsuperscript{134}. Carriers scattering off acoustic phonons lead to a $\lambda^{1.5}$ absorption coefficient increase, while scattering off optical phonons results in a $\lambda^{2.5}$ increase in absorption. Finally, for scattering by ionized impurities the dependence is $\lambda^3$ or $\lambda^{3.5}$. This interaction of carriers with its surroundings is necessary to conserve momentum. This is because in order to absorb a photon while remaining in the same energy band, the carrier must change its momentum. We assume that the absorption coefficient dependence of the wavelength implies that the absorbance and thus change in absorbance is also proportional to wavelength. This way we can test this relation in our TAS spectra (this is done for TiO$_2$ by Yoshihara et al.\textsuperscript{113}).
Figure 10.24: (a) TAS of BiVO$_4$ at a time delay of 700 fs in air at 3.0 mW pump power (blue), and the best fit to the spectrum with a power law function, \( dA(\lambda) = 7 \times 10^9 \lambda^3 \). (b) BiVO$_4$ absorption spectrum (blue, from Figure 10.22) with \( \text{Abs.}(\lambda) = 0.6 + 6 \times 10^{-11} \lambda^3 \) (black).

Figure 10.24a shows how we fit the steep rise of the spectrum in the IR region with a simple power law function. We found that out of the values for \( n \) in \( \lambda^n \) (\( n = 1.5, 2, 2.5, 3, 3.5 \)) discussed above, \( n = 3 \) clearly resulted in the best fit to the spectrum. Using \( n = 3 \), we also fit the absorption spectrum in Figure 10.24b which was successfully done. We note that in contrast to fitting the dA spectrum, the absorption spectrum could only be fit with a y-offset. We conclude that both spectra in Figure 10.24 can be fit with a power law function, which indicates a free carrier absorption. Only with a power law of order 3 could both the dA spectrum and the absorption spectrum be fit which indicates that the carriers are scattered by ionized impurities in BiVO$_4$. While we concluded above that the carriers are electrons, further investigation of the specific nature of the ionized impurities is required.
In Figure 10.25 we summarize our current understanding of the reaction species making up the dA spectrum. The strong negative feature (orange) around 450 nm corresponds to the ground state bleach associated with VB edge to CB edge transitions (emerges around 500 nm in the absorption spectrum above). This feature corresponds to the bandgap size of 2.4 eV (approximately 500 nm), but is convoluted with the large positive feature at 500 nm, and thus appears shifted to shorter wavelengths. This large positive feature (green) appears to be related to trapped holes according to differential absorption studies§§§§ conducted by J.K. Cooper at JCAP. As this study was not part of the work for this thesis, we will not go into further details. The positive feature ranging from approximately 600 to 1200 nm (red) is a broad spectral response caused by hole absorption. Evidence for this is found by Aiga et al.104 through in situ TAS measurements where, in the presence of electron scavengers, the amplitude of the traces increases. This indicates that due to a decrease in electron density, electron-hole recombination is retarded, thus the transient must be caused by a hole absorption. More evidence for this is found by J.K. Cooper through differential absorption. Finally, the absorption in the infrared (purple) is caused by free electrons as discussed above.

We will now discuss selected TAS traces at short (0 – 10 ps) and long (0 – 170 ns) timescales, beginning with the short traces. Below §§§§ In differential absorption one looks at the −log of the ratio between the absorption of a sample at open circuit potential versus the absorption at different biases, thereby investigating how the sample responds to different biases.
(Figure 10.26) we see measurements obtained with HELIOS at six wavelengths, each at four different pump intensities.

![BiVO₄ kinetic traces](image)

**Figure 10.26**: BiVO₄ kinetic traces at 1400 nm (a), 875 nm (b), 600 nm (c), 475 nm (d), 447 nm (e) at four different pump intensities (3.0 mW, 1.5 mW, 0.75 mW, 0.3 mW). Measurements performed in air.

Before we continue the discussion about the nature of the traces at short time delays, let us also look at the longer time delay traces obtained using the EOS mode of the setup in Figure 10.27 below. In order to get an indication of the carrier lifetimes we fitted the traces using a sum of exponential functions. All traces could be fit with a minimum of two exponential functions and a y-offset component. This offset excludes the longest time component in the signal. Finding a good fit for this longest component is impossible, because the traces have not yet decayed to zero at these timescales. For the other two components, we find the time constants to lie around 5 ns and 40 ns, at all wavelengths. The fact that the decay times on these longer timescales are similar, can indicate that the free carriers observed in the IR, decay by getting trapped at the defect states observed around 447 nm. Note that these time constants might include additional error due to the fact that the decays are much longer lived than the timescales we measure with this setup. It does however, give an indication of the carrier lifetimes. The finding that the time constants
are very similar is very interesting, and longer time delay measurements using our msTAS system can investigate this further.

![Graphs showing BiVO₄ kinetic traces at different wavelengths](image)

*Figure 10.27: BiVO₄ kinetic traces at 1400 nm (a), 875 nm (b), 600 nm (c), 475 nm (d), 447 nm (e) at a pump intensity of 3.0 mW from 0 to 0.17 µs. Measurements performed in air.*

In order to gain more insight into the kinetic traces at short timescales, we normalize the graphs to the peak intensity. Figure 10.28c – e (600 – 447 nm), show very little difference between the normalized traces. This indicates that the nature of the decay mechanisms is independent of pump intensity. However, this does not apply to Figure 10.28a – b where we can clearly observe non-linear effects as a consequence of the pump intensity.
Figure 10.28: Kinetic traces normalized to peak dA amplitude. (a) – (b) decay significantly faster at higher pump intensities. (c) – (e) show linear scaling with intensity, because the normalized traces do not show significant differences to each other.

At high pump intensity, the carrier concentration in the material becomes very high. At these carrier densities a new recombination pathway becomes available: Auger recombination. In Auger recombination the energy released when an electron-hole pair recombines is transferred to a third electron in the conduction band. We suspect that the accelerated decay in Figure 10.28a and b is due to more efficient recombination kinetics caused by Auger recombination. This effect is only visible at short time delays where the carrier density is still sufficiently high. In the previous section, we determined that the increasing dA response in the IR is due to free electron absorption. The fact that we observe Auger recombination at 1400 nm (Figure 10.28a) is consistent with the presence of free electrons at these longer wavelengths. In terms of the carrier lifetimes, fitting the traces of Figure 10.28a indicate that at these timescales, two fast components are present with time constants of approximately 0.5 and 2.5 ps (again excluding slower components that are also present). From Figure 10.27 we learn that longer time components of 5 and 40 ns are also present, as well as (an) even longer time component(s). To determine the specific recombination
pathways of these decaying electrons, further investigation is necessary.

At 875 nm, Figure 10.28b, we also observe Auger recombination. Earlier in this section, we assigned holes to be responsible for the dA spectrum in this wavelength range. We can thus conclude that at this wavelength we detect holes decaying through Auger recombination. Potentially there is also a component of the free electron absorption present that dominates in the IR. Further investigation will need to show the relative magnitudes of the electron and hole contribution to the signal. We also tentatively fit these kinetic traces using two exponential functions, which also resulted in time constants of approximately 0.5 and 2.5 ps. Further investigation into the precise nature of these components is necessary.

The kinetic traces at 600 and 475 nm appear to be of a similar nature when we look at Figure 10.28c and d, and are independent of pump intensity. After the initial rise associated with the pump laser, we observe a second rise. The amplitude of this feature peaks at 475 nm. The lifetime of the second rise is not very long as it is not visible in Figure 10.27c and d. We therefore conclude that the lifetime of this second rise component is in the order of less than a ns. See refer to the next section (10.2.2) on phonon oscillations for time constants of the rise components at 475 nm. We stated earlier that the absorption feature peaking at 475 nm is presumably due to trapped holes. Further investigation is necessary to uncover the complex mechanisms governing the kinetics at these wavelengths. According to I.D. Sharp, involved in the investigation into these features at JCAP, one explanation could be that this is an important defect in the overall electronic performance of the BiVO$_4$ thin films. We also see oscillatory behavior in the traces, which we will describe in detail in the next section. As a final note, we repeat that the long term time decay constants are very similar to the time constants at the other wavelengths, namely 5 and 40 ns.

The negative feature peaking at 447 nm (see Figure 10.27e, Figure 10.28e) is due to the band edge bleach. The bleach kinetics are intensity independent, which is surprising to us, as one would expect the bleach to decay through Auger recombination as we see at longer wavelengths because this transition creates holes in the VB and electrons in the CB. Additional experiments are required to clarify the relationship between the bleach and the band edge carriers.

As a conclusion to this section we note that we found BiVO$_4$ to be a complex, but interesting material. Considerably more work remains in order to obtain a thorough understanding of the charge carrier dynamics at these short timescales. Ultimately, we are interested in understanding the carrier dynamics at longer timescales to understand the dynamics responsible for water oxidation. In spite of the significant challenges at ultrafast timescales, we have gained a basic level of understanding that allows us to examine carrier dynamics at the longest timescales using our msTAS setup. We have
attempted these studies, but due to issues with the stability of BiVO₄ in solutions and under laser illumination we could not obtain reliable measurements. When we take another look at Figure 8.14 (below), the pace of sample degradation in BiVO₄ becomes clear. In the course of an hour, photocurrent density has been significantly reduced, indicating fast degradation of the sample. The stability needs to be significantly improved for consistent TAS measurements that are independent of sample degradation. Both JCAP and the artificial photosynthesis research community working at solving these issues.

![Figure 8.14: Linear sweep voltammetry (LSV) of spin coated BiVO₄ samples, while being periodically illuminated, resulting in a photocurrent during illumination. The three measurements were done before, during and after a 1.5 hr long TAS experiment in solution.](image)

In the next final section on BiVO₄, we turn to the oscillations observed on the short timescales, briefly discussed in the past section.

### 10.2.2 Phonon oscillations

In the first few picoseconds (Figure 10.26) of the kinetic traces, we see an oscillation in the TAS signal. Aiga et al.¹⁰⁴ attribute similar oscillations to phonons due to excited electrons and holes that are displaced after pump excitation. The pump beam pulse width is 100 fs, much shorter than the oscillations, thus the phonon wavepacket is coherently excited. The report compares the oscillation frequency (found by Fourier transformation and fitting) to Raman spectroscopy from Avakyants et al.¹³⁵, who found a phonon wavepacket frequency of 62 cm⁻¹. We fit the kinetic trace with a function reported by Aiga et al.:

\[
\frac{dA(t)}{dt} = \int_{-\infty}^{t} \left\{ e^{-\frac{(t-t')^2}{2\sigma^2}} \right\} dt \times \left[ A(t') + A(t') e^{\frac{t'}{\tau_c}} \cos(\omega t' + \phi) \right]
\]

\[
A(t) = \sum_{i=1,2} \alpha_i \left\{ 1 - e^{-\frac{t}{\tau_i}} \right\}
\]
With the first component of (23) a Gaussian time profile with a
duration of $\sigma$, representing the duration of the pump laser, $A(t)$ the
sum of two rise functions with rise time components $\tau_i$ of the transient
signal. This rise component is convoluted with a damped oscillation
represented by the exponential decay function of time constant $\tau_v$,
convoluted with a cosine function (angular frequency $\omega$ and phase $\phi$)
to represent the oscillation. We use (24) to fit the oscillations at 475
nm, shown below in Figure 10.29.

![Figure 10.29: Fit of kinetic trace of BiVO$_4$ at 3.0 mW pump power in
air at 475 nm. We found the oscillation of 56 cm$^{-1}$ to be in good
approximation to a value of 62 cm$^{-1}$ for a phonon oscillation from
literature.](image)

<table>
<thead>
<tr>
<th>$c_1$</th>
<th>$c_2$</th>
<th>$\sigma$</th>
<th>$t_0$</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
<th>$c_v$</th>
<th>$\tau_v$</th>
<th>$\omega$</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.28</td>
<td>0.27</td>
<td>104fs</td>
<td>0.24ps</td>
<td>0.21ps</td>
<td>23ps</td>
<td>0.58</td>
<td>0.43ps</td>
<td>56cm$^{-1}$</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 7: Fit parameters for fit in Figure 10.29 using Equations (23) and (24).

The fit was performed using Mathematica 9.0 (see Appendix for
code) and the fitting parameters are shown in Table 7. We find $\sigma$ to
be 104 fs, corresponding to the pump beam pulse width of
approximately 100 fs. The time constants for the rise of the dA signal
are found to be 0.21 ps and 23 ps, comparable to the parameters
found by Aiga et al. The phonon oscillation is fit with a decay time
constant of 0.54 ps and an oscillation frequency of 56 cm$^{-1}$****. This
value for the oscillation frequency compares very well with the
phonon oscillation frequency found by Avakyants et al. of 62 cm$^{-1}$.
We can thus conclude that the oscillation we observe is likely due to
a phonon oscillation.

Aiga et al. report that the amplitude of the phonon wavepacket
first increases and then subsides, presumably corresponding to the

**** Wavenumbers are calculated by $1/\lambda$ with wavelength in cm, with wavelength $2\pi c/\omega$. 

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creation of a surface trapped-hole concentration associated with the transient response. When we fit the upper section of the trace with an exponential function and subtract that from the trace we are left with the oscillation itself. We only observe a decrease in oscillation, as shown in the figure below.

![Graph](image)

*Figure 10.30: By subtracting an exponential fit from the graph, we single out the oscillation of the phonon.*

Our measurements show that the TAS signal at 475 nm is presumably due to trapped holes, as indicated in Section 10.2.1. On this timescale there is very limited time for the holes to travel to the surface, so the response must be mainly due to trapped holes in the bulk, potentially with a smaller influence of surface trapped holes. The phonon oscillations must thus be coupled to the trapped holes. The reason why Aiga et al. observe an initial increase in the oscillations might be due to slower hole trapping kinetics in their samples (Aiga et al. uses BiVO₄ nanocrystals). In our samples, the holes are trapped on a timescale much faster than we can observe with the TAS, thus we do not see increased oscillations as the population of surface trapped holes is already maximized.
11 Conclusion

We complete this thesis with the main conclusions of the research. First we will discuss the results from the experimental sections followed by the future steps to undertake following this study. We conclude with a review of the research goals we set out to accomplish.

11.1 Experimental results

We have successfully developed a millisecond transient absorption setup. By examining nanowire Fe₂O₃ samples with different dopants under varying biases, wavelengths and in different solutions we have acquired a considerable dataset. All data obtained correlates well with experiments from the literature. We have used two kinetic models to describe the charge carriers in the Fe₂O₃ photoanodes and discussed the different outcomes. While we succeeded in finding a mathematical description accurately capturing the kinetic traces over five orders of magnitude, both models have open questions in terms of the physical origin of the components and we conclude there is a need for a more advanced charge carrier dynamics model. From the SEM and XPS data we conclude that the four Fe₂O₃ nanowire samples are surprisingly more complicated in terms of morphology and their constituents. This complicates the interpretation of the results, as any change can be caused by a multitude of factors.

Using the ultrafast transient absorption setup we performed measurements on drop cast BiVO₄. In this work we presented the most detailed transient absorption spectra of BiVO₄ to date. We have identified Auger recombination and phonon oscillations in the data. Furthermore, in collaboration with other researchers at JCAP, first steps have been undertaken to interpret the spectra, employing techniques such as differential absorption and X-ray spectroscopy at the Advanced Light Source. Future work will be focused on long time delay transient absorption spectroscopy in order to conclusively identify long-lived holes in BiVO₄ that are responsible for oxygen evolution. Our attempts to perform transient absorption in situ at long time delays were unsuccessful due to the instability of the samples. We expect that by improving the sample quality and lowering pump beam intensities by improving the signal to noise of our millisecond transient absorption spectroscopy setup this is possible in the near future. Future research goals involve conducting global analysis of the BiVO₄ spectra and finding compelling evidence for the identification of the transitions in the material.

11.2 Future steps

The research objectives following this work are threefold. First of all, in order to perform transient absorption spectroscopy under conditions more closely resembling the sun, the sensitivity of the millisecond transient absorption spectroscopy setup need to be
improved. Through the use of quartz substrates and sample holders, we can eliminate fluorescence. Also, through carefully shielding the system components of their mutual radiation, we can decrease noise. Effective use of the spectrometer through careful wavelength selection should increase signal to noise, provided the probe light intensity is sufficiently conserved. These factors combined should allow us to significantly decrease the pump intensity.

Second of all, in the case of Fe₃O₅, the next step is to synthesize and analyze a set of samples that only changes in one parameter. Systematic variation of one parameter (such as dopant concentration) should allow for a useful comparative study of the role of impurity doping on the photo-electrochemical behavior of this material. Measuring the decay traces at an increased number of applied biases will allow more accurate monitoring of the changes in the components convoluted in the data.

Thirdly, improving the stability of the BiVO₄ samples is a crucial goal not only of JCAP, but also of the entire artificial photosynthesis community. When improved stability is combined with lower laser intensities in our transient absorption spectroscopy system, it should be possible to gain further insight in the nature of the long-lived charge carriers expected in BiVO₄ for oxygen evolution.

11.3 Research goals

The aim of this thesis was to investigate charge carrier dynamics in photoanodes for solar water splitting. With the development of an experimental setup for transient absorption spectroscopy, reproducing results from literature on Fe₃O₅ and BiVO₄ photoanodes, developing and comparing kinetic models describing carrier dynamics Fe₃O₅, and taking important first steps into identifying the energy transitions in BiVO₄, this goal has been reached. However, many questions remain unanswered, which provides an exciting opportunity for many more experiments to unravel the inner workings of these complex semiconductor materials for solar water splitting.
12 Appendix

12.1 BiVO$_4$ - Large fitting graphs

![Graphs showing fitting parameters for BiVO$_4$ at different potentials.](image)
12.2 Mathematica 9 BiVO$_4$ phonon fit model

Import the kinetic trace at 475 nm:

\[
\text{trace475} = \text{Import["C:/[path]/475.csv"]};
\]

Plot the data:

\[
\text{ListPlot[trace475]}
\]

Load the model based on Equation (23) and (24):

\[
\text{model} = \{\text{Integrate[Exp[-((t - t0)^2/(2*\[Sigma]^2))].\{t, -\[Infinity], t\}}, (A + 0.45* A \text{Exp[-((t-t0)/(\[Tau]v))]} \text{Cos[\[Omega]*(t - t0) + \[Phi]])};
\]

\[
A = (a (1 - \text{Exp[-((t - t0)/\[Tau]1)]] + b (1 - \text{Exp[-((t - t0)/\[Tau]2)]]));
\]

Use the function NonlinearModelFit to fit the model to the data. It was helpful to provide starting values (inside the curly brackets).

\[
\text{nlmfit} = \text{NonlinearModelFit[trace475, model, \{\{a, 0.284\}, \{b, 0.272\}, \{\[Sigma], 0.104\}, \{t0, 0.24\}, \{\[Tau]1, 0.21\}, \{\[Tau]2, 23\}, \{\[Tau]v, 0.4\}, \{\[Cv], 0.55\}, \{\[Omega], 10.6\}, \{\[Phi], -12.07\}}, t, \text{MaxIterations} \to 100];
\]

Plot the fit and the kinetic trace in one graph and show the best fit parameters.

\[
\text{Show[ListPlot[trace475], Plot[nlm475[x], \{x, -3, 10\}], Frame -> True, ImageSize -> Full, PlotRange -> \{\{-3, 10\}, \{0, 0.1\}\}]}
\]

par475 = nlm475["BestFitParameters"]
13 Bibliography


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