

**Imperial College
London**

**Dynamics of Charge Carriers in
Bismuth Vanadate Photoanodes
for Water Splitting Using Solar
Energy**

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Abstract

This thesis described an investigation of charge carrier dynamics in dense, flat bismuth vanadate (BiVO_4) photoanodes using transient absorption spectroscopy and photoelectrochemical measurements including transient photocurrents. Transient absorption spectroscopy was employed to probe directly the photogenerated charge carrier population change as a function of time from microsecond (μs) to second (s) timescales. Transient photocurrent measurements were used to monitor charge extraction under chopped light conditions. Photo-induced absorption spectroscopy was employed to investigate charge carriers under working photo-electrochemical (PEC) conditions.

The transient absorption signals due to photogenerated holes in BiVO_4 were determined through using electron/hole scavengers and applied electrical bias in a complete photoelectrochemical cell. In 'un-doped' BiVO_4 , photogenerated holes were found to absorb from 500 nm to 900 nm. The dynamics of photogenerated holes were studied as a function of applied potential and excitation intensity. The population of long-lived (milliseconds–seconds) holes increased with increasing the width of space charge layer as a function of applied potential. A recombination process in kinetic competition with water oxidation on these long timescales was found to limit the photocurrent amplitude and onset potential in un-doped BiVO_4 photoanodes. Using transient photocurrent measurements, this recombination process was identified as recombination of surface-accumulated holes with electrons from the bulk of the semiconductor (back electron/hole recombination).

Doping molybdenum (Mo^{VI}) in un-doped BiVO_4 has been reported to be an effective method to increase photocurrent amplitude. Impedance measurements were carried out to determine the donor density increased by the presence of Mo^{VI} doping. The increased donor density limited efficient generation of the space charge layer to retard fast recombination on microseconds to milliseconds timescales, thus limiting the long-lived hole yield under modest applied potentials. Mo^{VI} dopants were shown to improve the electron transport determined by front/back side illumination in PEC and transient absorption spectroscopy (TAS) measurements.

Cobalt phosphate (CoPi) surface-modified un-doped BiVO_4 photoanodes were also studied using transient absorption spectroscopy and transient photocurrent measurements. Transient absorption spectra of CoPi-modified BiVO_4 were similar to those of unmodified BiVO_4 , and the kinetics on milliseconds to seconds did not change in the presence of CoPi surface modification. Both results indicated that photogenerated holes in BiVO_4 rather than CoPi species were monitored by transient absorption spectroscopy. However, the negative shift of photocurrent onset and increased photocurrent could be explained by efficient suppression of back electron/hole recombination in BiVO_4 photoanodes.

In terms of the function of CoPi water oxidation catalysts on BiVO_4 , photo-induced absorption (PIA) was employed to further study the CoPi/ BiVO_4 system. CoPi species oxidised by BiVO_4 holes were observed in PIA measurements due to the high extinction coefficient of oxidised CoPi and significant hole accumulation generated by continuous illumination. However, these oxidised CoPi species did not appear to drive catalytic water oxidation, as evidenced by results from spectroelectrochemical measurements of CoPi/FTO electrodes; water oxidation still occurred via BiVO_4 , consistent with the transient absorption results. Therefore, I concluded that in the CoPi/ BiVO_4 system, CoPi did not act as a catalyst, although hole transfer to CoPi can take place.

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List of Symbols and Abbreviations

A	active geometric area (cm^2)
$abs(\lambda)$	absorbance
ALD	atomic layer deposition
$AM\ 1.5$	air mass 1.5
$APCVD$	atmospheric pressure chemical vapour deposition
A_{TAS2}	amplitude of the slow, exponential decay phase
C	concentration (mol L^{-1})
CB	conduction band
C_{light}	speed of light ($3 \times 10^8\ \text{m s}^{-1}$)
C_{SCL}	space charge capacitance (F)
DAQ	data acquisition
DFT	density-functional theory
d_{sc}	width of the space charge layer (nm)
e	electronic charge ($1.6 \times 10^{-19}\ \text{C}$)
$E(\lambda)$	photon energy (J)
$E_{F,n}$	quasi-Fermi level for electrons
$E_{F,p}$	quasi-Fermi level for holes
EIS	electrochemical impedance spectroscopy
$Flux$	solar photon flux ($\text{m}^{-2}\ \text{s}^{-1}\ \text{nm}^{-1}$)
FTO	fluorine-doped tin oxide
h	planck constant ($6.626 \times 10^{-34}\ \text{J s}$)
I_i	intensity of the incident light
$IPCE$	incident photon-to-current efficiency
I_{ph}	photocurrent (mA)
I_t	intensity of the transmitted light
j	current density (mA cm^{-2})
j_{hole}	hole flux approaching to the surface and accumulate
j_{max}	theoretical maximum photocurrent density (mA cm^{-2})
k_B	Boltzmann constant ($1.381 \times 10^{-23}\ \text{m}^2\ \text{kg s}^{-2}\ \text{K}^{-1}$)
k_{rec}	rate constants for back electron/hole recombination
k_{WO}	rate constant of water oxidation by BiVO_4 holes
k_{WO}	rate constants for water oxidation
L	optical path length of the film
l	film thickness (m)
LED	light emitting diode
L_p	light penetration depth (m)
m_e^*/m_o	electron effective mass

<i>MOD</i>	metal-organic deposition
<i>ms</i>	Monoclinic scheelite
N_d	donor density (cm^{-3})
<i>OD</i>	optical density
OD_{OC}	absorption signal at open circuit
<i>P</i>	solar power flux ($\text{W m}^{-2} \text{ nm}^{-1}$)
<i>PEC</i>	photoelectrochemical
<i>PIAS</i>	photo-induced absorption spectroscopy
P_{mono}	power intensity of the monochromatic light (mW cm^{-2})
p_s	density of surface holes (holes nm^{-2})
<i>RHE</i>	reversible hydrogen electrode
<i>SEC</i>	spectroelectrochemical
<i>SECM</i>	scanning electrochemical microscopy
<i>SEM</i>	scanning electron microscopy
<i>T</i>	temperature (K)
$t_{50\%}$	halftime (s)
<i>TAS</i>	transient absorption spectroscopy
<i>TOF</i>	turnover frequency
<i>TPC</i>	transient photocurrent
<i>U</i>	applied electrode potential (V)
U_{fb}	flat-band potential
<i>VB</i>	valence band
<i>XRD</i>	X-ray diffraction
α	reaction order of water oxidation
$\alpha(\lambda)$	absorption coefficient (m^{-1})
ΔOD	change in absorbance
$\Delta OD(t)$	transient absorption optical density
ΔOD_{SEC}	SEC amplitude
ϵ	relative permittivity
$\epsilon(\lambda)$	extinction coefficient of the absorbing species at λ
ϵ_0	vacuum permittivity ($8.854 \times 10^{-12} \text{ F m}^{-1}$)
ϵ_{hole}	extinction coefficient of surface accumulated holes ($\text{M}^{-1} \text{ cm}^{-1}$)
λ	wavelength (nm)
μ_e	electron mobility ($\text{m}^2 \text{ V}^{-1} \text{ s}^{-1}$)
σ	electric conductivity (S m^{-1})
$\tau(TAS2)$	exponential decay time constant (s)
τTPC	time constant of the negative transient recovery (s)
ϕ_{REC}	yield of holes which recombine in the slow phase
ϕ_{TAS2}	yield of long-lived holes

List of Publications

- a) Dynamics of Photogenerated Holes in Un-doped BiVO₄ Photoanodes for Solar Water Oxidation
Ma, Y.; Pendlebury, S. R.; Reynal, A.; Le Formal, F.; Durrant, J. R. *Chem. Sci.* 2014, **5**, 2964.
- b) Efficient Suppression of Back Electron/hole Recombination in Cobalt Phosphate Surface-Modified Un-doped Bismuth Vanadate Photoanodes
Ma, Y.; Le Formal, F.; Kafizas, A.; Pendlebury, S. R.; Durrant, J. R. *Submitted*.
- c) Time-Resolved Absorption Study of Cobalt Phosphate on Bismuth Vanadate Photoanodes for Photoelectrochemical Water Oxidation
Ma, Y.; Kafizas, A.; Le Formal, F.; Pendlebury, S. R.; Durrant, J. R. *In preparation*.
- d) Transient Absorption Study of Photogenerated holes in Mo^{VI}-doped BiVO₄ Photoanodes
Ma, Y.; Kafizas, A.; Le Formal, F.; Pendlebury, S. R.; Durrant, J. R. *In preparation*.

Clarification of Contributions

I declare that I carried out most of the experiments and interpretations reported in this thesis. Some of the work was contributed by members of our group listed below:

Dr Stephanie Pendlebury, Dr Florian Le Formal, Mr Ernest Pastor and Dr Anna Reynal and I carried out construction, maintenance and update of the μ s-s transient absorption spectrometer and photo-induced absorption spectrometer.

Dr Florian Le Formal provided the training session of electrochemical impedance spectroscopy technique.

Dr Florian Le Formal, Dr Stephanie Pendlebury, Prof James Durrant and I together conceived and developed the simple kinetic model used in Chapters IV and VII.

Dr Andreas Kafizas carried out XRD measurements and provided guidance for the SEM measurements.

Chapter I

1. Introduction and Background

1.1 Background and Introduction to Solar Water Splitting

The CO₂ content in the earth's atmosphere has reached its highest level of over 400 ppm.¹ This value is thought to be responsible for increasing levels of climate change and also linked with other environmental issues. Such an increase in CO₂ concentration results from our dependence on fossil fuels (i.e. coal, oil and natural gases) for energy supply. Therefore, reducing the energy demand from fossil fuels and promoting the use of renewable energy resources could potentially slow down the speed of CO₂ increase in the atmosphere. In other words, there is an urgent need to develop a clean, alternative and renewable energy resource to replace current fossil energy resources.

Solar energy is one candidate as a renewable energy among others including wind power, biomass, geothermal and hydropower. The power of annual incident solar radiation on the earth's surface is ca. 120 000 TW of electromagnetic radiation. Such a quantity far exceeds the total need for energy consumption.² The most developed technology is to transform photons from the sun to electricity by solar cells. Such electrical energy, however, has to be stored for use during the night due to the intermittent nature of sunlight. Direct conversion of sunlight into energy dense chemical fuels is a promising method to overcome this problem. Solar water splitting into hydrogen using semiconducting materials is of particular interest to the scientific community as it is a carbon free process, resulting in zero net emission of CO₂. Materials used for water splitting need to be earth-abundant, highly stable in a wide range of pH, have a suitable band gap to efficiently use solar energy and have low cost for fabrication and operation. The first photoelectrochemical (PEC) water splitting device was developed by Fujishima and Honda in 1972 using semiconducting TiO₂ photoelectrodes.³ Nowadays the highest efficiency in a solar-

to-fuel device has reached over 12 % using GaAs photoelectrochemical / photovoltaic cells⁴ or perovskite photovoltaics⁵ to produce solar hydrogen. However, such highly efficient techniques are based upon rare materials (Ga) or toxic chemicals (lead in perovskite) with poor stability.

PEC water splitting using earth-abundant metal oxides has been considered to be an effective way for H₂ production. Research is mainly based around the most commonly available oxide materials such as WO₃, TiO₂, α -Fe₂O₃, BiVO₄ and Cu₂O.⁶ The former four materials are often developed as photoanodes for water oxidation to produce oxygen, and the latter Cu₂O is a promising photocathode for reduction of water to produce hydrogen. Since the first reported PEC water splitting by Fujishima and Honda, TiO₂ has been substantially studied. It has a band gap of 3.2 eV, giving the maximum efficiency around 1.5 %.⁷ However, this efficiency is far from meeting the threshold of efficiency for a commercial water splitting device. WO₃ is similar to TiO₂ with a 2.8 eV band gap, providing a maximum efficiency of 5%.⁷ Other materials have been taken into consideration for more efficient photoelectrochemical water splitting. Hematite (α -Fe₂O₃) has a suitable band gap around 2.1 eV resulting in a theoretical efficiency > 12 % due to efficient harvesting of solar energy from 600 nm.⁸ However the conduction band edge is below water reduction potential, unable to reduce water to hydrogen. Despite its conduction band edge, α -Fe₂O₃ has been considered as a photoanode material for water oxidation with applied electrical potential. Promising results have been reported in recent years for highly efficient water oxidation with α -Fe₂O₃.^{9,10} However, this material is limited by the high energy input (typical onset potential of photocurrent: > 1 V_{RHE}) to initiate water splitting in a PEC device, therefore current research is focussing on reducing the onset potential for water splitting using α -Fe₂O₃.^{11,12}

Similar to $\alpha\text{-Fe}_2\text{O}_3$, bismuth vanadate (BiVO_4) has been studied as a water oxidation material in recently years.^{6,13} The band gap of BiVO_4 is 2.5 eV, absorbing light from *ca.* 500 nm to the UV region. Accordingly, the maximum efficiency is *ca.* 10 %, suitable for a water splitting device. However, the conduction band is still 100 mV below the water reduction potential, limiting hydrogen production directly from BiVO_4 . The fabrication of BiVO_4 photoanodes has been reported with various techniques.¹³ The most promising method is based around solution-processed coating techniques, including spray-pyrolysis,¹⁴ spin-coating¹⁵, and dip-coating or drop-casting.¹⁶ The working principle and more detailed properties of BiVO_4 are introduced in the following sections.

1.2 Theory of Photoelectrochemical Water Splitting

The interface between the semiconductor and the electrolyte is analogous to the metal-semiconductor junction. When the semiconductor is in contact with the electrolyte, the Fermi level in the semiconductor equilibrates with the electrolyte's redox potential by transferring charges to the electrolyte. In a n-type semiconductor, electrons, as the majority charge carriers, near the junction are transferred to the electrolyte. As a result, the electron density near the semiconductor surface decreases, changing the Fermi level of the semiconductor down to match to the electrolyte's redox potential. The surface of the semiconductor is depleted by losing electrons to the electrolyte, forming band bending from the surface towards the bulk. The length of the band bending can be described as a depletion region, or a space charge layer (**Scheme 1.1**).

The length of the space charge layer (d_{sc}) is determined from Equation 1.1,

$$d_{sc} = \sqrt{\frac{2\epsilon\epsilon_0(U-U_{fb})}{eN_d}} \quad (1.1)$$

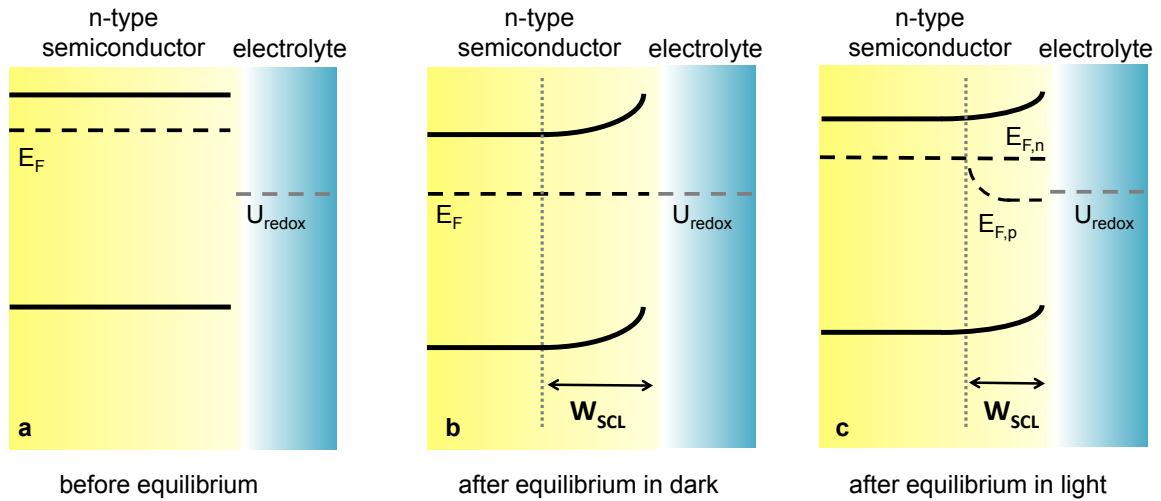
where N_d is the donor density; e is the electronic charge; ϵ is the relative permittivity of the electrode; ϵ_0 is the vacuum permittivity; U is the applied potential; U_{fb} is the flat-band potential.

To obtain the value of d_{sc} from Equation 1.1, N_d and U_{fb} need to be determined. Using impedance spectroscopy, such parameters can be quantified by modelling the impedance results using Mott-Schottky equation (Equation 1.2),¹⁷ assuming the space charge region is a parallel-plate capacitor with the spacing equal to the width of the space charge layer.

$$\frac{1}{C_{SCL}^2} = \frac{2}{\epsilon\epsilon_0 A^2 e N_D} (U - U_{fb} - \frac{k_B T}{e}) \quad (1.2)$$

where C_{SCL} is the space charge capacitance; k_B is the Boltzmann constant; T is the temperature; A is the active geometric area;

When the semiconductor is under illumination (i.e. band gap excitation), electrons are excited from the valence band to the conduction band. In the space charge layer, electrons in the conduction band migrate to the bulk by drift transport and holes in the valence band move towards the surface and accumulate. The band bending in the space charge layer provides an energy difference to drive electrons and holes movement inside the semiconductor.

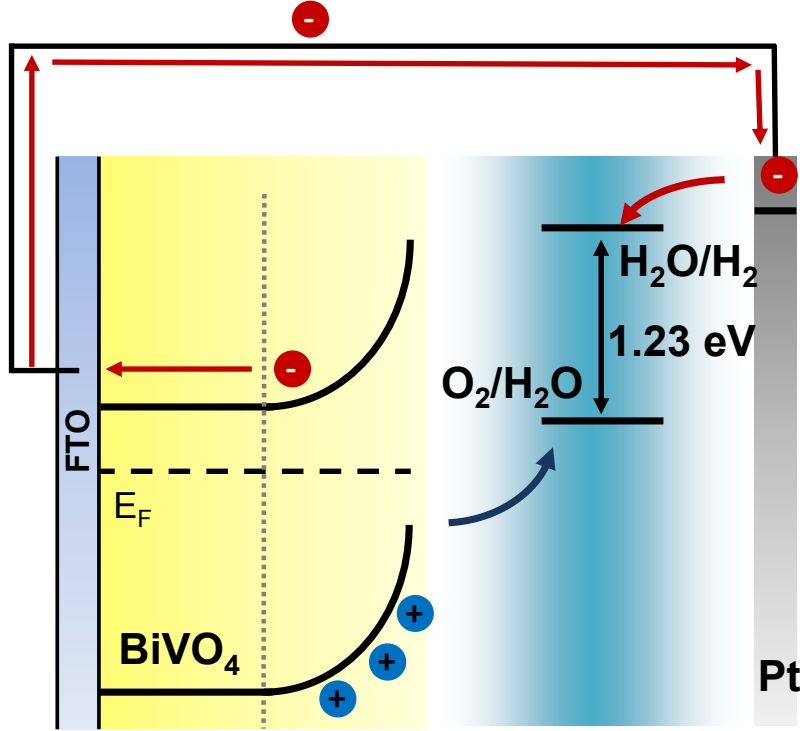


Scheme 1.1. (a): schematic of the Fermi level position of the n-type photoanode semiconductor before in contact with the electrolyte; (b): the semiconductor-electrolyte junction formed after the Fermi level in equilibrium with the electrolyte redox potential. (c) Quasi-Fermi levels formed under light excitation.

In a photoelectrochemical cell, the amplitude of band bending may be modulated by the applied potential. Under the flat band condition, the band bending is zero (**Scheme 1.1a**). The flat band potential is the position of the Fermi level under the

flat band condition. Because there is no band bending, there is no charge separation occurring to form photocurrent and water oxidation. Only fast bulk recombination can occur. Under anodic bias conditions, the band bending moves downwards (**Scheme 1.1b**). In the dark, when the Fermi level is positive enough to overcome overpotentials of water oxidation (Fermi level $> 1.23 V_{\text{RHE}} + \text{overpotential}$), water oxidation proceeds in the dark electrochemically at the semiconductor surface. When band gap excitation is present, the Fermi level splits into two quasi-Fermi levels ($E_{\text{F},n}$ and $E_{\text{F},p}$) near the semiconductor-electrolyte interface (**Scheme 1.1c**). Near the interface, photogenerated holes (minority charge carriers in a n-type semiconductor) accumulate at the interface. The band bending results in a decreased electron density at the interface. As the result, $E_{\text{F},p}$ near the surface shifts down and the surface is more likely to be p-type due to the accumulation of holes. The excited electrons may flow to the back contact (fluorine-doped tin oxide, FTO) and transfer to the counter-electrode. However, such change in electron density does not change the electron density significantly; therefore, the $E_{\text{F},n}$ in then bulk nearly remains unchanged.

In a working PEC cell, the whole processes of water splitting is illustrated in **Scheme 1.2**. Electrons are excited from the valence band to the conduction band and then extracted to the external circuit under applied anodic potential. The electrons reduce water on the counter electrode. The holes generated within the space charge layer move to the surface for water oxidation.



Scheme 1.2. Schematic of water splitting using a n-type photoanode in a PEC cell. After band-gap excitation, electrons (red dots) are generated to the conduction band and holes (blue dots) in the valence band. Electrons are collected at the FTO and holes accumulated at the interface for water oxidation to produce O₂. Electrons transfer to the counter electrode, platinum (Pt), to reduce water to produce H₂.

In terms of the water splitting reactions, half reactions are considered separately. The water oxidation process proceeds at the photoanode and the water reduction occurs on the cathode. For simplicity, each part of the PEC cell is studied separately. In this thesis, the charge carrier dynamics of a n-type photoanode semiconductor were studied, and a Pt electrode was employed as a cathode. The water oxidation reaction is written as follows:



while on the cathode, usually Pt, water reduction occurs



Therefore, the overall reaction is written:



To evaluate the materials, the water splitting efficiency is one valuable parameter. There are several methods to calculate the efficiency of water splitting. The most useful one is the incident photon-to-current efficiency (IPCE) defined in Equation 1.6, which has been commonly used for comparison between materials or devices,

$$IPCE = \frac{I_{ph} \times 1239.8}{P_{mono} \times \lambda} \quad (1.6)$$

where I_{ph} (mA cm⁻²) is the photocurrent density under applied potential; 1239.8 (V nm) is a multiplication of Planck's constant and the speed of light; P_{mono} (mW cm⁻²) is the power intensity of the monochromatic light and λ (nm) is the wavelength of the incident light.

The IPCE represents the efficiency at which photons generated from the light source (monochromatic) are converted into electrons. The IPCE is also useful for the calculation of the estimated photocurrent under AM 1.5 condition. The spectrum of the sunlight under AM 1.5 condition is often different from the simulated light source (Xe lamp or W lamp). The method of calculation AM 1.5 photocurrent is introduced in Chapter III.

It is apparent that the applied potential is not taken into account for the calculation of IPCE. Therefore, IPCE is a potential-dependent efficiency in a PEC water splitting device. In addition, IPCE has also been used in solar cells research, to investigate charge carrier transport properties, such as electron diffusion length in mesoporous TiO₂ electrodes for dye-sensitised solar cells.¹⁸

Water oxidation to generate oxygen has been thought to be the rate-limiting factor in overall water splitting because it is kinetically slower than hydrogen evolution.^{19,20} Therefore, it is important to consider making improvements in photoanode materials to promote the water splitting efficiency.

1.3 Literature Review of Bismuth Vanadate for Solar Water

Oxidation

1.3.1 General Requirements of Photoelectrode Materials for Water Splitting

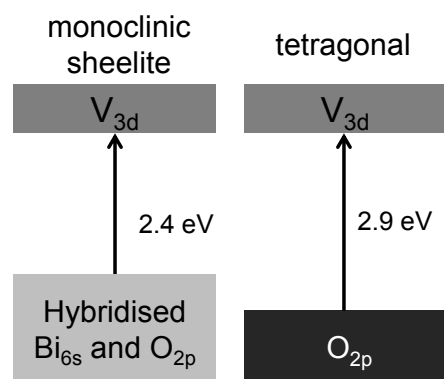
Using semiconducting materials for solar water splitting requires the potential of photogenerated holes in the valence band to be greater than 1.23 V_{RHE} (i.e. water oxidation potential), and the potential of photoexcited electrons in the conduction band to be more negative than 0 V_{RHE} (i.e. water reduction potential). Therefore, the overall band gap required in an ideal water splitting material is > 1.23 eV. Titanium dioxide (TiO_2) is one of these materials which meets the criteria mentioned above. However, the band gap is too large (3.0 eV), only absorbing light in the UV region of the solar spectrum. Cadmium sulfite (CdS) has a band gap of 2.4 eV with suitable band positions for overall water splitting. However, the stability of CdS is reported to be poor and the element of cadmium is toxic, limiting its development for application.⁶

Despite the limited choice of materials for overall water splitting, half reaction (water oxidation or water reduction) can be achieved by many materials. For example, hematite ($\alpha\text{-Fe}_2\text{O}_3$) and BiVO_4 cannot reduce water to hydrogen because the conduction bands are more positive than 0 V_{RHE} ; however, the valence bands (2.5 V_{RHE}) provide sufficient driving force for photogenerated holes to oxidise water. Therefore, the requirements for photoelectrode materials need to: be stable across a wide range of pH, nontoxic; have suitable band gap and band positions; low cost for mass production. These requirements will be addressed in the following sections.

1.3.1 Semiconducting Properties of BiVO₄

There are several crystal structures of BiVO₄ of which the monoclinic scheelite is the most photo-active for water oxidation. The monoclinic scheelite BiVO₄ has a band gap *ca.* 2.5 eV (absorption edge: *ca.* 500 nm, determined by absorption spectra), giving a theoretical maximum photocurrent about 6.9 – 7.5 mA cm⁻² (see Chapter III for details of calculation). The conduction band edge is reported to be 0.1 V_{RHE} and the valence band edge is 2.6 V_{RHE}, determined from impedance measurements and Mott-Schottky analysis.¹⁶ The band structure of ms-BiVO₄ crystal was initially proposed in Kudo *et al.*'s first synthesis paper, in which the conduction band was attributed to the 3d orbital of vanadium and the valence band to hybridisation of the 6s orbital of bismuth and 2p orbital of oxygen, as shown in **Scheme 1.3**.²¹ Computational chemistry using density functional theory (DFT) to study the BiVO₄ crystal structure was published in 2009, suggesting that the hybridised valence band may exist.²² However, experimental evidence for the hybridised valence band was not found until Payne *et al.* utilised X-ray photoelectron, X-ray absorption and X-ray emission spectroscopies to confirm that the valence band in BiVO₄ is due to hybridisation of Bi_{6s} and O_{2p}, narrowing the band gap to 2.5 eV.²³

Electron transport in BiVO₄ is facile and only a few reports focused on quantification of electron mobility or conductivity. The electron mobility in an undoped BiVO₄ was reported to be $4 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ measured by transient microwave conductivity method.²⁴ The slow charge transport has been reported to result in severe charge recombination and modest water oxidation performance in BiVO₄.^{16,24-26}



Scheme 1.3. Schematic of two BiVO₄ band structures, monoclinic sheelite (left) and tetragonal (right).

1.3.2 Synthesis

The synthesis of BiVO₄ photoanodes has been developed since Kudo and co-workers first introduced BiVO₄ to solar water splitting.²¹ The initial investigation was carried out using BiVO₄ nanoparticles in the presence AgNO₃ electron scavengers for photo-assisted water oxidation. The first synthesis of BiVO₄ materials by Kudo²¹ was reported by calcining Bi₂O₃ and NH₄VO₃ at 1170 K for several hours, forming a monoclinic scheelite structure of BiVO₄ which is suitable for visible light absorption. Then Kudo's group developed a facile method for synthesis of BiVO₄, in which Bi(NO₃)₃ was mixed with K₃V₅O₁₄ in water and the product was calcined to form BiVO₄ photocatalysts.²⁷ This method for synthesis of BiVO₄ nanoparticles was further modified by many groups using hydrothermal synthesis, to control crystal growth and facet modifications.^{28,29}

Initially, there was no consideration of BiVO₄ photoanode fabrication. In 2000, Galembeck and Alves first synthesised BiVO₄ thin films using a metal-organic deposition (MOD) and spin-coating method.³⁰ This method was further modified by Sayama *et al.* for a photoelectrochemical study of BiVO₄ photoanodes for solar water oxidation.^{15,31} This has since been the most popular method of synthesis, as discussed below. The MOD method facilitated the modification of the surface morphology in order to achieve flat³² or mesoporous³³ structures depending on the

parameter settings and surfactants applied. Additionally, doping BiVO₄ with tungsten (W^{VI}) or molybdenum (Mo^{VI}) was also realised easily using this MOD-spincoating method.^{34,35} Instead of spin-coating, based on the initial MOD recipe developed by Sayama *et al.*, van de Krol's group^{14,34,36} further modified this method using spray-pyrolysis to fabricate nanostructured BiVO₄ photoanodes with doping, producing increased photocurrent to 1 mA cm⁻² for water oxidation.

In 2012, Seabold and Choi³⁷ first developed an electrodeposition method for BiVO₄ fabrication. The photoelectrochemical performance was vague without any surface modification. However, it provided a new route for facile synthesis of BiVO₄ without using hazardous precursors and harsh conditions. Following the initial reports, Choi's group further optimised the electrodeposition conditions and significant enhancement was achieved, especially for an outstanding performance obtained when depositing electrocatalysts.³⁸

1.3.3 Performance enhancement of BiVO₄ photoanodes

1.3.3.1 Doping Tungsten (W^{VI}) or Molybdenum (Mo^{VI})

The poor electron transport in BiVO₄ was considered a key reason for the modest performance of PEC water oxidation.^{24,26} Hence, one strategy for improvement was to improve charge transport of BiVO₄ by doping electron-rich elements into the BiVO₄ lattice. Abdi and van de Krol studied un-doped BiVO₄ thin films using photoelectrochemical,^{25,34} and transient microwave conductivity measurements.²⁴ They concluded that the low mobility (ca. 4×10^{-2} cm² V⁻¹ s⁻¹) of electrons in BiVO₄ was compensated by their long lifetime (40 ns) and thus a long diffusion length (70 nm). Tungsten (W^{VI}) and Molybdenum (Mo^{VI}) doping were first reported by Bard's group using scanning electrochemical microscopy (SECM) to evaluate the effect of

W^{VI} and Mo^{VI} dopants.^{16,39,40} The DFT results also suggests that one excess electron in W^{VI} or Mo^{VI} could improve the conductivity of $BiVO_4$.¹⁶ Parallel to this, various doping elements were investigated by Parmar et al, where W^{VI} and Mo^{VI} were found to be the top candidates for the efficient PEC performance in doped $BiVO_4$.³⁵

It is commonly recognised that Mo^{VI} and W^{VI} doping in $BiVO_4$ improves the PEC water oxidation performance due to improved charge transport. The effect of doping however has not been systematically elucidated experimentally, particularly with regard to its impact upon the space charge layer formed at the semiconductor-electrolyte interface and the impact upon the recombination kinetics. It is generally agreed that this n-type doping by Mo^{VI} and W^{VI} increases the electron density (i.e. donor density, N_d) determined from electrochemical impedance analysis (Mott-Schottky).^{16,35} Additionally, the flat band potential was also measured to more negative electrode potentials shift by ca. 100 mV following doping. Van de Krol and co-workers used a gradient tungsten (W^{VI}) doped structure to form an energy cascade for driving electrons towards FTO and holes towards the surface due to different U_{fb} with doping content.³⁶ It is however not clear if such small energy offsets could provide enough driving force for charge separation. There is also an issue of diffusion of doping elements during the calcination procedure, which may further reduce the effect of gradient doping (i.e. the concentration of W^{VI} dopants gradiently increased from 0 % at the surface to 1 % at the FTO- $BiVO_4$ interface).

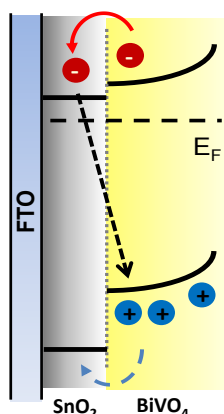
The width of the space charge layer was reduced following an increase of the donor density (N_d). This narrower space charge layer may be less effective at retarding charge recombination, and thus may limit the yield of charges for water oxidation. However, enhanced performance was indeed obtained with W^{VI} or Mo^{VI} doping, indicating that the limitation of a narrower space charge layer was overcome

by more efficient charge separation or transport. Additionally, there was no report addressing the behaviour of photogenerated holes in such doped BiVO_4 photoanodes. The mechanism of enhanced water oxidation by BiVO_4 due to doping still remains unclear.

1.3.3.2 Interfacial Layers

Charge separation in BiVO_4 has been considered to be key for efficient water oxidation. The modest photocurrent (i.e. water oxidation performance) however demonstrates that efficiency losses must be severe due to recombination. Electrons need to be excited and then separated in the film from the space charge layer to the back contact; during this process electrons may recombine, thus limiting photocurrent generation. One approach to minimise this effect is to generate a wide and deep space charge layer, which produces a large driving force to avoid recombination. This method on the other hand costs significant energy in terms of potential input, decreasing the overall water splitting efficiency.

To realise spatial charge separation, another approach was proposed by using interfacial layers with a lower conduction band and valence band edge between BiVO_4 and the FTO back contact.¹³ This structure aimed to collect electrons at the interfacial layer's conduction band and then send them to the FTO. Due to the energy offset between conduction bands of the interfacial layer and BiVO_4 , recombination may be mitigated. The photogenerated holes, on the other hand, should be blocked from moving towards the FTO side due to the deeper valence band of the interfacial materials. Therefore, electrons are collected by FTO via the interfacial layer and holes remain in the BiVO_4 readily for water oxidation.



Scheme 1.4 Schematic of the structure of a SnO_2 interfacial layer between FTO and BiVO_4 , and the proposed charge separation mechanism

The first material used for such an interfacial layer was tin oxide (SnO_2). The conduction band of SnO_2 is *ca.* $0.4 V_{\text{RHE}}$, $0.3 V$ lower than the BiVO_4 conduction band edge. The valence band of SnO_2 is deeper than the valence band of BiVO_4 . Therefore, the band positions in SnO_2 are suitable for this interfacial layer. The first study of this approach was reported by Nosaka *et al.*, who used SnO_2 in between BiVO_4 and FTO.⁴¹ Enhancement of photocurrent was obtained by a factor of three. Control measurement was also carried out using SnO_2 on the surface, showing a significantly reduced photocurrent. These results clearly demonstrated the importance of spatial charge separation in BiVO_4 photoanodes. Further studies of SnO_2 interfacial layer were reported by van de Krol *et al.*, who optimised the structure in terms of SnO_2 and un-doped BiVO_4 thicknesses.¹⁴ The latter case was more important as electrons were needed to be collected efficiently in a relatively short distance. This requires the BiVO_4 film to be thin. It is surprising that only 10 nm of SnO_2 can improve IPCE from 10% to 30% in a 200 nm thick BiVO_4 photoanode, clearly suggesting that significant recombination occurs during electron migration from the surface to the back contact.

Apart from SnO_2 , tungsten oxide (WO_3) is another candidate considered as an interfacial material. It has been used as a guest-host structure in $\alpha\text{-Fe}_2\text{O}_3$ photoanodes.⁴² The band position of WO_3 is similar to SnO_2 but more favourable for

the interfacial layer. The conduction band edge is closer to 0.1 V_{RHE} , whilst the valence band edge is ca. 2.9 V_{RHE} , allowing it to absorb visible light from 440 nm. Nosaka *et al.* first investigated the effect of WO_3 on BiVO_4 .^{43,44} Significant improvement was observed in the presence of a WO_3 interfacial layer, especially using illumination > 420 nm to rule out the contribution of WO_3 to photocurrent. When considering the light absorption by WO_3 under simulated AM 1.5 illumination, WO_3 may behave as a hole donor / electron acceptor to promote charge separation. Hong *et al.* studied the impact of WO_3 / BiVO_4 thicknesses in planar photoelectrodes on photocurrent and water oxidation efficiency.⁴⁵ They suggested that thin BiVO_4 was important for the best performance. Such photoanodes consisted of a thinner layer of BiVO_4 to allow efficient charge collection. Thicker BiVO_4 photoanodes were also compared, showing much decreased photocurrents, attributed to difficulties in charge transport across the bulk of BiVO_4 .⁴⁵

Sayama's group integrated SnO_2 and WO_3 in a BiVO_4 photoanode, where they found an enhanced photocurrent of up to 3 mA cm^{-2} in a $\text{FTO}/\text{WO}_3/\text{SnO}_2/\text{BiVO}_4$ architecture.⁴⁶ This structure was suggested to form an energy cascade for electron collection at the FTO side, which was suggested to replicate the charge separation process in Photosystem II.²⁰ However, the photogenerated holes on the WO_3 are trapped in WO_3 and therefore cannot contribute to water oxidation.

Although much effort has been made to increase photocurrents in BiVO_4 photoanodes using interfacial layers between the FTO and BiVO_4 , none of these approaches succeeded in reducing the onset potential for photocurrent generation. The onset potential (0.6 – 0.8 V_{RHE}) in BiVO_4 photoanodes is lower than other photoanode materials such as $\alpha\text{-Fe}_2\text{O}_3$ (1.0 – 1.2 V_{RHE}). However, comparing the flat band potential of BiVO_4 , there was still a gap with ca. 600 mV. This extra energy cost

could not be overcome by interfacial layers, although it has been thought that charge separation in such structure is improved. This could also be due to the lower conduction band edge of the interfacial layers. Materials such as SnO_2 and WO_3 have ca. 100 – 200 mV lower conduction band edges, which may need extra applied potential input to compensate the applied potential losses in electrons for water reduction. Therefore, the requirement of reducing onset potential in BiVO_4 was not solved by simply applying a back interfacial layer. Hence, other methods to improve the water oxidation performance are required, as is discussed in the following section.

1.3.3.3 Surface Modification

Surface modification using electrocatalysts (CoPi , FeOOH , NiOOH),^{32,36-38,47,48} and non-active layers (e.g. Al_2O_3)¹¹ on n-type photoanodes has shown effectiveness in terms of reducing onset potential, increasing photocurrent and increasing stability.⁴⁹ It has been proposed that the function of surface modification is to passivate surface traps by Al_2O_3 , and / or facilitate charge separation at the surface and catalyse water oxidation by electrocatalysts. The former case, using Al_2O_3 , has been considered for $\alpha\text{-Fe}_2\text{O}_3$ because of reported presence of surface trap states determined by impedance spectroscopy; the latter is commonly used in both BiVO_4 and Fe_2O_3 because it shows particularly improved performance, especially for much reduced onset potential.

One of the possible catalysts that has been used to modify BiVO_4 surfaces is cobalt phosphate (CoPi), which was introduced by Kanan and Nocera in 2008.⁵⁰ X-ray absorption studies indicated that the structure of CoPi composite is amorphous, forming a cubane-like CoO_x reaction centre with phosphate ligands.⁵¹⁻⁵³ CoPi has been reported to effectively reduce the overpotential for electrocatalytic water

oxidation^{50,54} and photocurrent onset potential for photo-assisted water oxidation on both BiVO_4 ^{25,32} and $\alpha\text{-Fe}_2\text{O}_3$ ^{48,55} photoanodes. In general, the onset potential can be reduced to ca. 200 – 300 mV vs U_{fb} by CoPi overlayer deposition on the BiVO_4 surface. The most striking performance was demonstrated by Abdi and van de Krol, who used a tungsten (W^{VI}) gradient doped BiVO_4 photoanode modified with CoPi on the surface to achieve 3.6 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$. The conventional deposition method is electrodeposition in a Co^{2+} containing electrolyte.⁵⁰ Zhong and Gamelin modified the deposition method by introducing illumination to the photoanode.^{32,48} CoPi was therefore deposited on the surface where photogenerated holes accumulate, which has been suggested to result in improved performance in terms of the onset potential and photocurrent.

Seabold and Choi developed a new electrocatalyst, FeOOH , for surface modification of BiVO_4 .³⁷ The onset potential was reduced to ca. 100 mV vs U_{fb} , clearly showing the effectiveness of this surface modification. The BiVO_4 was further developed in the Choi's group using a dual layer catalysts, $\text{FeOOH}/\text{NiOOH}$, to achieve $> 4 \text{ mA cm}^{-2}$ at $> 1.2 \text{ V}_{\text{RHE}}$ under simulated AM 1.5 excitation source.³⁸ Such a photocurrent is the highest reported so far for any kind of oxide photoanode system. However, the mechanism of performance enhancement from such modification, including CoPi and $\text{FeOOH}/\text{NiOOH}$, has not been clarified unambiguously.

The function of such electrocatalysts on BiVO_4 , or more general photoanodes, is not fully understood. In particular there has been no study on elucidation of the onset shift in a CoPi-modified BiVO_4 photoanode. Zhong *et al.*³² first attempted to answer this question using photoelectrochemical measurements. Comparing the unmodified BiVO_4 photocurrent measured with hole scavenger with the photocurrent of

CoPi/BiVO₄ measured in H₂O. They came to the conclusion that the performance enhancement (i.e. negative shift of onset potential) resulted primarily from a hole transfer process from BiVO₄ to CoPi to suppress surface recombination. They also suggested that the better performance, besides the suppression of surface recombination, was also due to the catalysis of water oxidation by CoPi. Such an observation and conclusions were also reported by van de Krol and co-workers.³⁴

Hamann and his group in parallel with Gamelin investigated the CoPi-modified α -Fe₂O₃ photoanodes using impedance spectroscopy. The processes of recombination, charge transport and water oxidation were modelled according to a previous impedance analysis of α -Fe₂O₃ photoanodes in Bisquert' group.⁵⁶ They concluded that the function of CoPi was to accept photogenerated holes from the photoanode in α -Fe₂O₃.⁵⁷

The mechanism reported above, is all based around the photoelectrochemical response of the photoanodes, in which the excited electrons, the majority charge carriers, were monitored. The electron dynamics obtained from the impedance data were then used to elucidate the behaviour of the minority charge carriers, photogenerated holes, for water oxidation.

Our group has previously reported a transient absorption study of CoPi-modified α -Fe₂O₃ photoanodes for water oxidation. Instead of hole transfer to CoPi, the photogenerated holes were found to remain in the α -Fe₂O₃ side and water oxidation was observed to proceed directly from α -Fe₂O₃. The CoPi overlayer reduced the potential required to suppress recombination, but no catalytic function was detected.^{55,58}

The function of CoPi became less clear after these two different conclusions reported by different techniques. The Gamelin group recently published their latest report on CoPi-modified α -Fe₂O₃, unravelling the function of CoPi deposited on photoanodes. Different morphologies and thicknesses of α -Fe₂O₃ substrates were investigated following CoPi deposition with different thickness.⁴⁷ Using photoelectrochemical measurements, they concluded that the CoPi was responsible for the onset shift by accepting holes and catalysing water oxidation; under higher applied potentials, the catalytic function of CoPi became trivial, with water oxidation increasingly resulting from direct oxidation of water by α -Fe₂O₃. However, this analysis was still based on electron signals measured from the photocurrents. In addition, when comparing different morphologies, the activity of water oxidation must be taken into account. It has been well-known that porous α -Fe₂O₃ prepared by atmospheric pressure chemical vapour deposition (APCVD) has the best photoactivity of water oxidation; however the α -Fe₂O₃ prepared by atomic layer deposition (ALD) is still modest. Therefore, when comparing the activity of water on these two CoPi-modified α -Fe₂O₃ surfaces, the activity/water oxidation performance needs to be normalised for comparison. Directly comparing the amplitude of photocurrents may not give useful information in terms of the water oxidation mechanism for revealing the mechanism.

1.3.3.4 Kinetic Study of Charge Carriers in BiVO₄ Photoanodes

Although there have been many studies of performance enhancement in BiVO₄ photoanodes, the understanding of charge carriers kinetics in BiVO₄ is still modest. There are many studies using phototransfer methods, impedance spectroscopy and computational methods to understand the water oxidation performance, semiconductor properties and energy levels of traps.¹³ The direct

detection of charge carriers, especially for minority charge carriers (i.e. photogenerated holes), is still lacking.

Transient absorption spectroscopy is one powerful technique to monitor charge carriers in semiconductors. It is particularly useful in observing changes in concentration of photogenerated holes in n-type photoanodes as a function of time. The time range can be tuned from femto-seconds to seconds timescales, depending on the objectives of an individual study.

Transient absorption spectroscopy has been used mainly to study charge carriers in TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$ photoanodes for solar water splitting. Currently, there is little research in transient absorption study of BiVO_4 .^{59,60} Aiga *et al.* studied particle-compacted BiVO_4 photoanodes using transient absorption spectroscopy on fs-ms timescales. The transient absorption signature of photogenerated holes in BiVO_4 was identified using Fe^{3+} and methanol as electron and hole scavengers, respectively. Two types of photogenerated holes were identified according to different decay kinetics between 600 nm and 900 nm. The 633 nm decay was assigned to photogenerated holes at the BiVO_4 surface actively reacting with the scavengers, whereas the 850 nm transient absorption signals was determined to be bulk photogenerated holes as no significant difference in decay kinetics was observed in the presence of scavengers. Electron-phonon coupling effects was also observed near the absorption edge of BiVO_4 , which was used to explain the oscillation of transient absorption signal within 10 ps near the absorption edge of BiVO_4 (ca. 500 nm). However, such studies focused on the ultra-fast (fs) timescales. The charge trapping/detrapping mechanisms were discussed. The water oxidation occurring with photogenerated holes in BiVO_4 was not elucidated due to their slow reactions on longer timescales, thought typically to be on ms-s timescales.

1.4 Project Objectives

. The maximum experimental photocurrent density for water oxidation at BiVO₄ photoanodes has been reported to be 4 mA cm⁻² under simulated solar excitation.³⁸ However, since then, the progress in the development of BiVO₄ materials has been slowed down. This is probably due to the lack of understanding of kinetics of charge carriers in BiVO₄, including generation, recombination and the reaction with water. Therefore, this thesis focuses on the charge carrier dynamics, based on photoelectrochemical and transient absorption measurements. Particularly, the dynamics of photogenerated holes in BiVO₄ photoanodes were addressed, giving a clearer understanding of the kinetic limitations in achieving higher photocurrent densities / water oxidation efficiencies.

The project objectives were:

a) Identification of transient absorption signals of photogenerated holes in

BiVO₄. The optical signature of charge carriers (photoexcited electrons/holes) has been reported using ultra-fast transient absorption spectroscopy previously. However, the charge carrier identified was on fs-ns timescales. On such timescales, the transient absorption signals were mainly associated with free charges, and may overlap between electron and hole signals. On longer timescales, identification of charge carriers in BiVO₄ has not been reported in the literature. Therefore, it was important to identify the charge carriers on longer timescales from milliseconds to seconds, especially important for photogenerated holes in BiVO₄ photoanodes by transient absorption spectroscopic measurements.

b) Understanding of charge carrier dynamics in un-doped BiVO₄ photoanodes for photo-assisted water oxidation. The dynamics of

photogenerated holes for water oxidation in BiVO₄ photoanodes are not clear yet. Water oxidation is a slow process determined from frequency-resolved and time-resolved techniques on α -Fe₂O₃, WO₃ and TiO₂ photoanodes. However the water oxidation rate for BiVO₄ was not determined under the condition of transient absorption measurements prior to these thesis studies. In addition, the water oxidation dynamics, in terms of the concentration of photogenerated holes and rate constants, were not studied. In addition, the flat-potential of BiVO₄ is 0.1 V_{RHE} but the photocurrent onset potential is 0.7 V_{RHE}, giving a 600 mV gap. It is important to understand which process limits the photocurrent generation, especially under the condition of low applied potential between 0.1 V_{RHE} and 0.7 V_{RHE}. The objective of this section is was identify the dynamics of photogenerated holes for water oxidation using transient absorption spectroscopy, and to understand the kinetic limitation of photogenerated holes for water oxidation under modest applied potentials (0.1 V_{RHE}–0.7 V_{RHE}).

- c) **Understanding of the effects of doping on the properties and kinetic behaviour of BiVO₄ photoanodes.** It has been reported that doping Mo^{VI} or W^{VI} can significantly improve the photocurrent in BiVO₄ for water oxidation. DFT calculations suggested that the improvement of photocurrent is associated with the improved electron transport. However, the impact of doping upon the dynamics of long-lived holes is not reported. In addition, another significant change following n-type doping is the potential change in space charge layer thickness, which had not been considered specifically. The objective of this section was to compare the dynamics of photogenerated holes for water oxidation in un-doped and doped BiVO₄ photoanodes using transient absorption spectroscopy, with particular interest in how doping changes the

width of the space charge layer and therefore change the dynamics of photogenerated holes in these BiVO_4 films.

d) Understanding the effects of surface modification on BiVO_4 photoanodes.

Surface modification using electrocatalysts has been considered as an effective method to improve water oxidation efficiency in BiVO_4 photoanodes. However, the function of such surface overlayer has not been elucidated. Previous studies of CoPi-modified $\alpha\text{-Fe}_2\text{O}_3$ using transient absorption spectroscopy suggest that CoPi does not behave as an electrocatalyst in this system. It is not clear if this effect is a general effect for all n-type photoanodes or only specific to $\alpha\text{-Fe}_2\text{O}_3$. Also, it is important to investigate the CoPi-modified BiVO_4 under the PEC working condition with continuous illumination. The objective of this section was to understand: 1) how CoPi overlayers on BiVO_4 photoanodes increase photocurrent and reduce the onset potential for photocurrent generation. Transient absorption spectroscopy was used for this study; 2) identify the catalytic function of CoPi overlayers on BiVO_4 photoanodes under the simulated AM 1.5 condition, using photo-induced absorption spectroscopy.

e) Understanding the reaction kinetics of water oxidation on BiVO_4 photoanodes under simulated working conditions.

Besides the transient absorption studies on BiVO_4 , the water oxidation behaviour in BiVO_4 under working conditions is also important. The current understanding of charge carrier dynamics is based on the short-pulsed transient absorption measurements, which is far different from continuous illumination measurements. The objective of this section was to carry out photo-induced absorption studies to understand the kinetics of water oxidation by

photogenerated holes by continuous illumination, rather than pulsed laser in transient absorption spectroscopy, using a simple rate law analysis.

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Chapter II

2. Materials and Methods

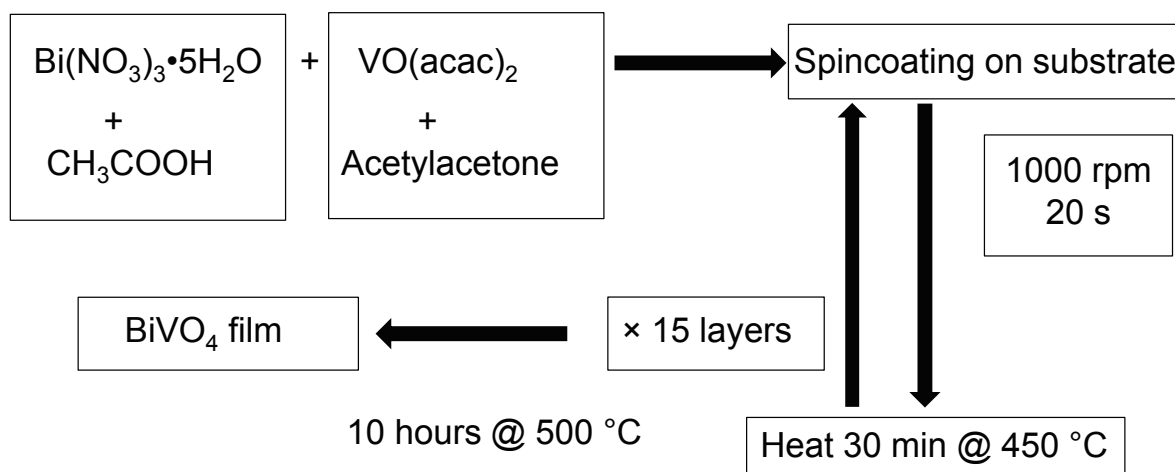
In this chapter, details of various BiVO_4 photoanodes (un-doped, molybdenum-doped, CoPi surface modified) and physical characterisations, including X-ray diffraction (XRD) and scanning electron microscopy (SEM), were given. The main techniques used to characterise the charge carrier dynamics of BiVO_4 photoanodes, including UV-Vis absorption spectroscopy, photoelectrochemistry (PEC), transient photocurrent (TPC), electrochemical impedance spectroscopy (EIS), transient absorption spectroscopy (TAS) and photo-induced absorption spectroscopy (PIAS), were also described.

2.1 Fabrication of BiVO₄ Photoanodes

2.1.1 Fabrication of Un-doped BiVO₄ Photoanodes Using Modified Metal-Organic Deposition

Unless otherwise stated, chemicals used in studies reported herein were purchased from Sigma-Aldrich in the highest purities available in store and used without further purification. Un-doped BiVO₄ photoanodes were fabricated using the metal-organic deposition (MOD) method, initially reported by Sayama, *et al.*,¹ with modifications. Bismuth nitrate pentahydrate (0.2 mol L⁻¹) was dissolved in acetic acid (1.5 mL, BDH), and vanadyl acetylacetonate (0.2 mol L⁻¹) was dissolved in acetylacetone (10 mL, Merck). These solutions were stirred at room temperature for 30 minutes. FTO (fluorine-doped tin oxide) glass (2.5 × 2.5 cm, TEC 15, Hartford Glass Co.) was cleaned by sonication in de-ionized water (Millipore, 18.2 MΩ cm at 25 °C) then acetone (VWR). After sonication, the cleaned glass was heated at 500 °C for 30 minutes to remove all organic residues. BiVO₄ films were prepared by depositing the precursors by spin coating. Spin-coating parameters were set at 1000 rpm for 20 s for each layer of deposition. For each layer, a small piece of the substrate was covered with a piece of tape to leave blank FTO for electrical connection. After each layer was deposited by spin-coating, the film was calcined at 450 °C for 30 min. This spincoat/calcine procedure was repeated 15 times, shown in **Scheme 2.1**. After depositing the final layer layer, the coated glass was calcined at 500 °C for 10 hours to ensure formation of the monoclinic- scheelite structure. The thickness of BiVO₄ was 450-500 nm determined by cross-sectional SEM shown in Chapter III.

Fabrication method: metal-organic deposition



Scheme 2.1. Schematic of un-doped BiVO₄ photoanode fabrication procedures using the MOD-spincoating method.

2.1.2 Fabrication of Mo^{VI}-doped BiVO₄ photoanodes using modified Metal-Organic Deposition

Molybdenum (Mo^{VI}) doped BiVO₄ photoanodes (Mo^{VI}-doped BiVO₄) were fabricated following the same procedures as described above for un-doped BiVO₄ photoanodes. As previously reported for Mo^{VI} or W^{VI} doped BiVO₄ photoanodes,^{2,3} when preparing the MOD precursors, bis(acetylacetonato)dioxomolybdenum(VI) was used to substitute vanadyl acetylacetonate from 1% to 10% in molar ratio, so the total ratio of Bi:(V+Mo^{VI}) remained 1:1. The spincoating and calcination procedures were the same as for the un-doped BiVO₄ fabrication.

2.1.3 Photo-electrodeposition of CoPi on un-doped BiVO₄ photoanodes

CoPi was photo-electrochemically deposited on un-doped BiVO₄ surface. A three-electrode configuration was employed in the PEC cell for the deposition (for electrochemistry details see Section 2.2.2). The precursor for CoPi deposition was

prepared using cobalt(II) nitrate hexahydrate dissolved with 0.1 M KPi buffer (0.1 mol L⁻¹ K₂HPO₄ and KH₂PO₄). The concentration of cobalt in the precursor was 0.1 mM. Photo-electrodeposition of CoPi on un-doped BiVO₄ was carried out by applying 1.2 V_{RHE} potential (details see below) to the BiVO₄ film under back-side illumination from a Xe lamp. The illumination was calibrated, using a Si photodiode, to be one sun equivalent in terms of photon flux emitted (m⁻² s⁻¹) with wavelengths shorter than 650 nm.

2.2 Characterisation methods

2.2.1 X-ray diffraction (XRD), UV-vis Absorption Spectroscopy, and Scanning Electron Microscopy (SEM)

X-ray diffraction (XRD) measurements was conducted using a micro-focus Bruker GADDS powder X-ray diffractometer with a monochromated Cu K α (1.5406 Å) source. UV-vis spectra were obtained using a Perkin Elmer UV-vis spectrometer (Lambda 25). SEM imaging was carried out with a LEO 1525 scanning emission microscope (field emission gun SEM with acceleration voltage of 5 kV).

2.2.2 Photoelectrochemical Measurements

Photoelectrochemical (PEC) measurements were carried out in a home-made PTFE cell with quartz windows on front and back sides. A three-electrode configuration was used, comprising a platinum mesh counter electrode, a reference electrode (Ag/AgCl/saturated KCl, 0.197 V_{SHE} at 298 K, Metrohm) and the BiVO₄ working electrode. Unless otherwise stated, all PEC and transient absorption spectroscopic measurements were carried out via back-side illumination. The scan rate was 10 mV s⁻¹, as reported in literature

for comparison, in the current-potential (j-U) measurements. Potassium phosphate (KPi) buffer (0.1 mol L⁻¹ K₂HPO₄ and KH₂PO₄) was employed to maintain a constant pH of 6.7. The hole scavenger, Na₂SO₃ (1 mol L⁻¹), and the electron scavenger, AgNO₃ (6 mmol L⁻¹), were employed in the transient absorption study to determine the transient absorption signals of electrons and photogenerated holes. The applied electrode potential used in this thesis was converted to be *versus* the reversible hydrogen electrode (RHE) at 298 K concerning the impact of the AgCl/Ag reference electrode. The reaction of the AgCl/Ag reference is:



$$E_{AgCl/Ag}(SHE)/V = 0.220 - 0.0592 \log(a_{Cl^-}) \quad (2.2)$$

where Equation 2.1 is the reaction in the reference electrode. Equation 2.2 describes that the equilibrium (relative) electrode potential at 298 K is dependent on the activity of Cl⁻ (a_{Cl^-}). By definition, the equilibrium electrode potential for a hydrogen electrode is:

$$E_{H^+/H_2}(SHE)/V = -0.0592 pH \quad (2.3)$$

so that

$$E_{H^+/H_2}(AgCl/Ag)/V = 0.220 - 0.0592 \log a_{Cl^-} + 0.0592 pH \quad (2.4)$$

Therefore, the applied electrode potential versus reversible hydrogen electrode used in this thesis is:

$$U_{RHE}/V = U_{AgCl/Ag} + E_{H^+/H_2}(AgCl/Ag) = U_{AgCl/Ag} + 0.220 - 0.0592 \log a_{Cl^-} + 0.0592 pH \quad (2.5)$$

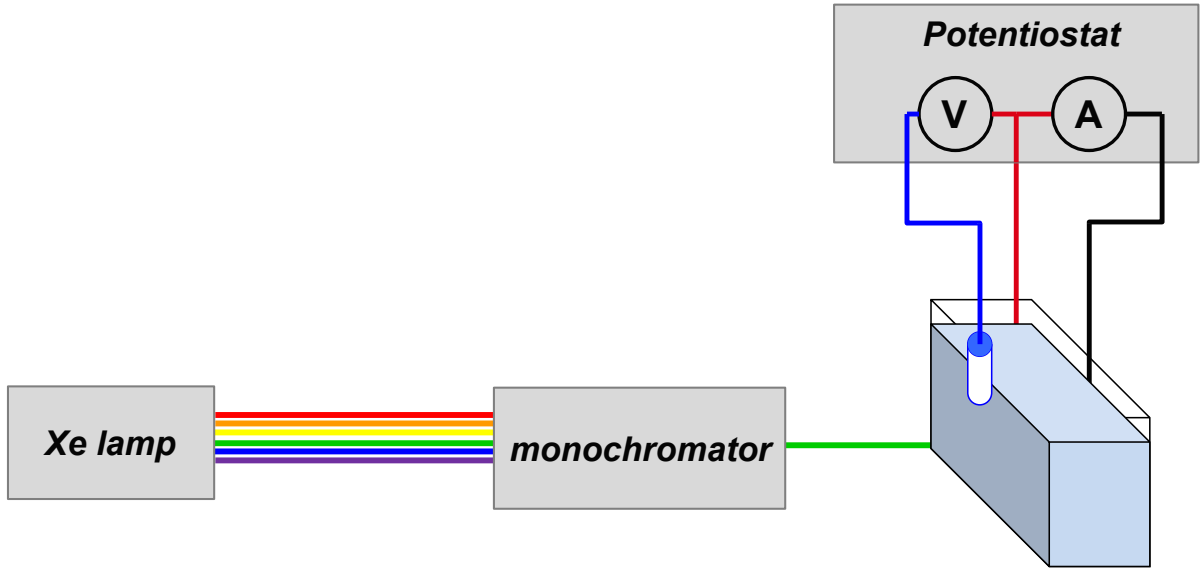
where $U_{AgCl/Ag}$ is the applied electrode potential versus the Ag/AgCl reference electrode. In the reference electrode used for this thesis studies, saturated KCl

was used as the electrolyte. The reference electrode potential was 0.197 V_{SHE} at pH=0.

The light source used was a 75 W ozone-free xenon lamp (Hamamatsu) coupled, for IPCE measurements, with a monochromator. For photocurrent measurements, the light used was generated from the Xe lamp without coupling with the monochromator. An Autolab potentiostat (PGSTAT 12 equipped with FRA2 module) was used to record all PEC and impedance data with Nova software. For incident-photon-to-current efficiency (IPCE) measurements, the intensity of the monochromated light was measured using an optical power meter (PM 100, Thorlabs) with a power sensor (S120UV, Thorlabs). The IPCE values were calculated using the following equation (Equation 2.6),⁴

$$\text{IPCE} = \frac{j_{\text{ph}} \times 1239.8}{P_{\text{mono}} \times \lambda} \quad (2.6)$$

where j_{ph} (mA cm⁻²) is the photocurrent density under applied potential; 1239.8 (V nm) is a multiplication of Planck's constant and the speed of light; P_{mono} (mW cm⁻²) is the power intensity of the monochromatic light and λ (nm) is the wavelength of the incident light.



Scheme 2.2. Schematic presentation of the PEC setup for j-U and IPCE measurements.

2.2.3 Transient Photocurrent Measurements (TPC)

The equipment for TPC measurements was based on the PEC equipment. The measurements were carried out by fixing constant applied bias to the sample and then measuring the current response under chopped light conditions. The light on/off condition was controlled by a shutter with a time interval of 5 s or 10 s.

2.2.4 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) measurements in the dark were conducted to determine the flat-band potential (U_{fb}) of BiVO_4 . The frequencies were between 0.01 Hz and 100 kHz. The semiconductor-electrolyte interface is assumed to be a plate capacitor, so the U_{fb} can be calculated using the Mott-Schokky equation (Equation 2.7),

$$\frac{1}{C_{sc}^2} = \frac{2}{\epsilon \epsilon_0 A^2 e N_d} \left(U - U_{fb} - \frac{k_B T}{e} \right) \quad (2.7)$$

where C_{sc} (F) is the space charge capacitance; A (cm²) is the active geometric area, N_d (cm⁻³) is the donor density; e is the electronic charge (1.602×10^{-19} C); ϵ is the relative permittivity of BiVO₄ (68);⁵ ϵ_0 is the vacuum permittivity (8.854×10^{-12} F m⁻¹); U vs RHE (V) is the applied electrode potential; U_{FB} vs RHE (V) is the flat-band potential; k_B is the Boltzmann constant (1.381×10^{-23} J K⁻¹) and T is the temperature (298 K). The impedance data were acquired using the Autolab potentiostat and analysed using Zview (Scribner Associates). Full range of frequencies (0.01 Hz-100 kHz) were used to model and obtain the space charge capacitance using the Randles circuit (shown in Chapter III **Figure 3.4**). After determining the donor density and flat-band potential, the width of the space charge layer (d_{sc}) as a function of applied potential was also determined using Equation 2.8.⁶

$$d_{sc} = \sqrt{\frac{2\epsilon\epsilon_0(U-U_{fb})}{eN_d}} \quad (2.8)$$

2.2.5 Transient Absorption Spectroscopy (TAS)

Transient absorption spectroscopy is a pump-probe technique which monitors the photo-induced charge carrier population as a function of time. A short laser pulse (pump) was used to excite electron from the valence band to the conduction band in a semiconductor sample. A second, continuous wave, light beam generated from a tungsten or xenon lamp (probe) was used to monitor the charge carrier's population as a function of time after the photoexcitation. The photogenerated species can absorb the probe light at certain wavelength, thus changing the absorbance of the semiconductor sample. Therefore the change in absorbance (ΔOD) can be translated directly into the population of charge carriers, giving a profile of dynamics.

Mathematically, the working principle is based on Beer-Lambert law. The absorbance (optical density, OD) is determined from:

$$OD = \varepsilon(\lambda)CL = \log\left(\frac{I_i(\lambda)}{I_t(\lambda)}\right) \quad (2.9)$$

where I_i is the intensity of the incident light; I_t is the intensity of the transmitted light; the probe wavelength is λ ; $\varepsilon(\lambda)$ is the extinction coefficient of the absorbing species at λ ; C is the concentration and the L is the optical path length of the film.

The change in absorbance (ΔOD) as a function of time (t) at a certain wavelength (λ) can be therefore calculated from:

$$\begin{aligned} \Delta OD(t) &= OD_1(t) - OD_0(t_0) = \log\left[\frac{I_i}{I_{t1}(t)}\right] - \log\left[\frac{I_i}{I_{t0}(t_0)}\right] = \log\left[\frac{I_{t1}(t)}{I_{t0}(t_0)}\right] \\ &= \log\left[1 + \frac{I_{t1}(t) - I_{t0}(t_0)}{I_{t0}(t_0)}\right] = \log\left(1 + \frac{\Delta I(t)}{I_{t0}(t_0)}\right) \end{aligned} \quad (2.10)$$

In the transient absorption equipment, the change in light intensity is measured by a photodiode, in which incident photons result in a photo-induced potential change. Therefore, the transient absorption signal is translated into:

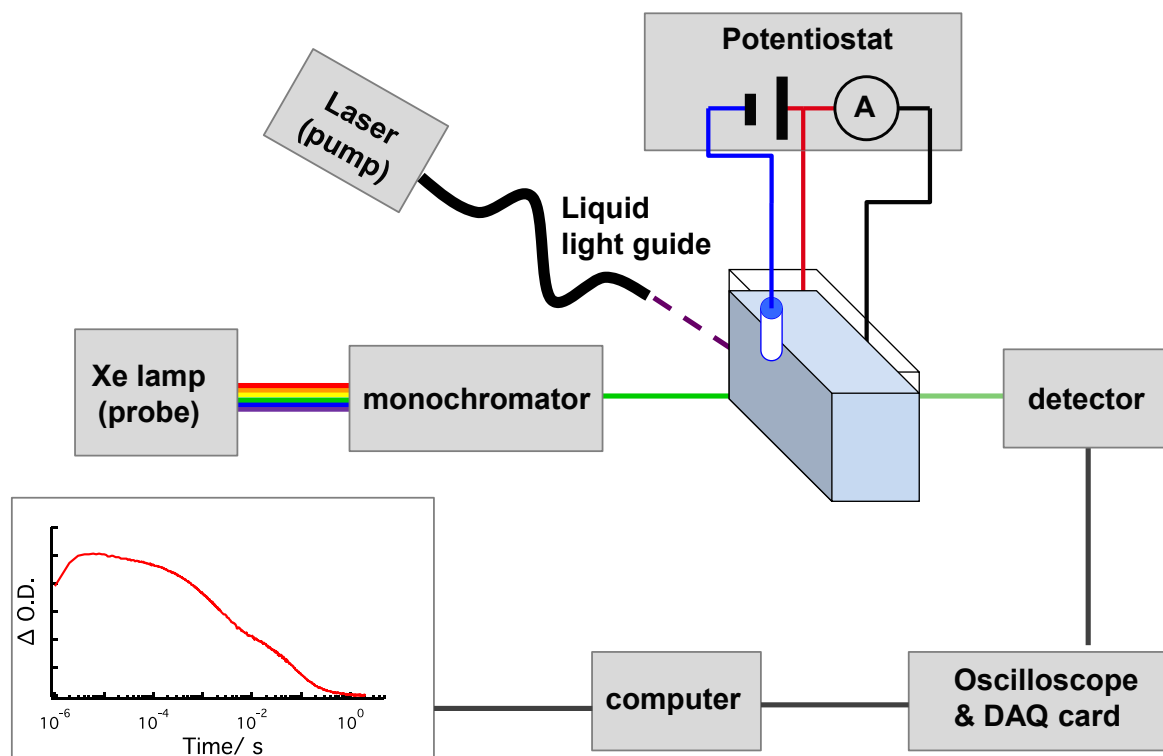
$$\Delta OD(t) = \log\left(1 + \frac{\Delta I(t)}{I_{t0}(t_0)}\right) = \log\left(1 + \frac{\Delta V(t)}{V_{t0}(t_0)}\right) \quad (2.11)$$

Because such ΔOD is a very small value, the equation above can be simplified:

$$\Delta OD(t) = \log\left(1 + \frac{\Delta V(t)}{V_{t0}(t_0)}\right) = \frac{1}{\ln(10)} \frac{\Delta V(t)}{V_{t0}(t_0)} = \frac{1}{2.303} \frac{\Delta V(t)}{V_{t0}(t_0)} \quad (2.12)$$

The transient absorption spectrometer used for the studies reported in this thesis is shown in **Scheme 2.3**. It consisted of a Nd:YAG laser (Big Sky Laser

Technologies, Ultra CFR Nd:YAG laser system, 6 ns pulse width) at 355 nm (3rd harmonic) to excite the band gap of BiVO₄ photoanodes; the frequency of the laser flash was 0.33 Hz; the laser intensity was adjusted to be 100 $\mu\text{J cm}^{-2}$ using neutral density filters (Comar Instruments). The probe light source was a 100 W Bentham IL1 tungsten lamp equipped with a monochromator (OBB-2001, Photon Technology International). The transmitted probe light was filtered by a number of long-pass filters and a band-pass filter (Comar Instruments) in order to filter the scattered laser light. A silicon photodiode (Hamamatsu S3071) was used to detect transmitted photons. Collected data were processed in an amplifier (Costronics), and then were recorded with an oscilloscope (Tektronics TDS 2012c) on the timescale of μs – ms. For the transient absorption data on ms-s timescales, the signal passed by the amplifier and was recorded by a data acquisition (DAQ) card (National Instruments, NI USB-6211). Each transient absorption decay was recorded by averaging 300-1000 laser pulses. All data were acquired by software built using the LabviewTM software. The transient absorption signals were very small, so the signal was represented as milli- ΔOD (m ΔOD) for convenience.

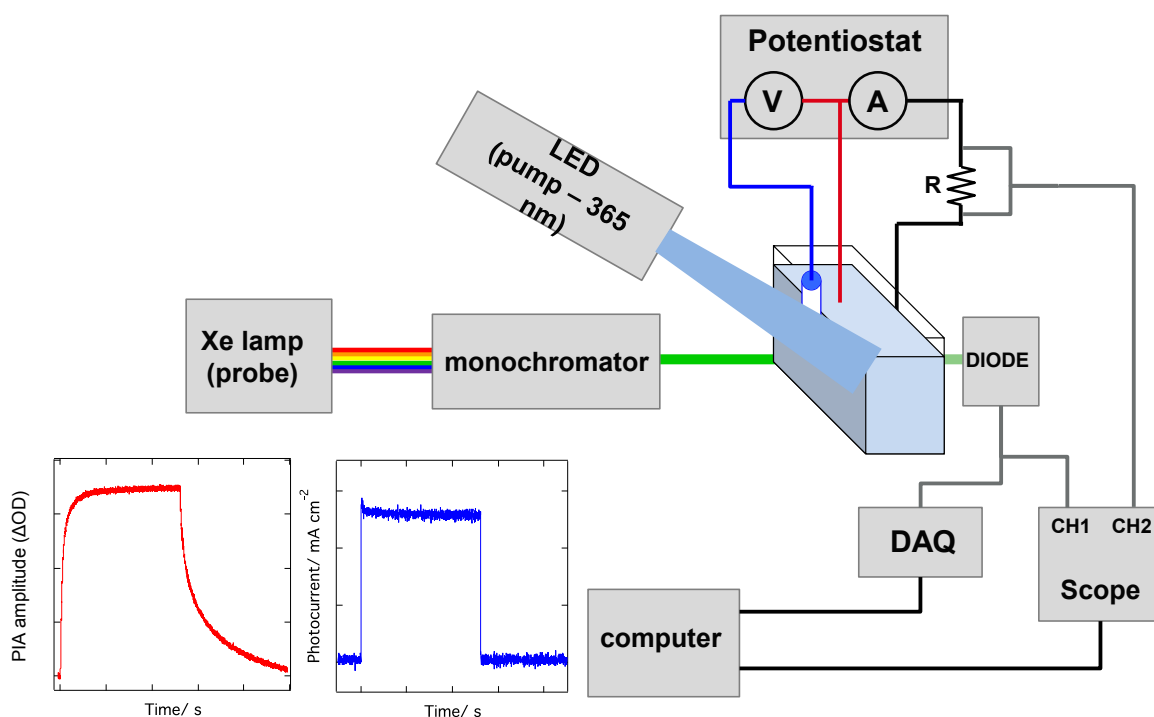


Scheme 2.3. Schematic of the transient absorption spectrometer for studying a photoelectrode in a photoelectrochemical cell under applied electric potential.

2.2.6 Photo-Induced Absorption (PIA) Spectroscopy

The equipment for photo-induced absorption spectroscopy was a modified version of the transient absorption spectrometer, where the laser excitation source was replaced with a long-pulsed LED at 365 nm (LZ1-10U600, LedEngin. Inc.). The excitation frequency was controlled by a frequency generator (TG300, Thurlby Thandar Instruments), with light on/off times ranging from 5 s to 8.5 s. The PIA signal was collected by the photodiode and sent to the amplifier and the DAQ card, as described in Section 2.2.5. The transient photocurrent response was monitored by recording the voltage response across a resistor in a potentiostat (Ministat 251, Sycopel Scientific Ltd). The photocurrent was calculated from the voltage

measurement using Ohm's law. The applied potential was controlled by the potentiostat.



Scheme 2.4. Schematic of the photo-induced absorption spectrometer for studying a photoelectrode in a PEC cell under applied potential.

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Chapter III

3. Photoelectrochemical and Transient Absorption Characterisations of Un-doped BiVO₄ Photoanodes

In this chapter, the fabrication of un-doped BiVO₄ photoanodes was discussed. Photoelectrochemical measurements were carried out to characterise the photoactivity of water oxidation by BiVO₄. A transient absorption study of un-doped BiVO₄ photoanodes on microsecond to second timescales was discussed. These measurements enabled the detection of charge carriers' dynamics during the recombination and water oxidation processes. Using electron/hole scavengers, the transient absorption signature of photogenerated holes in un-doped BiVO₄ were assigned, with the support of a transient absorption study in a PEC cell under anodic potential. The identification of the hole signal enabled further study of the hole reaction with water.

3.1 Introduction

In a previous report of charge carrier dynamics of BiVO_4 photoanodes, photogenerated holes on fs-ms timescales were identified from 500 nm to 800 nm probing range, using Fe^{3+} in de-ionised water as an electron scavenger.¹ No electron signal was found in the probing wavelength range. In addition, two types of photogenerated holes were assigned to trapped holes and free holes in the valence band, based on different rise times on fs-ns timescales. However, it is not clear if these holes were responsible for water oxidation on a longer (ms-s) timescales.

Our group has previously applied electron/hole scavengers to identify hole and electron signal on μs -s timescales in transient absorption studies of TiO_2 ,^{2,3} WO_3 ⁴ and $\alpha\text{-Fe}_2\text{O}_3$ ⁵ photoanodes: the electron scavenger can react with excited electrons in the conduction band before the time of recombination. Therefore, photogenerated holes can be probed. In addition, hole scavengers can reaction with photogenerated holes, leaving electrons to be probed. Both electron and hole signals were identified in TiO_2 and WO_3 . The photogenerated holes signal was broad across UV and near IR with maximum absorption around the blue spectral region (460 nm for TiO_2 and 500 nm for WO_3) and electron signals was observed in near IR region around 900 nm.^{3,4} However, in $\alpha\text{-Fe}_2\text{O}_3$, the hole signal was observed around 580 nm and electron signal was not observed, which requires the electron signal to be probed further in the IR region.⁵

In addition to scavengers, applying anodic potentials can also assist in identifying electron/hole signals. Previously TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$ hole signals were observed when positive potentials were applied, with the same spectral feature as measured in the presence of electron scavengers.^{2,5}

In this chapter, the fabrication of un-doped BiVO₄ photoanodes was reported. Transient absorption characterisations were carried out to identify the photogenerated hole signals using electron/hole scavengers and applied positive potentials. The assignment of photogenerated hole signals is also compared with previously reported transient absorption results.

3.2 Results

3.2.1 Material Characterisation

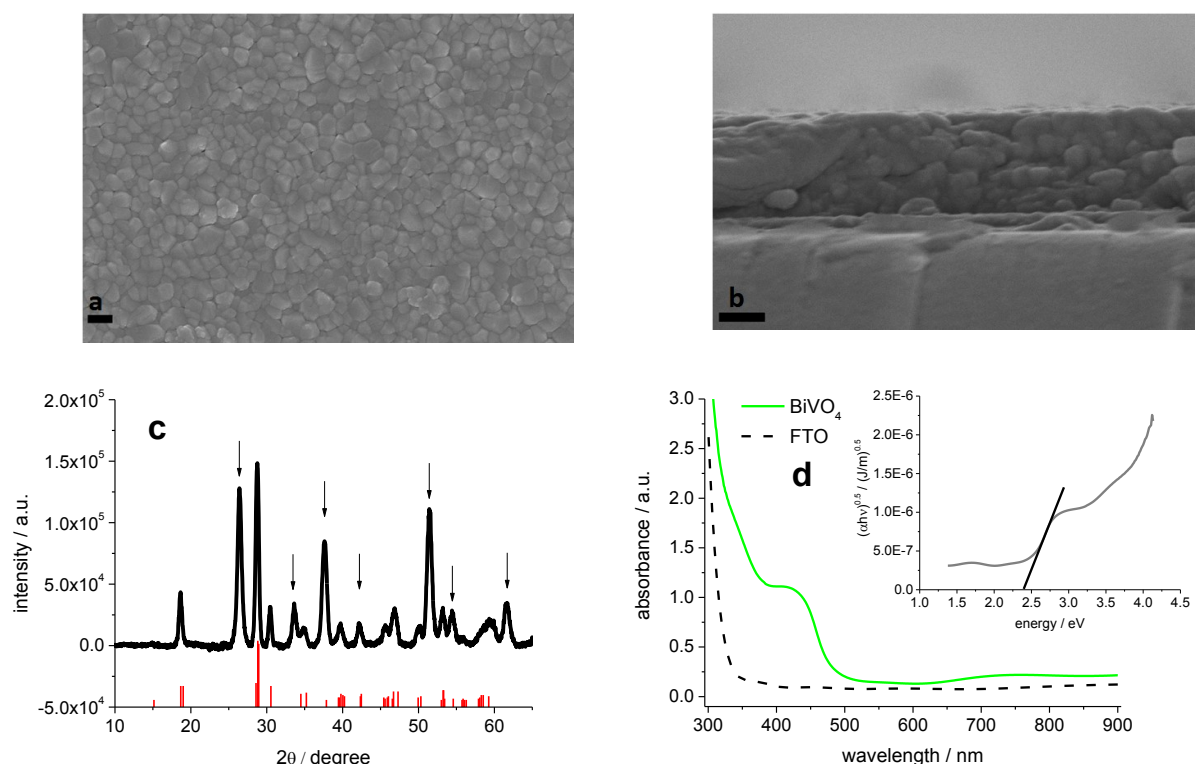


Figure 3.1. (a) SEM top view of the BiVO₄ photoanode. (b) SEM cross-sectional view of the BiVO₄ photoanode. The scale bars in (a) and (b) indicate 200 nm in length. (c) XRD pattern of BiVO₄ fabricated using the MOD method. Arrows are indications of SnO₂ peaks in FTO substrates. BiVO₄ XRD reference (red bars): 00-014-0688. (d) UV-vis absorption spectrum of BiVO₄ (green) and the FTO glass substrate (black dashed line); Inset: Tauc plot to determine the optical band gap of the BiVO₄ photoanodes.

Samples used in this chapter were un-doped BiVO₄ photoanodes (see Chapter II). The photoelectrode was characterised by XRD (**Figure 3.1**), showing a monoclinic sheelite structure, matching the reference pattern (reference code: 00-014-0688). SEM imaging shows that un-doped BiVO₄ prepared by the MOD-spincoating method was a flat and dense thin film with *ca.* 500 nm thickness and *ca.* 100 nm particle size (**Figure 3.1d**). These features enable apply the Schottky-type model to be used to interpret the semiconductor-electrolyte interface.

UV-vis absorption spectroscopy was used to characterise the BiVO₄ absorption edge (**Figure 3.1d**). The onset of light absorption is at *ca.* 500 nm, corresponding to 2.4 eV band gap (**Figure 3.1b**, inset), which gave a maximum theoretical photocurrent density of *ca.* 6.45 mA cm⁻², as calculated below (Equation 3.5).

According to the thickness of BiVO₄, the absorption coefficient was obtained from Beer-Lambert law, shown in Equation 3.1.

$$\alpha(\lambda) = \frac{\text{abs}(\lambda)}{l} \quad (3.1)$$

Where $\alpha(\lambda)$ is the absorption coefficient (m⁻¹), *abs*(λ) is the absorbance measured by UV-vis spectroscopy and *l* is the film thickness (m).

The light penetration depth is then determined by Equation 3.2.

$$L_p = 1/\alpha(\lambda) \quad (3.2)$$

Where L_p (m) is the light penetration depth. Therefore, the optical penetration depth was calculated to be *ca.* 270 nm at the 355 nm excitation used for the transient absorption measurements.

3.2.2 Photoelectrochemistry

Figure 3.2 (a) and (b) shows the stability of un-doped BiVO₄ photoanodes during photoelectrochemical measurements. The photocurrent dropped by *ca.* 40 % over two hours measurement under simulated AM 1.5 illumination, indicating the importance of improving the stability of BiVO₄, which will be discussed in Chapter VI. It has been reported that the stability of BiVO₄ appeared to be poor under simulated AM 1.5 illumination,⁶ and under high energy laser pulse⁷ during transient absorption spectroscopy. However, photoelectrochemical measurements were carried out with prolonged illumination to the photoelectrodes, producing a short-term stability over 10-15 minutes. Additionally, transient absorption measurements were carried out

with weak laser pulse compared to the reported transient absorption studies. No obvious photocorrosion was observed during both measurements and constant photocurrent performances were obtained before and after PEC and transient optical measurements.

The pH of the electrolyte was selected to be close to neutral (pH 6.7). The photocurrent performance as a function of pH is shown in **Figure 3.2 (b)**. The BiVO_4 electrode was not stable in the electrolytes with $\text{pH} < 4$ or > 10 , as oxidation peaks were observed. However, BiVO_4 showed a stable performance as a function of pH between 4 and 10.

At pH close to 3, Bi^{3+} was likely to be reduced in the acidic solution. The negative current observed in the photocurrent result at pH 3 could be associated with Bi^{3+} reduction (i.e. probably monolayer of Bi^{3+} was reduced). The oxidation peak at $0.5 V_{\text{RHE}}$ suggested that the reduced bismuth could be re-oxidised following positive sweep of electrode potential.

At pH close to 10, vanadium was not stable and likely to be dissolved in the alkaline solution, probably forming Bi_2O_3 on the electrode surface. The negative current may be indicative of a combination of O_2 reduction, Bi^{3+} reduction and V^{5+} reduction. At $1.1 V_{\text{RHE}}$, the oxidation peak at $0.9 V_{\text{RHE}}$ suggested that the reduced bismuth was re-oxidised, evidenced by the potential shift corresponded to the pH difference, i.e. $E_{\text{shift}} = 0.0591 \Delta \text{pH} + 0.5 V_{\text{RHE}}$ ($\Delta \text{pH} = 7$, $E_{\text{shift}} = \text{c.a. } 0.9 V_{\text{RHE}}$). However, it was not clear what reaction occurred at the second peak at $1.1 V_{\text{RHE}}$. This oxidation peak could be associated with vanadium oxidation which caused stability problems. After the j-U measurements, photocorrosion was observed in the sample at pH 10, suggesting that vanadium had been dissolved in the solution.

At pH between 4 and 10, the electrolyte could maintain a reasonable stability of BiVO_4 . The shift of photocurrent onset potential was due to different water oxidation mechanism, which is beyond the scope of this chapter. The electrolyte was then selected to be neutral to avoid severe photocorrosion.

Figure 3.2 (c) shows the current-potential performance of a typical BiVO_4 photoanode employed in this study, consistent with a previous study reported by Sayama *et.al.*⁸ The dark current onset for water oxidation was 1.9 V_{RHE} , which is indicative of a large overpotential for dark water oxidation on BiVO_4 . At 1.2 V_{RHE} , the photocurrent was 0.86 mA cm^{-2} . The corresponding incident photon-to-current efficiency spectrum (IPCE, shown in **Figure 3.3**) shows an onset at 500 nm, corresponding to the BiVO_4 absorption edge (**Figure 3.1 d**). The photocurrent onset was at ca. 0.8 V_{RHE} , consistent with literature data.^{9,10}

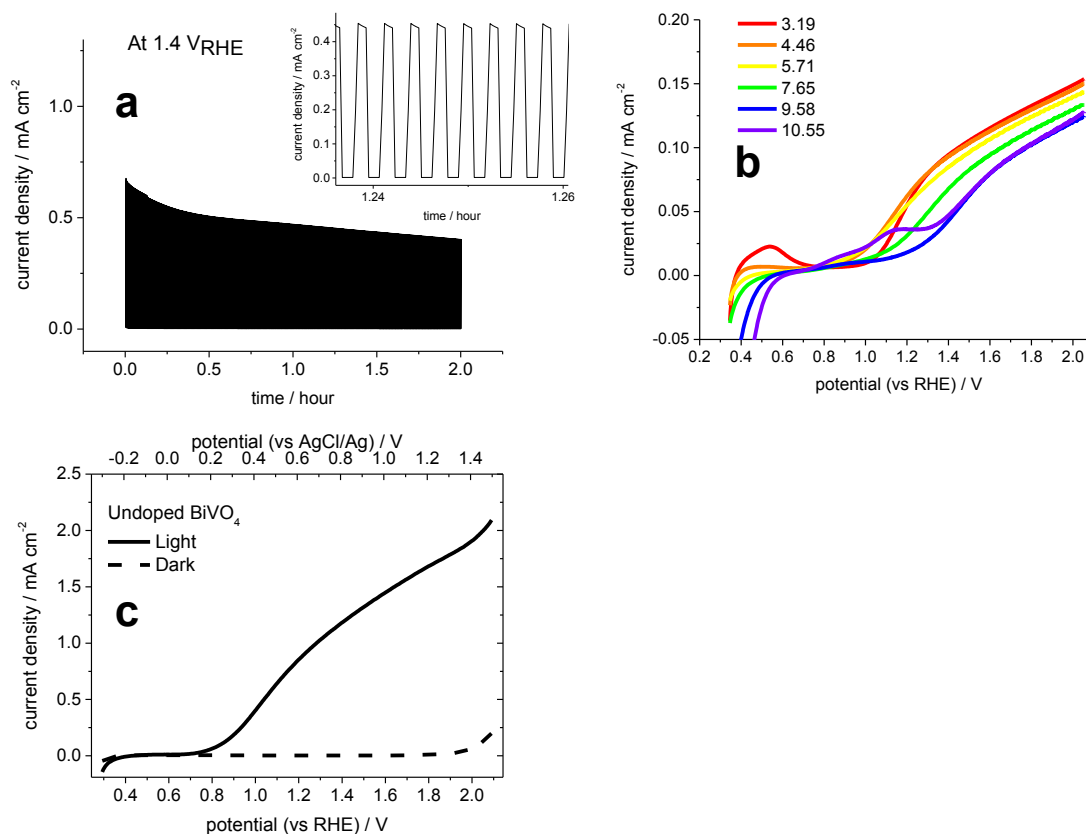


Figure 3.2. (a) Chopped light transient photocurrent measurements of un-doped BiVO₄ photoanodes at 1.4 V_{RHE} applied potential over 2 hours; inset: the details of photocurrent during the chopped light measurements. (b) Photocurrent measurements of a BiVO₄ photoanode as a function of the pH of electrolytes. (c) Effect of electrode potential on the current density of a BiVO₄ photoanode, measured in 0.1 M KPi buffer (pH 6.7) is shown as a function of the applied potential versus RHE and AgCl/Ag reference potentials. The current density measured under illumination (solid line) is compared to dark conditions (dashed line). Light intensity: approximately 100 mW cm⁻². Scan rate: 10 mV s⁻¹.

The IPCE corrected AM 1.5 photocurrent was also calculated by the following steps.

The single photon energy was calculated from Equation 3.3

$$E(\lambda) = h \times \frac{C_{light}}{\lambda} \quad (3.3)$$

where $E(\lambda)$ is the photon energy (J), h is the planck constant (6.626×10^{-34} J s), C_{light} is the speed of light (3×10^8 m s⁻¹) and λ is the photon wavelength (m).

The solar photon flux is then calculated according to Equation 3.4

$$\text{Flux}(\lambda) = \frac{P(\lambda)}{E(\lambda)} \quad (3.4)$$

where $\text{Flux}(\lambda)$ is the solar photon flux (m⁻² s⁻¹ nm⁻¹), $P(\lambda)$ is the solar power flux (W m⁻² nm⁻¹).

The theoretical maximum photocurrent density, j_{max} (A m⁻²), is then calculated by integrating the solar photon flux, shown in Equation 3.5:

$$j_{max} = e \times \int_{\lambda_2}^{\lambda_1} \text{Flux}(\lambda) d\lambda \quad (3.5)$$

Where λ_1 is the absorption edge of BiVO_4 , ca. 500 nm (2.5 eV band gap) in this study, λ_2 is the lower limit of the measured solar spectrum, and e is the elementary charge (1.602×10^{-19} C). A maximum theoretical photocurrent of such BiVO_4 photoanodes is accordingly calculated to be 64.5 A m^{-2} (6.45 mA cm^{-2}), assuming that photons absorbed were converted to current with 100 % efficiency from 500 nm to 280 nm (lower boundary of the NREL solar spectrum).

The integration of the photon flux converted to chemical energy (H_2 and O_2) by BiVO_4 photoanodes (i.e. $\text{IPCE} \times \text{AM1.5G spectrum}^{11}$), measured at 1.2 V_{RHE} and 1.7 V_{RHE} , gives photocurrent densities of 0.58 and 1.38 mA cm^{-2} , according to Equation 3.6, taking into account that the photons absorbed below 360 nm were neglected in the IPCE measurement due to strong absorption of FTO below 360 nm. The difference between the calculated photocurrent and the measured photocurrent is considered due to the different excitation source. In the PEC measurements, a Xe lamp was used to measure the PEC response, in which the excitation energy consists of strong contribution from the UV photons. As BiVO_4 absorbed strongly in the UV region, the photocurrent was expected to be higher than the calculated AM 1.5 photocurrent. However, such difference did not affect the interpretation of charge carrier kinetics in BiVO_4 as is discussed below.

$$j(V) = e \times \int_{\lambda_2}^{\lambda_1} \text{Flux}(\lambda) \times \text{IPCE}(\lambda, V) d\lambda \quad (3.6)$$

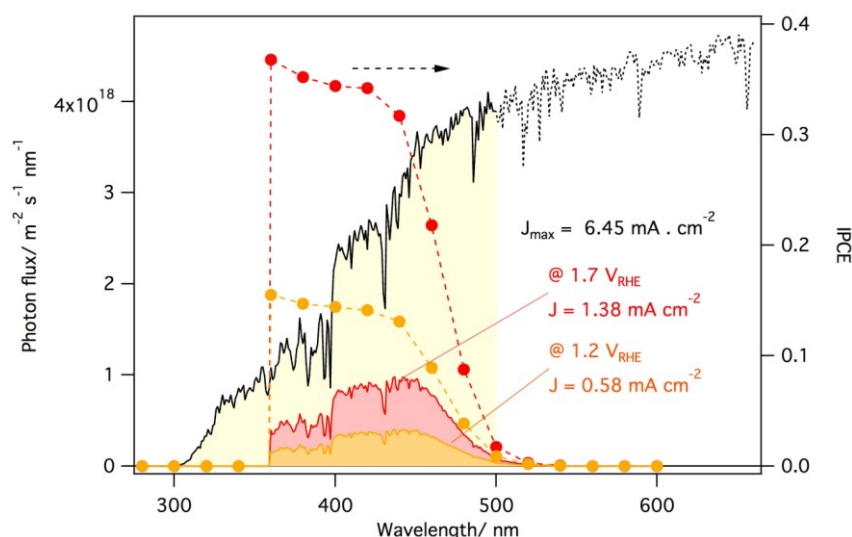


Figure 3.3. Absorbed photon flux converted to chemical energy by the BiVO_4 photoanode, measured at $1.2 V_{\text{RHE}}$ (orange) and $1.7 V_{\text{RHE}}$ (red), and compared to the AM1.5 solar photon flux spectrum (black). The BiVO_4 photon flux spectrum is calculated according to the IPCE data under $1.2 V_{\text{RHE}}$ (orange circles) and $1.7 V_{\text{RHE}}$ (red dots) conditions. Accordingly the theoretical maximum photocurrents under 1.2 and $1.7 V_{\text{RHE}}$ (under AM1.5 conditions) were indicated in the inset text.

Mott-Schottky analysis using electrochemical impedance spectroscopy was employed to calculate the width of the space charge layer in these photoanodes (see **Figure 3.4a**). Details of impedance measurements have been introduced in Chapter II. The use of CPE to interpret the space charge capacitance is due to the non-ideal property of space charge layer capacitance. It is often caused by the inhomogeneous capacitance at the surface. The SEM shows that the surface of BiVO_4 surface was not perfectly flat, composited by particles. Using a parallel capacitor to interpret the space charge capacitance will cause over-fitting of the impedance result. Such problem can be corrected by using CPE to obtain the best fit and therefore obtain the corrected space charge capacitance. The flat-band potential (U_{fb}) was determined to be *ca.* $0.1 V_{\text{RHE}}$, which is 700 mV more negative than the onset of photocurrent generation. This analysis also yielded a donor density of 10^{18}

cm^{-3} , similar to that reported previously for 'un-doped' BiVO_4 films (i.e. without additional intentional dopants).¹² This donor density in un-doped BiVO_4 has been reported to result from oxygen vacancies.¹³ The value of donor density was used to calculate the width of the space charge layer (d_{sc}) as a function of applied potential using Equation 2.4, as discussed further below. The relatively low donor density measured for these un-doped BiVO_4 photoanodes results in a rather wide space charge layer (e.g. at $1.2 V_{\text{RHE}}$, d_{sc} was calculated to be *ca.* 90 nm),¹⁴ significantly wider than typically reported in, for example Si^{IV} -doped hematite photoanodes (*ca.* 10 nm at $1.23 V_{\text{RHE}}$).¹³

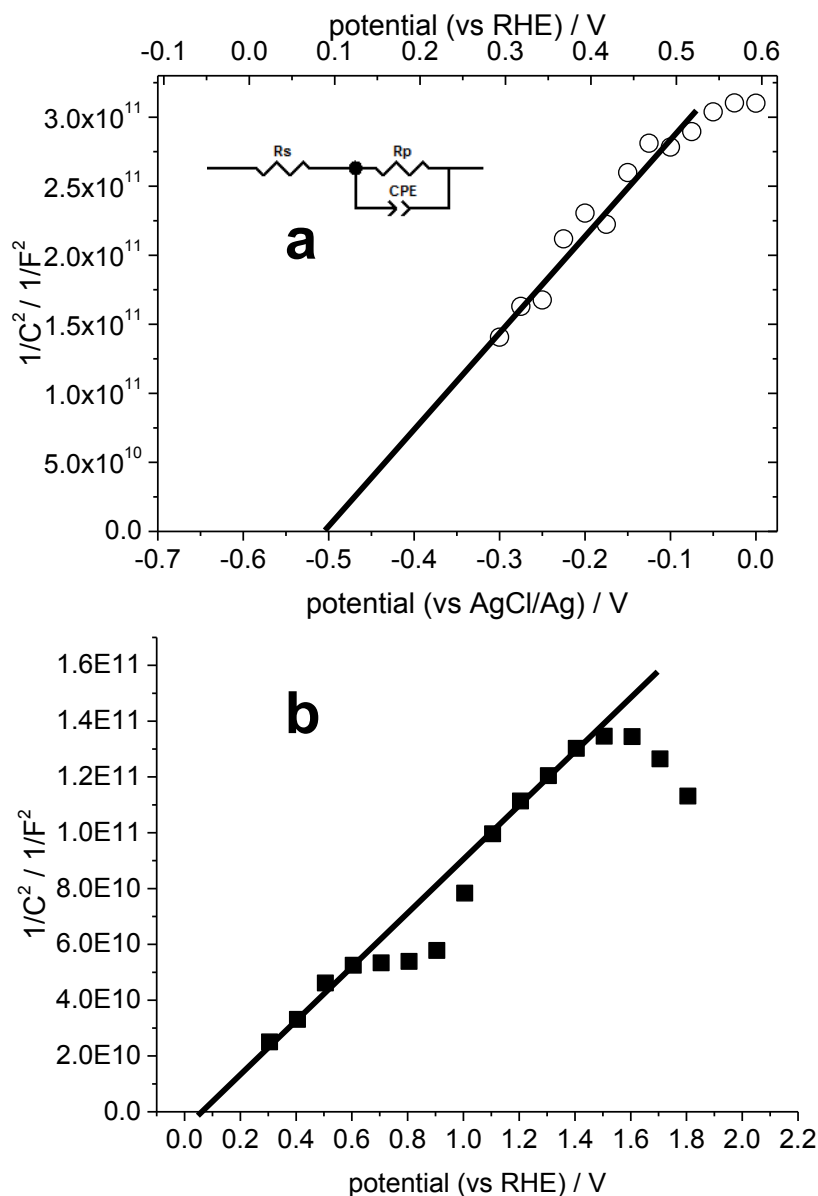


Figure 3.4. (a) Mott-Schottky plot of the BiVO_4 photoanode using the Randle model shown inset. The flat-band potential is determined to be ca. $0.1 V_{\text{RHE}}$. (b) Full range of Mott-Schottky plot of the BiVO_4 photoanodes between $0.3 V_{\text{RHE}}$ and $1.8 V_{\text{RHE}}$.

3.2.3 Transient Absorption Spectroscopic Study of Isolated Un-doped BiVO_4 Photoanodes in H_2O , and Electron and Hole Scavengers

Using transient absorption spectroscopy, charge carriers photogenerated in the BiVO_4 photoanode can be monitored directly by measuring the change in the intensity of a transmitted monochromatic probe light as a function of time after

pulsed band gap excitation. In order to understand the photogenerated holes' behaviour during the process of water oxidation on BiVO_4 , it is first necessary to identify the transient absorption signal of these holes. Employing electron/hole scavengers or applying a positive electrode potential can enable the identification of charge carriers' transient absorption signals by modulating their lifetimes and concentrations. Previous transient absorption studies have shown that electron/hole scavengers change the kinetics of charge carriers significantly in WO_3 and TiO_2 films;^{3,4} however, kinetics of photogenerated holes in $\alpha\text{-Fe}_2\text{O}_3$ were not affected by methanol (a hole scavenger) without applied potential.⁵

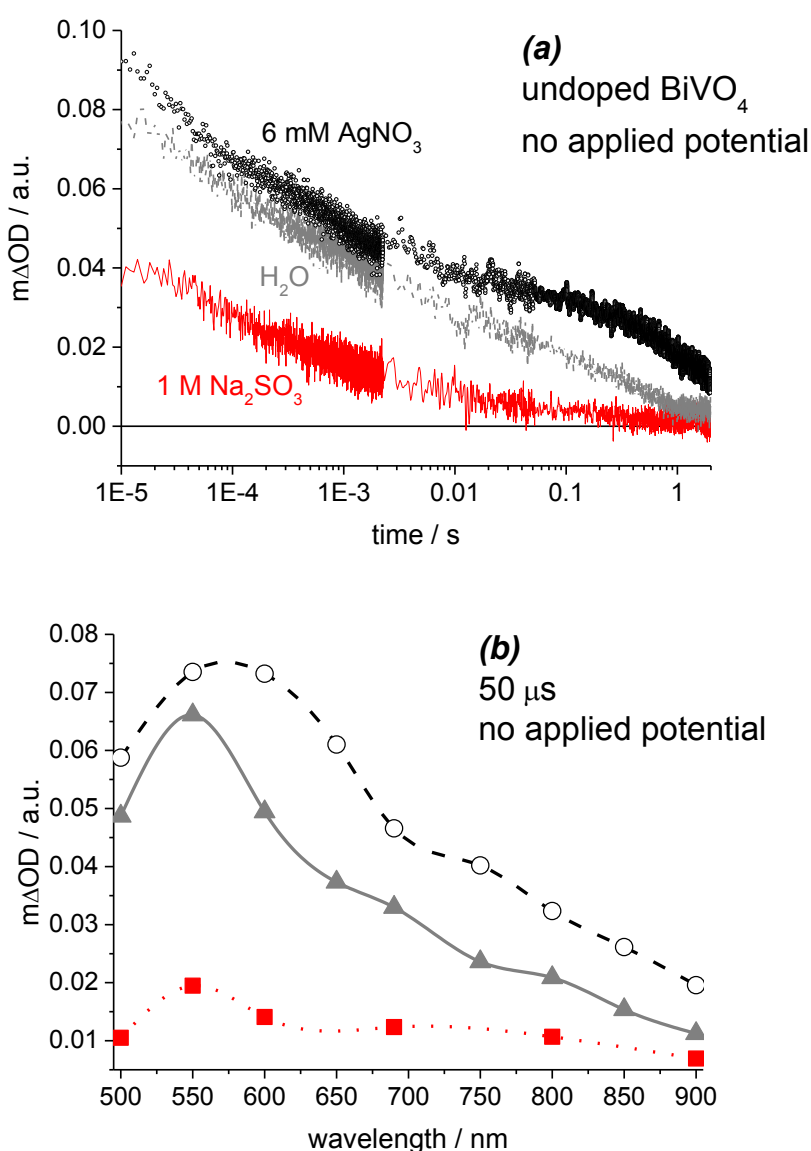


Figure 3.5. (a) Transient absorption decays of a $BiVO_4$ photoanode measured in 6 mM $AgNO_3$ (black, electron scavenger), de-ionized water (grey) and 1 M Na_2SO_3 (red, hole scavenger), probing at 550 nm. (b) Transient absorption spectra in $AgNO_3$, de-ionized water and Na_2SO_3 (colour matches Figure 3.5a), recorded 50 μs after laser excitation (355 nm, $100 \mu J cm^{-2}$, 0.33 Hz).

Figure 3.5 compares the transient absorption data collected for a $BiVO_4$ photoanode in de-ionised water, $AgNO_3$ solution, and Na_2SO_3 solution with no applied potential, measured at 550 nm. The transient absorption amplitude were

shown as milli- Δ OD (m Δ OD) as the signals was very small. We note that these films exhibited significant optical light scattering; the resultant negative scatter signal precluded the collection of transient absorption data for <10 μ s time delays in the apparatus. The transient absorption spectra measured under the same conditions are shown in **Figure 3.5b** at a time delay of 50 μ s after excitation. The observed enhancement of the transient absorption signal amplitude and the increased lifetime of charge carriers in the presence of the electron scavenger (AgNO_3) suggest that photogenerated holes were probed in this spectral region (500–900 nm). This assignment was supported by a significant decrease in the signal amplitude and lifetime on the addition of the hole scavenger Na_2SO_3 . The assignment of transient signals in this spectral region, peaking at 550 nm, to photogenerated holes was also supported by the transient absorption study of BiVO_4 with applied potential (see below), and with a previous transient absorption study of BiVO_4 employing FeCl_3 as an electron scavenger.¹ Absorption maxima for photoinduced holes in this spectral region have also been observed for other metal oxide photoelectrodes.³⁻⁵ No signals were observed that could be clearly assigned to electrons between 500 and 900 nm, suggesting that electrons may absorb in the near-IR (NIR) region, as was observed in some other metal oxide photoelectrodes.^{3,4} In any case, the dynamics of photogenerated holes and their reaction with water were the primary focus of this study; the assignment indicates that these holes can be monitored most readily at 550 nm.

3.2.4 Transient Absorption Spectroscopic Study of Un-doped BiVO_4 Photoanodes under Applied Potential

Under applied potential, the decay dynamics of photogenerated holes, probed at 550 nm, in a BiVO_4 photoanode as a function of applied potential from 0.1 V_{RHE} (flat-

band potential, U_{fb}) and $1.2 V_{RHE}$ are shown in **Figure 3.6a**. At U_{fb} , the small transient absorption signal decayed to zero within 20 ms, assigned to charge recombination occurring primarily on timescales faster than the instrument's response, consistent with a previous study of $\alpha\text{-Fe}_2\text{O}_3$ photoanodes.⁵ The amplitude and decay time constant of the photoinduced hole signal both increased with increasing positive applied potential throughout the wavelength range studied (**Figure 3.6b**). This is consistent with our assignment of these transient absorption signals to photogenerated holes, with applied anodic potential increasing the yield of these holes due to reduction of back electron/hole recombination losses. The transient kinetics of the isolated film in the absence of scavengers was closest to that observed under modest anodic potential (*ca.* $0.6 V_{RHE}$), indicative of the presence of significant band bending in these BiVO_4 electrodes in water in the absence of any applied potential or scavengers. The dark open circuit potential of the isolated BiVO_4 photoanode was measured to be $0.6 V_{RHE}$, which was in agreement with these results. Details of water oxidation reaction on the surface of BiVO_4 photoanodes will be discussed in Chapter IV and Chapter VII.

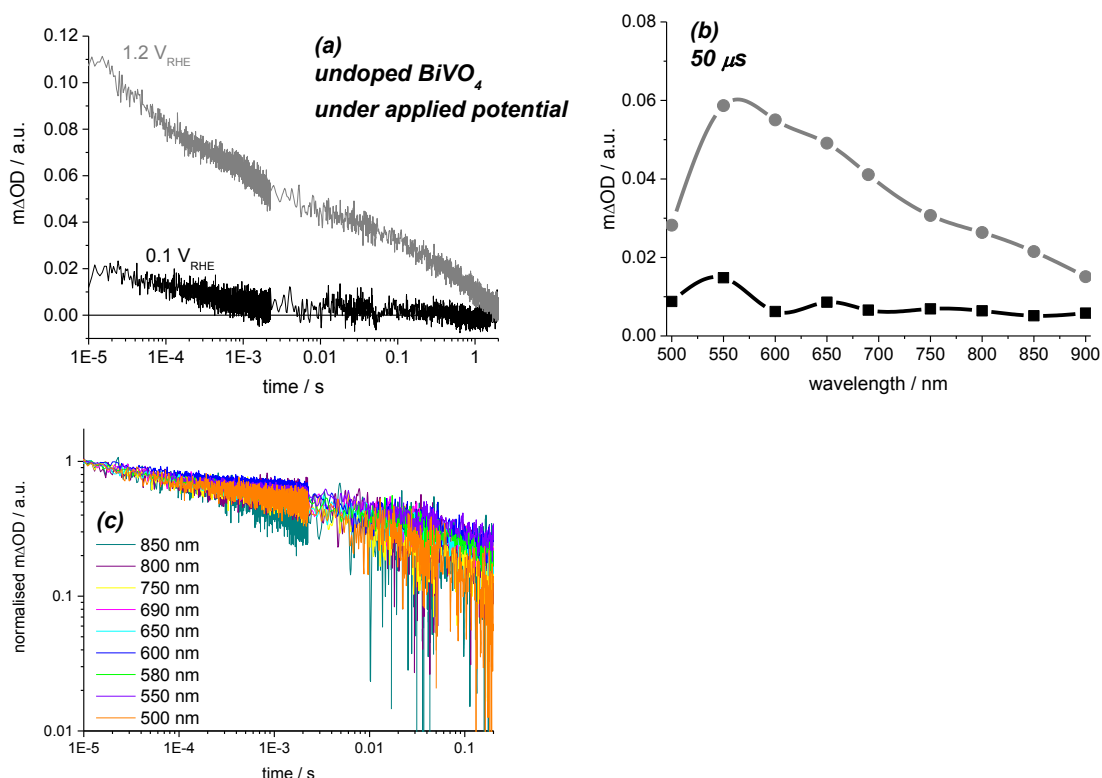


Figure 3.6. (a) Transient absorption decays of a BiVO_4 photoanode measured at $1.2 V_{\text{RHE}}$ (grey) and $0.1 V_{\text{RHE}}$ (black; near the flat-band potential), probing at 550 nm. **(b)** Transient absorption spectra of the BiVO_4 photoanode measured at $1.2 V_{\text{RHE}}$ and $0.1 V_{\text{RHE}}$ (colour matches Figure 3.6a) recorded at 50 μs after laser excitation (355 nm). **(c)** Transient absorption decays of undoped BiVO_4 measured at $1.2 V_{\text{RHE}}$ as a function of probing wavelength from 500 nm to 900 nm, normalised at 10 μs .

At high positive (anodic) potential, a biphasic decay was observed, with one phase on microsecond to millisecond timescales (defined herein as the ‘fast phase’), and a slower decay phase on millisecond to second timescales. This biphasic behaviour under anodic potential was similar to that which has been reported previously for TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$ photoanodes,^{2,5} where the faster μs -ms decay phase was assigned to bimolecular back electron/hole recombination following photoexcitation, and the slower ms-s phase to holes localised in the space charge

layer. The similarity with the data reported herein suggests similar assignments of these two phases could be made for the BiVO_4 photoanodes.

3.3 Discussion

Previously the transient absorption signatures of photogenerated holes in TiO_2 , hematite and WO_3 photoanodes were assigned using electron/hole scavengers and applied potential methods.²⁻⁵ The results of studies using electron/hole scavengers and applied anodic potential reported in this chapter indicate that the photogenerated hole species were probed in transient absorption measurements with probe wavelengths of 500-900 nm. The electron scavenger (AgNO_3) can react with excited electrons in an isolated BiVO_4 film, leaving holes to be probed in the valence band; the hole scavenger (Na_2SO_3) reacts with photogenerated holes in the valence band, giving rise to the electron signals in the transient absorption measurements. Applying electrode potential can also assist to determine charge carrier signals in transient absorption measurements. At U_{fb} , electron signals can be probed because there is no band bend to extract electrons to the external circuit; under high anodic potential, electrons were extracted to the external circuit to form photocurrent. Therefore holes were probed.²

Using the electron scavenger, increased transient absorption signals were observed from 500 nm to 900 nm and these signals decreased in the presence of the hole scavenger. Previously, the electron transient absorption signals were detected in the presence of hole scavengers in the near-IR region in TiO_2 ³ and WO_3 .⁴ However in BiVO_4 , the electron signal was not detected because the transient absorption signal was not increased by the hole scavenger. Therefore, the transient absorption signals measured between 500 nm and 900 nm indicate photogenerated holes in BiVO_4 .

The assignment of photogenerated hole signal was also supported by the transient absorption measurements under applied potentials. The transient absorption amplitude increased with increasing the applied anodic potentials; at U_{fb} , there was no electron signal probed. Therefore, the transient absorption signals measured under applied potential were assigned to the photogenerated holes from μs to s timescales.

Under these conditions (electron scavenger and applied potential), a biphasic decay were observed with first fast phase on μs -ms timecales and a slower decay on ms-s timecales. The μs -ms decay could be assigned to the fast bimolecular recombination with trapping-detrapping process,¹⁵ resulting in a linear transient absorption decay on a log-log plot (inset in **Figure 3.6b**); a power law decay.² Comparison with previous studies of hematite photoanodes suggested that this second, slower decay phase on ms-s timescales should be associated with the water oxidation process, as will be discussed in more detail in the following chapters.¹⁶ This slow phase was described by a single-exponential function (which has also been observed in TiO_2 ,² $\alpha-Fe_2O_3$ ¹⁷ and WO_3 ⁴ photoanodes for water oxidation in transient absorption spectra). Therefore, the overall decay function for a transient absorption trace on μs -s timescales is fit to a combination function of a power law and a single exponential functions, as represented in Equation 3.6.²

$$\Delta OD(t) = at^{-b} + A_{TAS2}e^{-t/\tau(TAS2)} \quad (3.6)$$

Here $\Delta OD(t)$ is the transient absorption optical density, a and b define the power law phase, A_{TAS2} is the amplitude of the slow, exponential decay phase and $\tau(TAS2)$ is the exponential decay time constant. A typical fit to the experimental data is shown in **Figure 3.7**. More details of these bimolecular recombination processes will be

discussed in the following chapters. At high positive electrode potential conditions, a slow exponential decay on ms-s timescales was assigned to a water oxidation process by accumulated photogenerated holes in the space charge layer. This potential-dependent behaviour will be discussed in the following chapter. At U_{fb} , the decay time of the hole signal became significantly faster, with a lifetime at least one order of magnitude lower than at $1.2 V_{RHE}$. This suggests that the fast bimolecular recombination became dominant under the flat-band condition, at which there was no band bending to maintain spatial charge separation. The hole scavenger, Na_2SO_3 , did not give rise to an enhancement of transient absorption amplitude or lifetime in the 500-900 nm region, suggesting that only holes were probed in $BiVO_4$ from the visible to near-IR region.

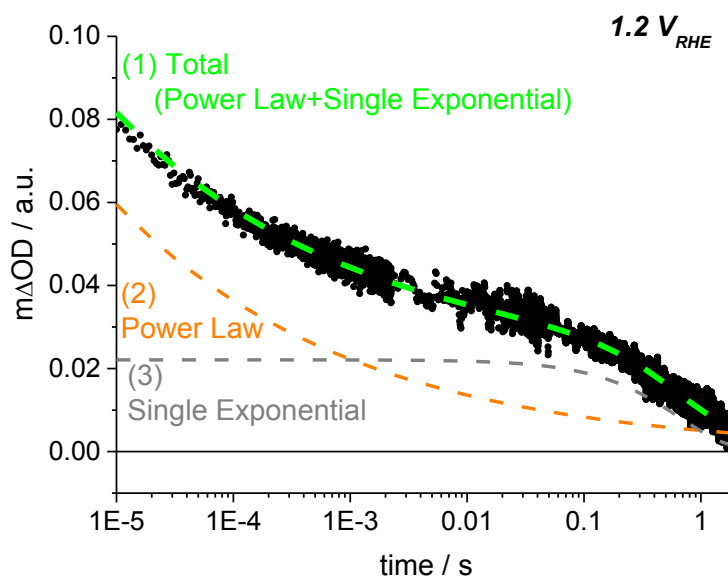


Figure 3.7. The fitting (green) to a transient absorption decay measured at $1.2 V_{RHE}$ applied potential at 550 nm, with a combination of a power law (orange) and single exponential (grey) functions.

The transient absorption spectra of $BiVO_4$ obtained in both measurements showed a similar shape in $AgNO_3$ and under strong anodic potential at $1.2 V_{RHE}$, with

a peak at 550 nm. This is qualitatively in agreement with a previously reported hole transient absorption signature of BiVO₄ using FeCl₃ as an electron scavenger.¹ Significant long-lived hole signal in de-ionised H₂O (without electron/hole scavengers) was observed in the isolated BiVO₄ transient absorption measurements (**Figure 3.5a**, the grey decay), suggesting that strong band bending occurs in BiVO₄ in contact with electrolyte even at open circuit. The SEM images in **Figure 3.1** showed a flat dense film, which allows to apply the model of space charge layer formation in order to interpret the transient absorption data as a function of applied potential (see Chapter IV). Thus, under the isolation condition (open-circuit condition), where there is no photocurrent generation ($j = 0$), efficient charge separation occurs due to the existence of significant band bending. This electric field overcomes fast bimolecular recombination on μ s-ms timescales. These long-lived holes result from significant band bending and space charge layer sufficient to achieve spatial charge separation. However, in the isolated BiVO₄ film, electrons cannot reduce water because the conduction band is 100 mV positive of the redox potential of hydrogen evolution reaction. These electrons eventually recombine with the long-lived holes with a faster time than water oxidation by holes, which therefore thus cannot contribute to water oxidation. This will be discussed in detail in the following chapter.

Previously, Matsumoto *et al.* suggested that two types of photogenerated holes in BiVO₄ could be observed on fs-ns timescales in a thick BiVO₄ film.¹ They described different rise times on fs–ns timescales and assigned these signals to trapped and free holes in the valence band. However, such differences were not observed in transient absorption data reported herein, probably due to different processes observed on different timescales. The time window used in this project was from microseconds to seconds, in which the transient absorption kinetics for BiVO₄

photogenerated holes were independent of probing wavelength from 500 nm to 900 nm (**Figure 3.6b**, inset). This suggests that identical hole species were monitored across this wavelength range, with only differences of molar absorption coefficients at different wavelengths.

Therefore, the following chapters in this thesis will discuss mainly transient absorption results measured with 550 nm probing wavelength, at which the maximum transient absorption signal was obtained. Different types of holes in BiVO_4 photoanodes were not required for the interpretation of the results discussed herein.

3.4 Conclusion

Dense un-doped BiVO₄ photoanodes with thickness of 450 nm were fabricated using the MOD-spincoating method. XRD characterisation confirmed the monoclinic scheelite structure and the band gap was *ca.* 2.4 eV with absorption edge of *ca.* 500 nm determined from UV-vis measurements. Such BiVO₄ films were studied using transient absorption spectroscopy. The photogenerated hole signal was assigned using electron/hole scavengers and applied potential in a PEC cell. The transient absorption hole signals had a very broad absorption range from visible to near-IR (500 – 900 nm); however, no electron transient absorption signal was observed in this spectral range. Decay kinetics were found to be independent of wavelength within this region, indicating only one type of hole signal was observed. These results provide information on the signature of photogenerated holes in un-doped BiVO₄, allowing further study of the dynamics of water oxidation on BiVO₄.

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Chapter IV

4. Kinetic Competition between Back Electron/hole Recombination and Water Oxidation in Un-doped BiVO₄ Photoanodes

The dynamics of photogenerated holes in an un-doped BiVO₄ photoanode were studied with transient absorption spectroscopy and transient photocurrent measurements. A potential-dependent behaviour of the photogenerated holes in the BiVO₄ film was observed. The impact of this potential-dependent behaviour upon charge recombination and water oxidation particularly was discussed.

4.1 Introduction

In this chapter, investigation of photogenerated holes in un-doped BiVO_4 photoanodes were reported. The main technique is transient absorption spectroscopy with supporting techniques such as photoelectrochemical (PEC) measurements, transient photocurrent measurements and impedance spectroscopy. The aim for this chapter is to understand how photogenerated holes in un-doped BiVO_4 react with water and what the limiting factor is for the modest PEC performances.

Previously our group has studied TiO_2 ¹ and $\alpha\text{-Fe}_2\text{O}_3$ ² photoanodes using transient absorption spectroscopy, particularly focusing on the potential dependent behaviour of long-lived (ms-s timescales) photogenerated holes for water oxidation. Applied electrical potential to the photoanode in a PEC cell can form a space charge layer which effectively retard the fast recombination on μs -ms timescales and result in the generation of long-lived holes.³ The most important behaviour of long-lived holes is that the amplitude of long-lived holes (at 100 ms) correlates with the amplitude of photocurrent, clearly addressing the importance of requiring sufficient hole accumulation at the photoanode surface due to the slow reaction rate of water oxidation on metal oxide surface between 100 ms and 1 s.^{3,4} This slow kinetics have also been reported by the Peter's group using intensity-modulated photocurrent spectroscopy.⁵

In addition to transient absorption studies, the Hamann's group investigated $\alpha\text{-Fe}_2\text{O}_3$ photoanodes using impedance spectroscopy.⁶ The impedance data was interpreted using a model consisting of intra band gap states at the $\alpha\text{-Fe}_2\text{O}_3$ surface. Such intra band gap state has been considered responsible for water oxidation by trapping

holes from the $\alpha\text{-Fe}_2\text{O}_3$ valence band and the modest performance of water oxidation by $\alpha\text{-Fe}_2\text{O}_3$ is due to severe recombination when the intra band gap state is fully occupied with photogenerated holes.

Our group has carried out independent study using transient absorption spectroscopy to investigate $\alpha\text{-Fe}_2\text{O}_3$ photoanodes for water oxidation.^{7,8} The recombination process in $\alpha\text{-Fe}_2\text{O}_3$ can be interpreted to be the recombination process between the surface accumulated holes in the valence band and the bulk electrons coming back from the external circuit (i.e. back electron/hole recombination). Such recombination process has been characterised to be a slow process from ms-s timescales, effectively competing against water oxidation with long-lived holes at the surface. The assignment of back electron/hole recombination was also supported by other techniques such as transient photocurrent and impedance spectroscopy without considering the intra band gap states. However, it should be noted that the onset of long-lived photogenerated holes in $\alpha\text{-Fe}_2\text{O}_3$ is 0.7 V_{RHE} , which is still *ca.* 200 mV more negative of the flat band potential (U_{fb}).⁷ The onset potential for photocurrent generation and water oxidation may not be improved beyond 0.7 V_{RHE} because there is no long-lived hole generated for water oxidation.

In terms of BiVO_4 , there was no report of the long-lived holes concerning its water oxidation behaviour yet. Therefore, in this chapter reported herein, the first functional transient absorption study of water oxidation on un-doped BiVO_4 photoanodes on microsecond to second timescales was discussed. The timescale was most relevance to water oxidation. In the PEC cell, the dynamics of photogenerated holes in BiVO_4 were studied as a function of applied potential and laser excitation intensity. These hole dynamics were correlated with the width of the space charge layer calculated from impedance analysis. Measurements of chopped light transient

photocurrents were employed to study the kinetics of recombination of bulk BiVO_4 electrons with long-lived surface holes. The impact of the relative rates of recombination and water oxidation upon the efficiency of water photo-oxidation were discussed.

4.2 Results

Figure 4.1 shows the decay dynamics of photogenerated holes, probed at 550 nm, in a BiVO_4 photoanode as a function of applied potential from 0.1 V_{RHE} (flat-band potential, U_{fb}) to 1.5 V_{RHE} . At U_{fb} , the small transient absorption signal decayed to zero within 20 ms, assigned to charge recombination occurring primarily on timescales faster than the instrument response, consistent with a previous study of $\alpha\text{-Fe}_2\text{O}_3$ photoanodes.² The amplitude and decay time constant of the photoinduced hole signal both increased with increasing positive (anodic) applied potential throughout the wavelength range studied. This was consistent with the assignment of these transient absorption signals to photogenerated holes, with applied anodic potential increasing the yield of these holes due to reduction of back electron/hole recombination losses.

At strong positive (anodic) potential, a biphasic decay was observed, with one phase on microsecond to millisecond timescales (defined herein as the fast phase), and a slower decay phase on millisecond to second timescales. This biphasic behaviour under anodic potential has been discussed in previous chapter (Chapter III), where the faster μs -ms decay phase was assigned to bimolecular electron/hole recombination following photoexcitation, and the slower ms-s phase to holes localised in the space charge layer. Similar results have been observed for TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$ photoanodes.^{1,2}

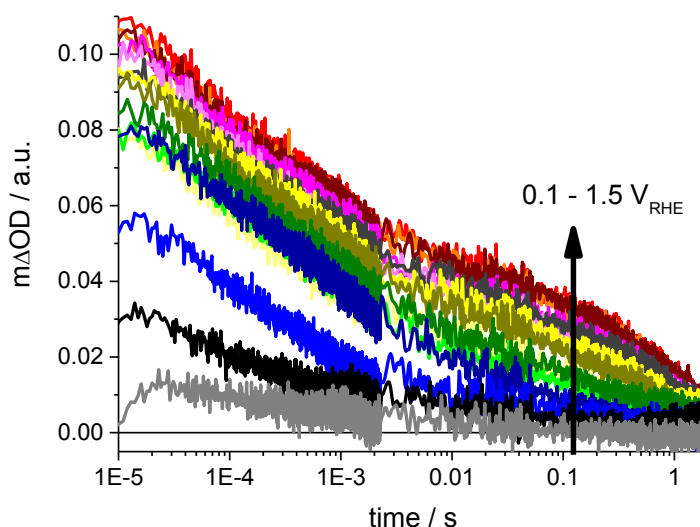


Figure 4.1. Dynamics of photogenerated holes (probed at 550 nm) in the BiVO₄ photoanode as a function of applied potential, measured from 0.1 V_{RHE} (corresponding to flat-band conditions) to 1.5 V_{RHE}, at intervals of 0.1 V. Data recorded in a three-electrode PEC cell with KPi electrolyte;

Support for assignment of the faster phase to electron/hole recombination came from the laser intensity dependence of the transient absorption decays at 1.2 V_{RHE}, as shown in **Figure 4.2**. It was apparent that the decay kinetics of the slow decay phase (ms–s) were almost independent of the excitation intensity (**Figure 4.2d**), whereas the fast phase becomes more pronounced and shorter lived as the laser intensity was increased (**Figure 4.2c**). The increased dominance and acceleration of the fast phase with increased laser intensity was analogous to behaviour which have been observed for α-Fe₂O₃⁸ and TiO₂⁹ photoanodes, and was consistent with the assignment of this phase to the bimolecular recombination of photogenerated electrons and holes. The saturation in the amplitude of the slow transient absorption decay phase under high excitation intensities (> 400 μJ cm⁻²) was attributed to the typical non-linear dependence of bimolecular recombination on charge carrier density (with an increasing proportion of this recombination occurring on sub-

microsecond timescales not reported herein). The measured amplitude of the slow phase (measured on millisecond timescales) saturates at $5 \times 10^{-5} \Delta OD$ (absorption) units as the laser intensity was increased, emphasising the high detection sensitivity required to monitor this slow decay phase.

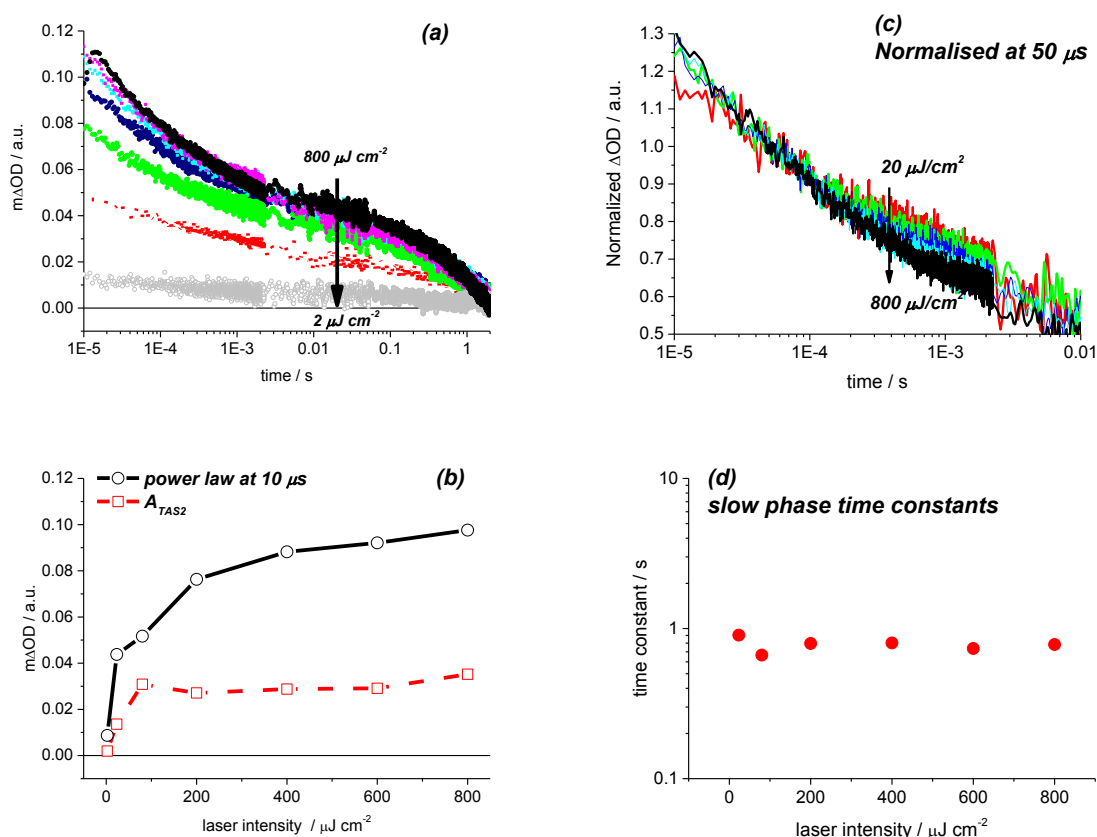


Figure 4.2. (a) Transient absorption decays of a BiVO₄ photoanode as a function of laser excitation intensity, ranging from 2 μJ cm⁻² (grey) to 800 μJ cm⁻² (black), at 1.2 V_{RHE}. The arrow in the figure indicates decreasing laser intensity. (b) Amplitude from the fit of the μs-ms phase (power law; black empty dots) and the amplitude of the ms-s phase (A_{TAS2} of the exponential function; red empty squares) as a function of laser excitation intensity. (c) Normalised transient absorption decays, normalised at 50 μs. Intensity-dependent kinetics were observed from 50 μs to 2 ms. Laser excitation intensity range: 20 μJ cm⁻² to 800 μJ cm⁻². (d) Lifetime of the slow phase decay (ms-s timescale), fitted by a single-exponential, as a function of laser excitation intensity under 1.2 V_{RHE} potential.

The transient absorption decays such as those shown in **Figures 4.1** were well fitted by a combination of a power law decay and a slower, single exponential function, as has been discussed in Chapter III. Here in this chapter, the same model

was applied to fit the transient absorption decays as a function of applied potential, as detailed in Equation 4.1:

$$\Delta OD(t) = at^{-b} + A_{TAS2}e^{-t/\tau(TAS2)} \quad (4.1)$$

Here ΔOD is the transient absorption optical density, a and b define the power law phase, A_{TAS2} is the amplitude of the slow, exponential decay phase and $\tau(TAS2)$ is its decay time constant. All values of all fit were shown in **Figure 4.3b**; the potential dependence of the four fit parameters was shown in **Table 1**. In this chapter, correlating the observed transient absorption data with the potential dependence of water oxidation was particularly concerned. Therefore, following analogies with previous studies of TiO_2 and $\alpha-Fe_2O_3$ electrodes, the amplitude and decay kinetics of the slower (ms–s), exponential decay phase, were the focus in this chapter.

Table 4.1. Fit parameters of transient absorption decays in Figure 4.2a, using a combination of power law and single exponential function, shown in Equation 4.1.

potential vs RHE / V	power law		single exponential function	
	$a / a.u.$	$b / a.u.$	$A_{TAS2} / a.u.$	$\tau(TAS2) / s$
1.5	4.0E-6	-0.28	3.1E-5	0.99
1.4	4.6E-6	-0.26	3.0E-5	0.77
1.3	5.9E-6	-0.24	2.7E-5	0.86
1.2	5.4E-6	-0.26	2.2E-5	0.76
1.1	5.1E-6	-0.26	2.2E-5	0.73
1	5.6E-6	-0.25	2.2E-5	0.77
0.9	6.0E-6	-0.24	1.7E-5	0.57
0.8	4.8E-6	-0.26	1.9E-5	0.40
0.7	3.4E-6	-0.26	1.8E-5	0.21
0.6	3.7E-6	-0.27	1.4E-5	0.19
0.5	4.9E-6	-0.26	1.3E-5	0.15
0.4	2.5E-6	-0.32	1.4E-5	0.075
0.3	2.7E-6	-0.27	8.4E-6	5.5E-4
0.2	1.6E-6	-0.26	4.5E-6	9.5E-4
0.1	4.3E-7	-0.26	1.0E-6	1.0E-3

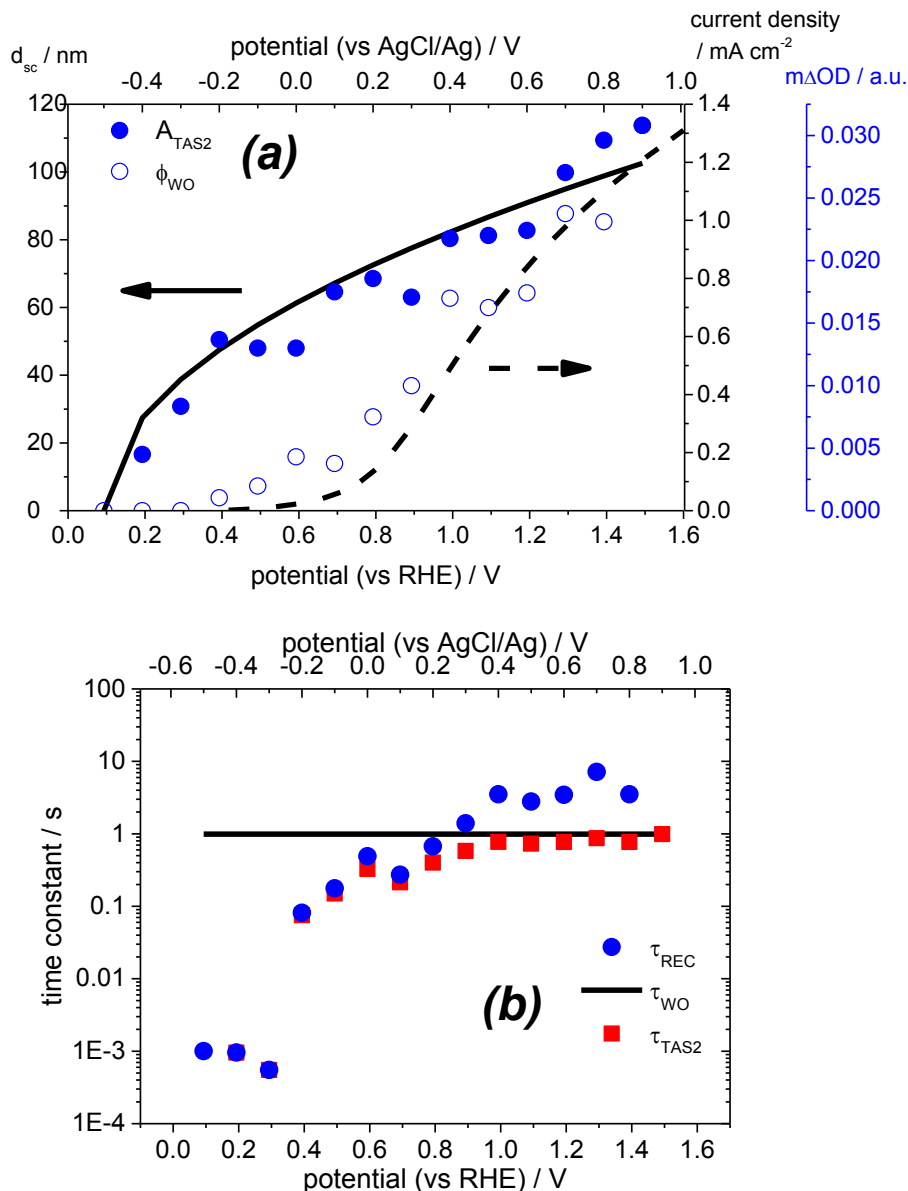


Figure 4.3. (a) Correlation of transient absorption amplitude of long-lived photogenerated holes (A_{TAS2} , blue solid squares, obtained from fitting with an exponential decay) with the width of the space charge layer (black solid line), and correlation of yield of water oxidation determined from the transient absorption data by Equation 4.1 (ϕ_{WO} , blue empty squares) with photocurrent density (black dashed line). (b) Time constants of slow decay kinetics (ms-s) of long-lived holes (τ_{TAS2} , red squares) determined from the single exponential fitting to the transient decays; time constants of recombination kinetics of long-lived holes (τ_{REC} , blue dots, determined by $1/k_{REC}$) determined from Equation 6 and time constants of water oxidation kinetics of long-lived holes (τ_{WO} , black solid line) determined from the transient absorption decay time constant at $1.5 V_{RHE}$.

It was apparent from **Figures 4.1** and **4.3** that the amplitude A_{TAS2} of the slow, exponential TAS decay phase increased with increasing anodic potential beyond a threshold potential of *ca.* $0.2 V_{RHE}$. The lifetime $\tau(TAS2)$ of this exponential decay

phase also increased with anodic potential, as was apparent from **Figure 4.1**, and was discussed further below (**Figure 4.5**). In **Figure 4.3a**, the amplitude of this decay phase (A_{TAS2} , filled squares) as a function of applied potential was overlaid with the photocurrent density measured under white light irradiation (dashed line), and with the width of the space charge layer determined by the electrochemical impedance analysis (solid line). Following previous studies of hematite photoanodes, this amplitude was assigned as an assay of the yield of photogenerated holes which avoid initial recombination with BiVO_4 electrons and were thus able to accumulate at the photoanode surface. It was apparent that the yield of these long-lived holes correlates with the width of the space charge layer; both had an onset potential of 0.2 V_{RHE} . It was also striking that for modest applied potentials, 0.2–0.7 V_{RHE} , these surface-localised holes did not result in significant photocurrent generation (i.e. water oxidation). This implied the presence, at these potentials, of a process that competes with water oxidation, which is considered below.

Transient photocurrent measurements¹⁰ was a complementary technique to study the kinetics of charge carriers and their correlation with the transient absorption data reported above. **Figure 4.4a** presents the result of a typical chopped light transient photocurrent measurement under modest anodic potential (0.8 V_{RHE}). When the light was switched on, a positive transient photocurrent was observed; when it was switched off, an analogous negative transient was observed, in qualitative agreement with a previous BiVO_4 report.¹¹ The asymmetric peaks between positive and negative current transients were probably due to the decreased space charge layer width under illumination, which decreased the band bending, so decreasing the efficiency of water oxidation. In order to rule out this effect, bias light as the background light was applied so that the excitation light was only a small

perturbation. The kinetic results using the bias light and small perturbation excitation were consistent with the TPC data in the chapter, and will be discussed in Chapter VI. These positive and negative photocurrent transients have been associated with accumulation of the holes in the BiVO_4 space charge layer under prolonged irradiation and the recombination of bulk electrons with these holes,¹¹ in agreement with analogous studies of $\alpha\text{-Fe}_2\text{O}_3$ photoanodes.^{5,7,10} In particular, the negative transient observed following light switch-off has been assigned to recombination of bulk BiVO_4 electrons with holes accumulated in the space charge layer during irradiation, resulting in a back flow of electrons into the photoanodes.¹¹

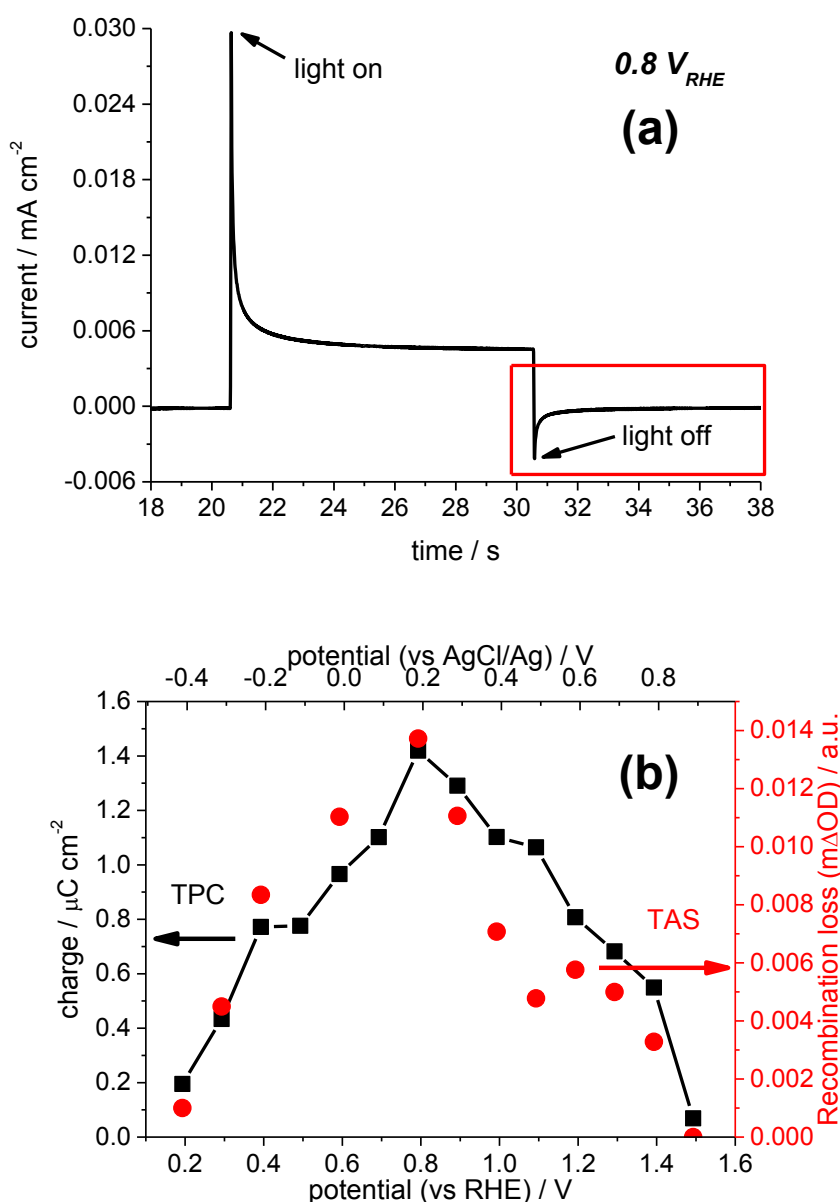


Figure 4.4. (a) Chopped light transient photocurrent measured at 0.8 V_{RHE}. **(b)** Black squares: charge due to surface accumulated holes which undergo ms–s recombination, as a function of applied potential, obtained by integration of the negative transient current (black box in (a)). Red dots: transient absorption amplitude of holes that undergo slow charge recombination, calculated from the fit amplitude of the exponential function and Equation 4.5.

Analogous chopped light photocurrent data were collected for applied potential between 0.2 and 1.5 V_{RHE}. The negative transients fitted reasonably to single exponential decays, shown in Equation 4.2,⁵

$$j(t) = j_0 + A_{\text{TPC}} e^{-t/\tau(\text{TPC})} \quad (4.2)$$

where $j(t)$ is the transient current density measured under a certain applied potential, j_0 is the dark steady-state current density, A_{TPC} is the amplitude of the exponential decay and $\tau(TPC)$ is the decay time constant.

Integration of the negative transient current quantifies the negative charge associated with this back electron/hole recombination process, as shown in **Figure 4.4b** (black squares). It is apparent that losses associated with this back electron/hole recombination were largest for potentials around the photocurrent onset (0.8 V_{RHE}), and negligible for potentials ≤ 0.2 V_{RHE} and ≥ 1.5 V_{RHE}. It is also apparent that the potential range where this recombination phase results in the largest losses corresponds to the range where high yields of long-lived holes but low photocurrent densities were observed (see **Figure 4.4b**).

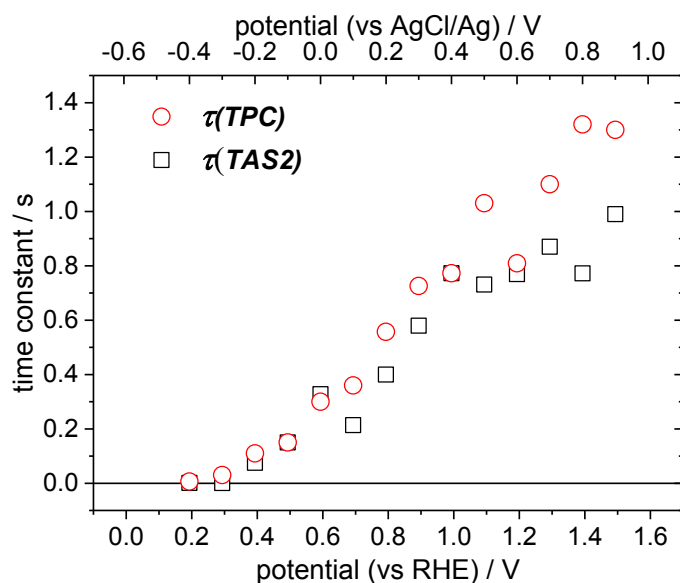


Figure 4.5. Effective of electrode potential on the time constants as a function of applied potential obtained from transient absorption spectroscopy and transient photocurrent. Red dots: $\tau(TPC)$, the time constants of negative transient current in the chopped light TPC measurements; black squares: $\tau(TAS2)$, slow phase time constants obtained from fitting the transient absorption slow decay phase with an exponential function.

The time constants of the negative photocurrent transients decays ($\tau(TPC)$), red circles) were shown as a function of applied potential in **Figure 4.5**, increasing from

10 ms to *ca.* 1 s with increasing anodic potential. The time constants of these ‘back electron/hole recombination’ transients appear to be very similar to the decay times of the slow decay phase observed in the transient absorption data, $\tau(TAS2)$, black squares in **Figure 4.5**, as is discussed below.

4.3 Discussion

4.3.1 Yield of Long-lived BiVO₄ Holes

The slower, exponential transient absorption decay phase (ms-s) observed under anodic potential was considered first. **Figure 4.3a** shows the transient absorption amplitude of long-lived holes after laser excitation as a function of applied potential (red solid squares), overlaid on the width of the space charge layer (W_{SCL} , black solid line) determined from the Mott-Schottky impedance analysis. The relatively large width of this space charge layer (e.g. *ca.* 90 nm at 1.2 V_{RHE}) was in agreement with a previous impedance analysis of un-doped BiVO₄,¹² and consistent with the relatively low doping density compared to intentionally doped metal oxide photoanodes.^{8,13} It was apparent that there was a quantitative correlation between this assay of long-lived photogenerated holes and the space charge layer width. This strongly suggests that the electric fields present in the space charge layer were essential for driving the spatial separation of initially generated electrons and holes, and thereby the generation of long-lived holes which accumulate at the electrode surface.

As discussed in Chapter III, the formation of the space charge layer could be limited by the grain boundaries between crystallites or Fermi level pinning, which mainly affected the increase of the space charge layer thickness between 0.6 V_{RHE} and 1.2 V_{RHE}. However, the transient absorption data shown in this chapter indicated that the amplitude (concentration) of long-lived holes and their decay lifetimes were not affected by such limitations. If Fermi level pinning occurred, the long-lived hole concentration and photocurrent would not have been changed by applied potential between 0.6 V_{RHE} and 1.1 V_{RHE} as the thermodynamic driving force (i.e. the energy difference between the Fermi level and 1.23 V_{RHE} for water oxidation) remained unchanged. Additionally, the kinetics and losses of back electron/hole recombination

should also remain unchanged in both transient absorption and transient photocurrent results, as the band bending did not increase. Therefore, such considerations may be unimportant for understanding the dynamics of photogenerated holes for water oxidation or recombination reported in this chapter.

It is also apparent from **Figure 4.3a** that this transient absorption assay of long-lived holes did not correlate with photocurrent density (black dashed line). Significant long-lived hole signals were observed in BiVO₄ at potentials cathodic of the photocurrent onset potential U_{on} (0.8 V_{RHE}). Since photocurrent was indicative of water oxidation, as has been shown previously for BiVO₄ photoanodes,¹⁴ the observation of long-lived holes at $U > U_{\text{on}}$ suggested that there must be a competing pathway that reduces the yield of water oxidation, particularly at modest applied potential. In the following section, the identity of this competing pathway is addressed.

4.3.2 Kinetic Competition between Water Oxidation and Back Electron/hole Recombination

The decay kinetics of the slow transient absorption decay phase correlated with the recovery time of the negative transient current assigned to electron/hole recombination, as illustrated in **Figure 4.4a**. The transient absorption signal on ms-s timescales monitored the density of long-lived holes. The observation that the negative current transient decays with the same time constant as the decay of this hole density supported the assignment of this current transient to back electron transfer into the photoanode. This back electron transfer was driven by recombination of bulk BiVO₄ electrons with holes accumulated in the space charge layer, analogous to recent analyses of hematite photoanodes.^{5,7,10}

A kinetic model was applied to the transient absorption results to quantify the proportion of long-lived photogenerated holes which gave rise to water oxidation *versus* those which decay due to back electron/hole recombination, as shown in **Scheme 4.1**. The water oxidation hole yield, $\phi_{WO}(V)$, assuming a 100% Faradaic efficiency for the water oxidation and reduction reactions (i.e. no side reactions of holes for water oxidation and of electrons for water reduction), according to previous reports of 100 % Faradaic efficiency for O₂ and H₂ evolution,^{15,16} could be calculated from,

$$\phi_{WO}(V) = \phi_{TAS2}(V) \times \frac{k_{WO}}{k_{rec}(V) + k_{WO}} \quad (4.3)$$

where $\phi_{TAS2}(V)$ is the yield of long-lived holes determined from the amplitude of the slow exponential transient absorption signal, A_{TAS2} , in Equation 4.1, determined from data shown in **Figure 4.1**; k_{WO} and $k_{rec}(V)$ correspond to the rate constants for water oxidation and back electron/hole recombination, respectively. In this simple analysis, the rate constant of the water oxidation, k_{WO} , was assumed to be independent of applied potential. The potential dependence of $k_{rec}(V)$ was determined from:

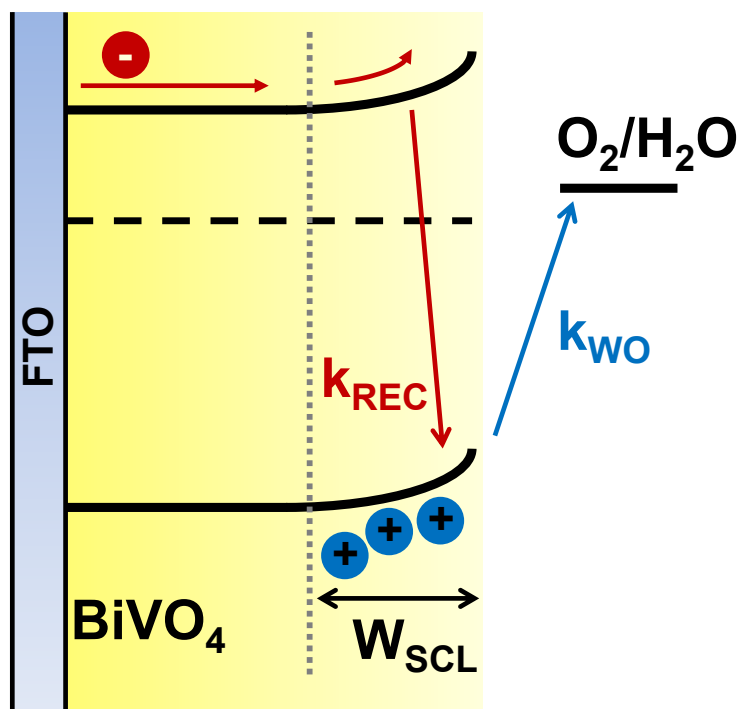
$$k_{rec}(V) = \frac{1}{\tau(TAS2)} - k_{WO} \quad (4.4)$$

where $\tau(TAS2)$ is obtained from fitting the transient absorption decays to Equation 4.1 above, shown in **Figure 4.3b**.

The transient absorption amplitude of slow recombination (ms-s) could be calculated using Equation 4.5 shown below,

$$\phi_{rec}(V) = \phi(V) \times \frac{k_{rec}(V)}{k_{rec}(V) + k_{WO}} \quad (4.5)$$

where $\phi_{rec}(V)$ is the yield of holes which recombine in the slow phase; $\phi(V)$ is the total yield of holes (slow phase amplitude of the exponential function, A_{TAS} , in Equation 4.1) from decay fittings of **Figure 4.1**, k_{WO} and $k_{rec}(V)$ correspond to the rate constants for water oxidation (k_{WO}) and back electron/hole recombination, respectively.



Scheme 4.1. Schematic representation of the photo-induced processes considered in the kinetic model of photogenerated charges in an un-doped BiVO_4 photoanode. The back electron/hole recombination is in kinetic competition with water oxidation, on ms-s timescales.

The transient absorption decay kinetics of long-lived photogenerated holes saturated (time constant ca. 0.8 s) at applied potential more positive than 1.3 V_{RHE} , as shown in **Figure 4.5**. Over this potential range, losses from back electron/hole recombination tended to zero (**Figure 4.4b**). This suggests that over this potential range, water oxidation was dominant, such that k_{WO} ca. 1.3 s^{-1} .

The yield of water oxidation, ϕ_{WO} , determined from analysing the slow transient absorption decay phase by **Equations 4.3** and **4.4** was shown as a function of

applied potential in **Figure 4.3a** (empty squares). It is apparent that the yield of water oxidation determined from this simple kinetic model correlated remarkably well with the photocurrent density. In particular, this kinetic analysis of the transient absorption data suggested that almost all long-lived holes recombined without contributing to water oxidation between $0.1 V_{\text{RHE}} (U_{\text{fb}})$ and $0.8 V_{\text{RHE}} (U_{\text{on}})$. Back electron/hole recombination decreased with increasing anodic potential after U_{on} and was strongly suppressed at strong anodic potentials. This observation was consistent with the transient photocurrent data, which indicated that losses resulting from back electron/hole recombination were maximal around the photocurrent onset ($0.8 V_{\text{RHE}}$), and become smaller for higher applied potentials. For potentials $>1.2 V_{\text{RHE}}$, the slow decay phase of photogenerated holes was dominated by water oxidation.

It has been previously reported that the yield of long-lived holes observed with $\alpha\text{-Fe}_2\text{O}_3$ and TiO_2 photoanodes showed strong correlation with photocurrent density,^{8,17} although these studies did not consider the potential dependence of the lifetime of these long-lived holes, nor the impact of back electron/hole recombination as discussed herein. An analogous study of Si^{IV} -doped, nanostructured $\alpha\text{-Fe}_2\text{O}_3$ photoanodes⁷ has been recently reported, where the consideration of such back electron/hole recombination was included, demonstrating that the model reported herein for BiVO_4 is also valid for other photoanode materials such as $\alpha\text{-Fe}_2\text{O}_3$, consistent with previous PEC analyses of $\alpha\text{-Fe}_2\text{O}_3$ electrodes.^{5,10} However the potentials relative to flat band required to generate long-lived holes, and to suppress back electron/hole recombination, differed between the results for BiVO_4 reported herein and those reported for Si^{IV} -doped $\alpha\text{-Fe}_2\text{O}_3$. For example, for the BiVO_4 photoanodes long-lived holes were observed at potentials immediately anodic of flat band, whereas for Si -doped $\alpha\text{-Fe}_2\text{O}_3$ such long-lived holes were only observed at

potentials 300 mV more positive than flat band potential, potentially due to the much narrower space charge layer in the doped $\alpha\text{-Fe}_2\text{O}_3$ compared to the BiVO_4 photoanodes studied herein.

The kinetics of the slow TAS decay phase at strong anodic potential, assigned to water oxidation, were observed to be independent of excitation intensity, and therefore hole density (**Figures 4.2b** and **4.2d**). This observation suggests that under the experimental conditions employed, this water oxidation process did not involve a concerted, multi-hole water oxidation, but rather the single hole water oxidation. In Chapter VII, the kinetics of water oxidation by BiVO_4 holes with different reaction pathways will be reported. It confirmed that under the transient absorption measurements reported in this chapter, the water oxidation reaction was first order reaction kinetics, involving a single hole oxidation process. This was due to the low quantum yield of long-lived photogenerated holes generated by the weak laser pulse. The processes during transient absorption measurements were dominated by the bimolecular recombination, strongly limiting the charge separation and hole accumulation at the BiVO_4 surface. In Chapter VII, different reaction kinetics, from the first order to the third order, will be reported when the surface hole concentration increases by one order of magnitude under 5 s pulsed LED. However, the first order kinetics measured under such condition was also consistent with the result reported in this chapter (also shown in **Figure 7.7** in Chapter VII), showing valid assignment of the water oxidation kinetics under the short laser pulse. As have been discussed previously, the single-hole oxidation of water by metal oxide holes such as BiVO_4 , $\alpha\text{-Fe}_2\text{O}_3$ and TiO_2 may be enabled by the highly oxidizing nature of such valence band holes.¹⁸ However, it should be noted that continuous solar irradiation may result in substantially higher densities of accumulated holes than those achieved by the

pulsed laser excitation employed herein, with therefore potentially greater opportunities for concerted, multi-hole reactions.

The mechanism of the back electron/hole recombination which is observed to be in kinetic competition with water oxidation was considered. It should be noted that electrons cannot reach the semiconductor-liquid interface without being thermally activated over or tunnelling across the space charge layer (or *vice versa* for holes moving into the electrode bulk). Tunnelling across the space charge layer was unlikely due to the relatively wide space charge layer in the photoanodes studied herein (ca. 80 nm at 0.8 V_{RHE}). More likely, the relatively slow timescale of back electron/hole recombination (100 ms) compared to bulk electron recombination (typically reported on picosecond timescales for metal oxides) could be attributed to the requirement for thermal activation across the space charge layer. For example, a 300 mV barrier height was equivalent to 12 $k_{\text{B}}T$ at room temperature, resulting in a retardation of recombination dynamics by e^{-8} or 1/200000 fold. It thus appeared more likely that back electron/hole recombination proceeded via thermal activation.

The formation of a space charge layer at the semiconductor-liquid interface was widely recognised as being critical in reducing recombination losses in photoelectrodes. The results presented herein suggest that two distinct, space-charge dependent, recombination processes must be considered for the BiVO_4 photoanodes studied herein. The space charge layer facilitates initial charge separation, leading to generation of long-lived holes with a yield that scales with the width of the space charge layer. However, for potentials only modestly anodic of flat band, the space charge layer field is insufficient to block the slow back recombination of bulk electrons with these long-lived holes localized in the space charge layer. This back electron/hole recombination can be avoided by significantly

deep band bending across the space charge layer with strong anodic potential. In the BiVO_4 photoanodes employed in these studies in this chapter, the potential required to prevent back electron/hole recombination appears to be *ca.* 600 mV greater than that required to achieve separation of the initially generated charge carriers, and is therefore the key reason for the high anodic potential required for photocurrent generation. As such, the results reported herein suggest that blocking the back electron/hole recombination should be prioritised in order to improve the water oxidation efficiency of BiVO_4 photoanodes. This could be achieved by increasing barriers to this recombination (by increasing the space charge layer band bending or introducing an additional junction) or using surface catalysts to increase the water oxidation rate constant.

4.4 Conclusion

In this chapter, the study of water oxidation and recombination dynamics of photogenerated holes in un-doped BiVO_4 photoanodes was discussed. Using transient absorption spectroscopy and photoelectrochemical methods, charge recombination on ms–s timescales has been found to occur due to back electron/hole recombination. This slow recombination competed kinetically with water oxidation, thus limiting the photoanode efficiency. These results suggest that future material design and optimisation should consider avoiding back electron/hole recombination in BiVO_4 photoanodes in order to enable efficient water oxidation at less anodic applied potentials.

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Chapter V

5. Transient Absorption Study of Photogenerated holes in Mo^{VI}-doped BiVO₄ Photoanodes

Molybdenum (Mo^{VI}) doped BiVO₄ photoanodes were studied using transient absorption spectroscopy and photoelectrochemical methods. Doping BiVO₄ could change the transport property of charge carriers, which was determined from the comparison of dynamics of photogenerated holes and photocurrent excited from front-side and back-side illumination. Impedance spectroscopy was used to determine the donor density and the flat-band potential in both un-doped BiVO₄ and doped BiVO₄ photoanodes. The impact of the width of the space charge layer in doped BiVO₄ upon the yield of long-lived holes required for water oxidation is discussed.

5.1 Introduction

In previous chapters, the dynamics of photogenerated holes in un-doped BiVO_4 were investigated using transient absorption spectroscopy and photoelectrochemical (PEC) methods. Significant losses due to back electron transfer across the space-charge layer, leading to recombination with long-lived surface-accumulated holes have been observed. However, the initial charge separation in the space charge layer in un-doped BiVO_4 was efficient, as observed with strong correlation of the long-lived hole yield and the width of the space charge layer. The back electron transfer process was in kinetic competition with water oxidation, such that at modest anodic potentials the long-lived holes were consumed by recombination and did not contribute to water oxidation. This significantly limited the water oxidation performance in un-doped BiVO_4 photoanodes. Therefore, modifying the un-doped BiVO_4 was important to enhance the photocurrent.

Electron transport has been qualitatively determined to be poor in BiVO_4 photoanodes by studying the photocurrent from front-side and back-side illumination.¹ Photo-induced charge carriers were generated near the semiconductor-electrolyte interface under front-side illumination, which was potentially favourable for charge separation in the space charge layer. However, electrons needed to migrate across the entire film under this condition. Therefore good electron transport was needed for electrons to reach the back contact without recombining. On the other hand, under back-side illumination charges were generated near the FTO back contact, which facilitated electron extraction to the external circuit. However, photogenerated holes needed to migrate to the surface, thus the performance was dependent on the transport of photogenerated holes.

Doping with molybdenum (Mo^{VI})², tungsten (W^{VI})³ or co-doping with Mo^{VI} and W^{VI} ^{4,5} is an effective method to improve photocurrent amplitude, which was first observed by Bard *et al.* using scanning electrochemical microscopy.⁴ It was suggested that one dopant added one extra electron in the BiVO_4 lattice increasing electron conductivity. The increased conductivity therefore facilitated electron transport in the BiVO_4 lattice, as has been proposed using DFT calculations.⁴ In this consideration, the electric conductivity of BiVO_4 is determined by Equation 5.1:

$$\sigma = en\mu_e \quad (5.1)$$

where σ is the electric conductivity; e is the elementary charge; n is the electron density of the material; μ_e is the electron mobility in the material. In the case of doped BiVO_4 , the term of electron density (n) was increased significantly by doping, thus enhancing the conductivity (σ).

However, this proposed mechanism was not fully understood yet. It was difficult to directly measure the conductivity. Instead, the conductivity of BiVO_4 could be calculated from Equation 5.1 by measuring the electron density (e.g. impedance measurement) and charge mobility. For example, van de Krol *et al.*⁶ investigated un-doped and 1% W^{VI} -doped BiVO_4 using the transient microwave technique. They found that the electron mobility was not primarily improved by the W^{VI} dopants (electron mobility: $2.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the W^{VI} -doped BiVO_4 and $4 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in un-doped BiVO_4). These values give the conductivity of $2.2 \times 10^{-3} \text{ cm}^{-1} \Omega^{-1}$ for the 1% W^{VI} -doped BiVO_4 , and $2.4 \times 10^{-1} \text{ cm}^{-1} \Omega^{-1}$ for un-doped BiVO_4 , taking the electron density of $6.4 \times 10^{19} \text{ cm}^{-3}$ for W^{VI} -doped and $3.8 \times 10^{19} \text{ cm}^{-3}$ for un-doped BiVO_4 .² These results contrast with Mullins *et al.*⁷ who applied Hall effect measurements to un-doped and $\text{Mo}^{\text{VI}}/\text{W}^{\text{VI}}$ co-doped BiVO_4 . The electron mobility in

the doped BiVO₄ was found close to $2 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ whereas un-doped BiVO₄ was too resistive for Hall Effect measurements.

There also have been many efforts attempting to clarify experimentally the relationship between doping and charge transport in BiVO₄.^{3,4,6,8-10} All experiments focused on the electron transport in BiVO₄, especially for the conductivity and mobility. The techniques measured the majority charge carriers in BiVO₄. However, the behaviour of minority charge carriers, photogenerated holes, by doping of BiVO₄ has not been observed.

In this chapter, a complementary investigation employing transient absorption spectroscopy to study the dynamics of photogenerated holes in Mo^{VI}-doped BiVO₄ photoanodes in a complete PEC cell was reported, with particular interest in the transient absorption timescales from microseconds to seconds. Charge transport was investigated by studies using photoelectrochemistry and transient absorption spectroscopy under front-side and back-side illumination. In addition, it was discussed whether or not doping was a useful strategy to improve PEC water oxidation efficiency in BiVO₄ photoanodes, in terms of photocurrent and onset potential improvement.

5.2 Experimental

Front-side and back-side illuminations were used in the study of charge transport in this chapter. The back-side illumination was carried out through the FTO side (FTO-BiVO₄). A piece of blank FTO was used in front of the cell window for the front-side illumination (BiVO₄-FTO) in PEC and transient absorption measurements to adjust the excitation intensity consistent with the back-side illumination.

5.3 Results

BiVO_4 photoanodes were fabricated with Mo^{VI} doping concentration from 0 % to 10 % (mol %). **Figure 5.1** shows the photoelectrochemical performances of these photoanodes measured at 1.2 V_{RHE} as a function of Mo^{VI} content, where 1 % Mo^{VI} dopant in BiVO_4 was found to be the most efficient water oxidation system. Therefore, 1 % Mo^{VI} -doped BiVO_4 photoanodes were studied to investigate the charge carrier dynamics.

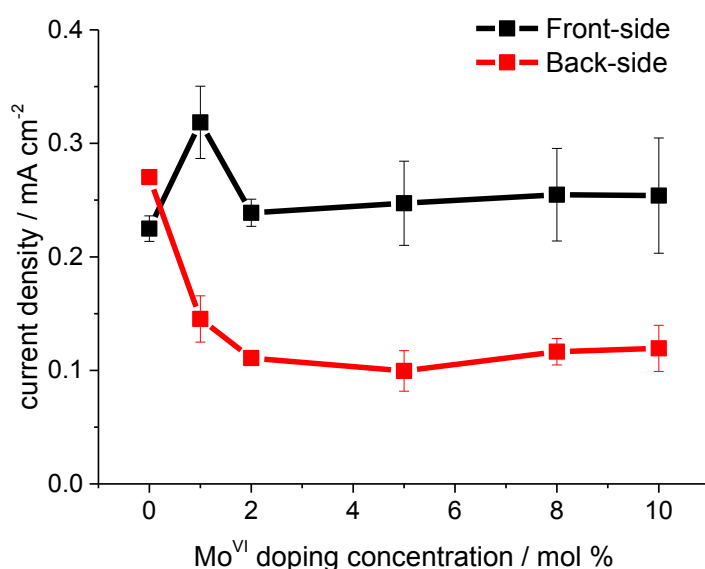


Figure 5.1. Comparison of photocurrent measured as a function of Mo^{VI} doping concentration (mol %) in BiVO_4 . Photocurrents were measured by front-side and back-side illumination. Light source: Xe lamp with monochromator at 420 nm (intensity: 1.2 mW cm^{-2}). Applied potential: 1.2 V_{RHE} .

Figure 5.2 a and **b** show the SEM images of 1 % Mo^{VI} doped BiVO_4 and undoped BiVO_4 . No significant change in morphology was observed, indicating that the Mo^{VI} dopant did not affect the morphology of BiVO_4 films. However, XRD results (**Figure 5.2c**) showed that the Mo^{VI} dopant was not detected in the 1% Mo^{VI} -doped BiVO_4 .

sample. The crystal structure of 1 % Mo^{VI} doped BiVO₄ remained monoclinic scheelite.

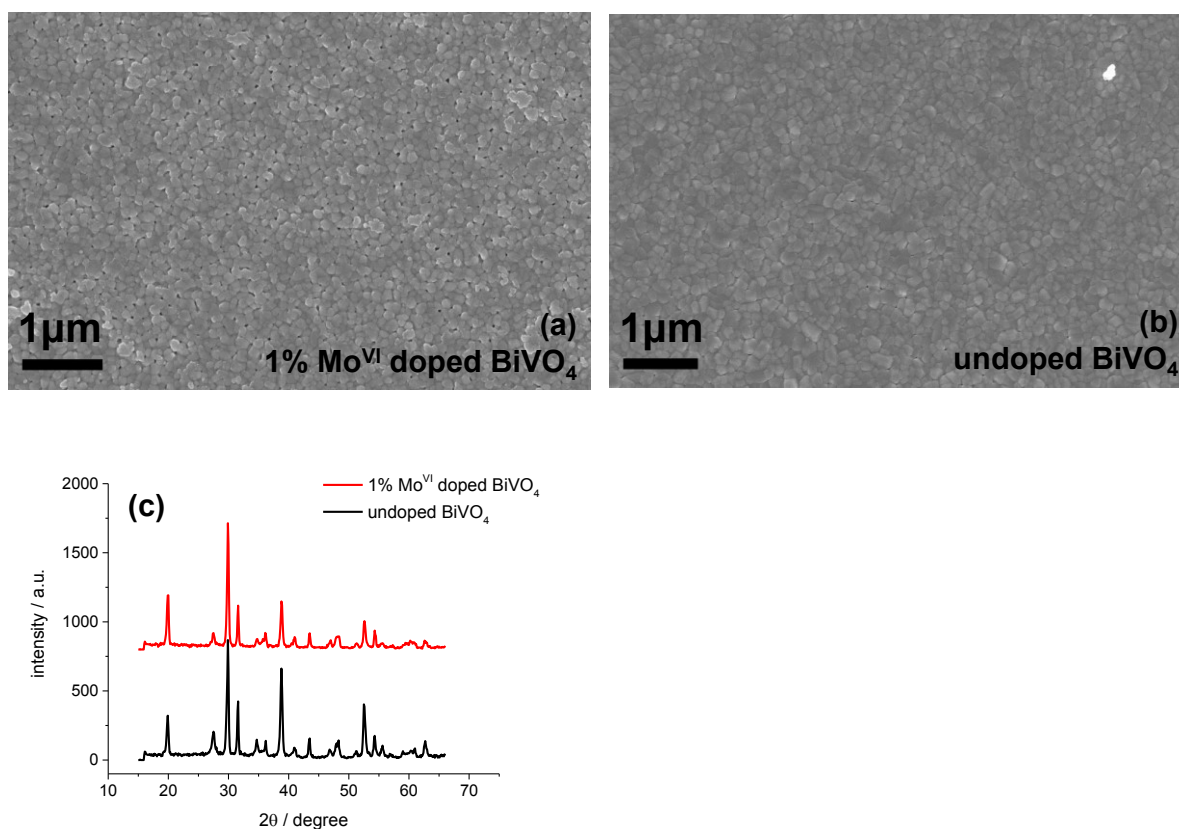


Figure 5.2. Top view SEM images of (a) 1% Mo^{VI}-doped BiVO₄ and (b) un-doped BiVO₄ photoanodes. (c) XRD patterns of 1 % Mo^{VI}-doped BiVO₄ (red) and un-doped BiVO₄ (black).

Current-potential performances of doped (1% Mo^{VI}) and un-doped BiVO₄ photoanodes were shown in **Figure 5.3**. Data were collected via front-side and back-side illumination in order to investigate the electron transport properties affected by doping. For front side excitation, the photocurrent increases with 1 % Mo^{VI}-doping in BiVO₄, however such doping did not result in a significant cathodic shift of onset potential (U_{on}). All onset potentials measured under both front and back side illumination were *ca.* 0.7 V_{RHE}, consistent with previous reports.^{3,9} In un-doped BiVO₄, the photocurrent measured under back-side illumination was higher than that under front-side illumination, whereas the doped BiVO₄ exhibited the opposite trend,

consistent with a previous report on W^{VI} -doped $BiVO_4$.³ As mentioned in Introduction section, the higher photocurrent observed was indicative of a better electron transport property in the doped $BiVO_4$ photoanodes, as discussed below.

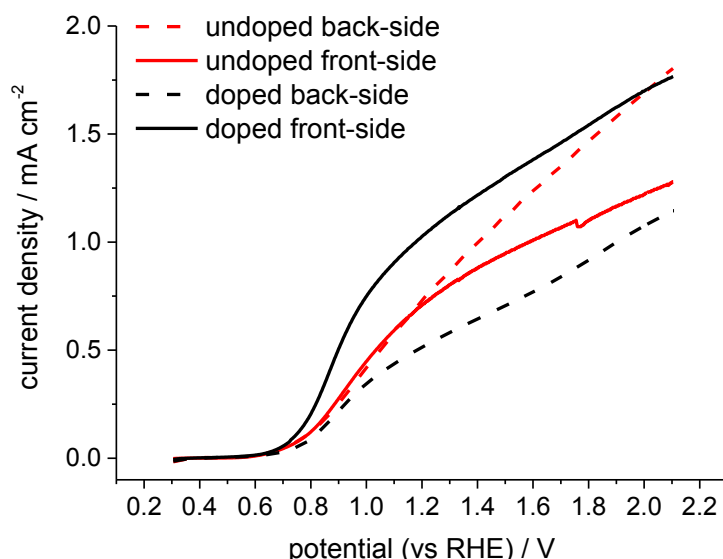


Figure 5.3. Current-potential comparison in un-doped $BiVO_4$ and 1 % Mo^{VI} -doped $BiVO_4$ photoanodes. Solid lines: front-side illumination; dashed lines: back-side illumination. Light source: Xe lamp with 100 mW cm^{-2} intensity. Scan rate: 10 mV s^{-1} .

Impedance measurements were carried out in the dark to determine the space charge layer width and donor density in doped $BiVO_4$. In **Figure 5.4**, the Mott-Schottky analysis showed that the flat-band potential is 0.18 V_{RHE} , *ca.* 80 mV more negative of the un-doped $BiVO_4$ (0.1 V_{RHE}). The donor density was calculated to be 10^{20} cm^{-3} , which was two orders of magnitude higher than the un-doped $BiVO_4$. The width of the space charge layer was calculated as a function of applied potential with maximum *ca.* 10 nm under strong anodic potential. The space charge layer in doped $BiVO_4$ was significantly narrower than in the un-doped $BiVO_4$, *ca.* 100 nm as reported in the previous chapter. It was clear that Mo^{VI} -doping increases the donor density, but narrowed the space charge layer.

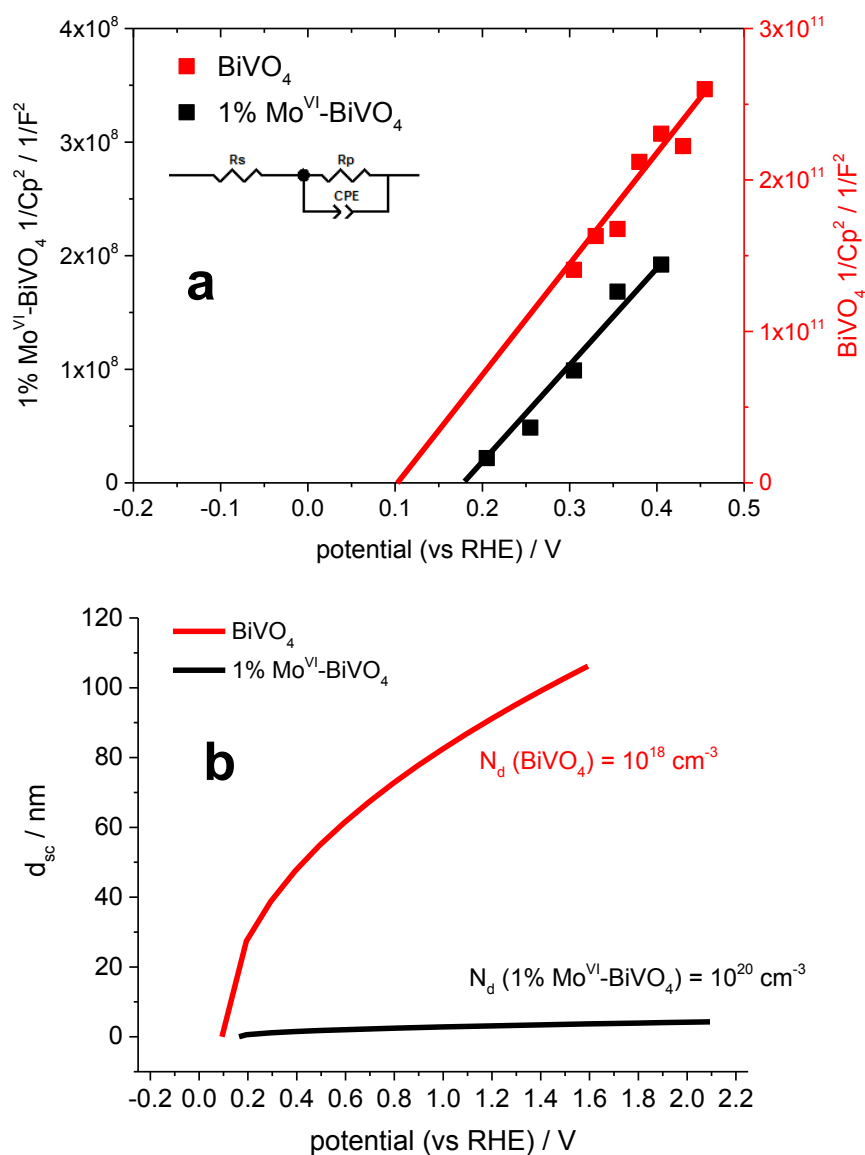


Figure 5.4. (a) Mott-Schottky analyses of un-doped (red) and 1% Mo^{VI} -doped (black) BiVO_4 photoanodes; inset: Randle circuit model used to interpret the impedance data. (b) The width of the space charge layer as a function of applied potential. Red: un-doped BiVO_4 ; black: 1% Mo^{VI} -doped BiVO_4 .

Transient absorption spectroscopy was employed to investigate the charge carrier dynamics of recombination and water oxidation from microseconds to seconds timescales. **Figure 5.5** shows the transient absorption decays of un-doped (a – c) and 1 % Mo^{VI} -doped (e – f) BiVO_4 at different applied potentials, from a modest

applied potential (negative of U_{on}) to a potential with significant photocurrent. The transient absorption decays were compared between front-side and back-side illumination. The kinetics on ms-s timescales do not change significantly with doping (i.e. $t_{50\%}$ from 10 ms: ca. 300 ms in un-doped BiVO_4 and ca. 200 ms in doped BiVO_4) under strong applied potential. However, the yield of photogenerated holes (i.e. the amplitude of the transient absorption signal) was strongly affected by the presence of Mo^{VI} dopants.

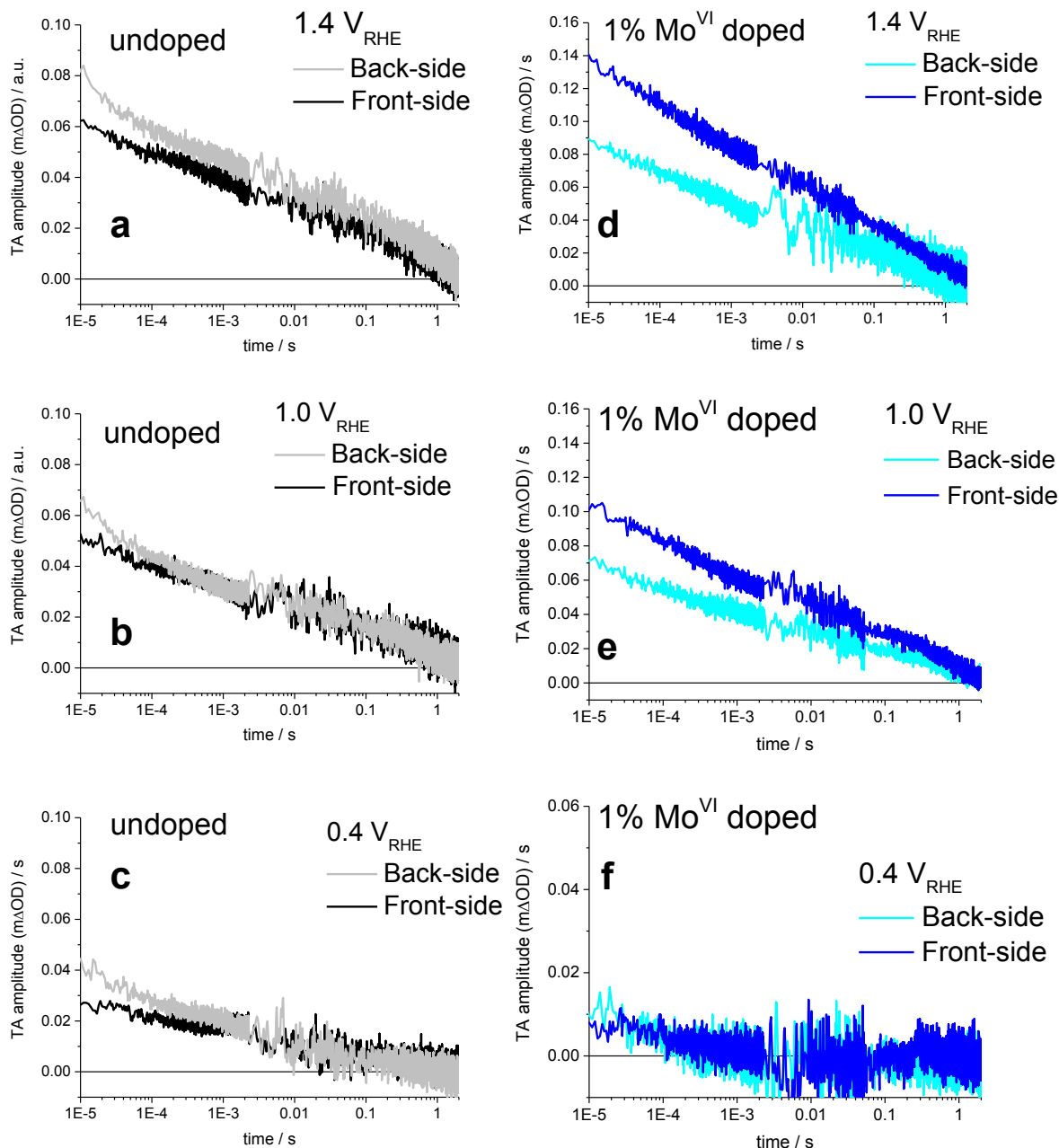


Figure 5.5. (a)–(c): Transient absorption decays of photogenerated holes in an un-doped BiVO_4 photoanodes (probed at 550 nm) under $1.4 V_{\text{RHE}}$, $1.0 V_{\text{RHE}}$ and $0.4 V_{\text{RHE}}$. All decays were compared under front-side (black) and back-side (grey) illumination. **(d)–(f):** Transient absorption decays of photogenerated holes in a 1 % Mo^{VI} -doped BiVO_4 photoanode under $1.4 V_{\text{RHE}}$, $1.0 V_{\text{RHE}}$ and $0.4 V_{\text{RHE}}$. All decays were compared under front-side (dark blue) and back-side (cyan) illuminations.

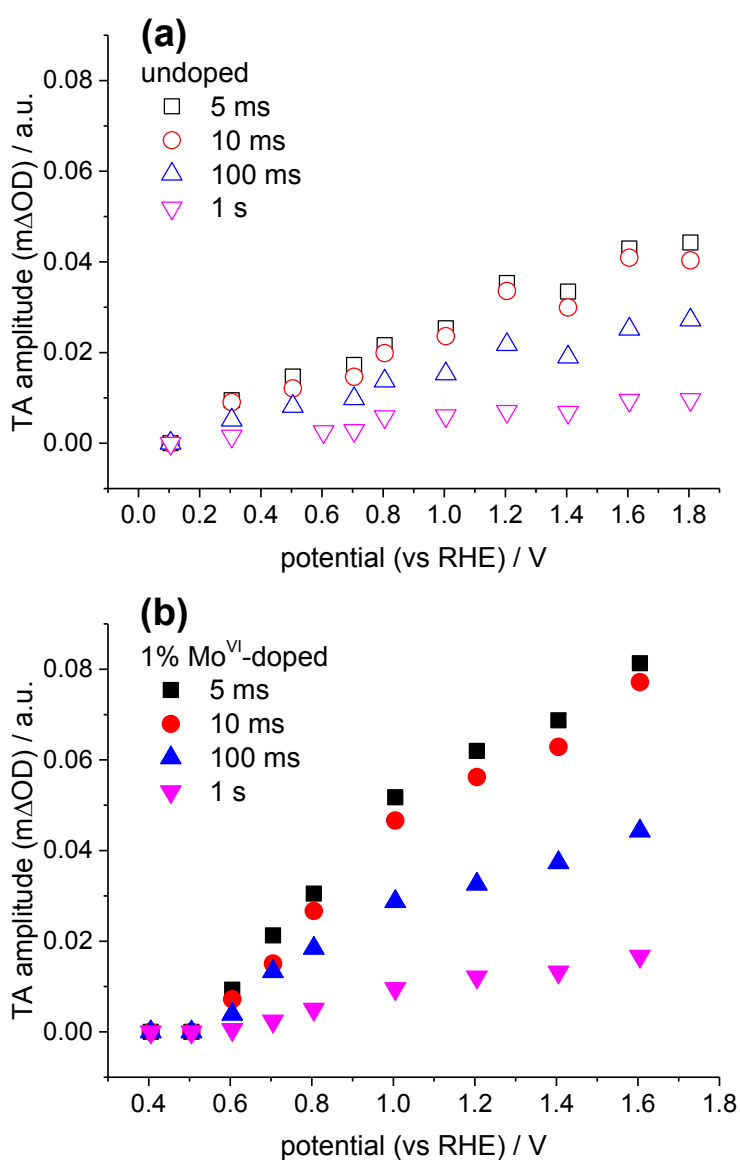


Figure 5.6 Transient absorption amplitude of long-lived photogenerated holes (from 5 ms to 1 s) probed at 550 nm in un-doped (a) and 1% Mo^{VI}-doped (b) BiVO₄ photoanodes as a function of applied potential. Data recorded via front-side illumination.

For the un-doped BiVO₄, a biphasic decay behaviour was observed, consistent with un-doped BiVO₄ decay dynamics presented in previous chapters. No significant difference in terms of the hole amplitude (probed at 550 nm) measured from front and back sides was observed under modest applied potential (**Figures 5.4 b** and **c**), whereas under strong applied potential a small difference becomes observable

at $>1.4 V_{\text{RHE}}$. Under such applied potential, the transient absorption amplitude measured from back-side excitation was higher than that from front-side excitation, consistent with the photocurrent behaviour.

For the doped BiVO_4 , it was apparent that there was a clear difference in terms of transient absorption amplitude when excited from the front-side versus the back-side of the photoanode. When the applied potential was greater than the onset potential for photocurrent generation, the transient absorption amplitude was higher in front-side illumination. Below the onset potential, the transient absorption signals decayed to zero within a few hundred of microseconds indicating that the fast recombination was dominant on sub-millisecond timescales (**Figures 5.5f and 5.6**).

5.4 Discussion

In this chapter, charge carrier dynamics in Mo^{VI} doped BiVO_4 studied using transient absorption spectroscopy and photoelectrochemical measurements were reported. The main focus of this chapter was the charge (electron and holes) transport in un-doped versus doped BiVO_4 photoanodes.

5.4.1 Charge Transport in Un-doped BiVO_4

First the photocurrent response measured by front and back-side illumination was considered. In the un-doped BiVO_4 under front-side illumination, electrons were excited near the semiconductor/electrolyte interface. These electrons migrated across the entire film to the FTO back contact. Photogenerated holes, on the other hand, were generated near the surface of BiVO_4 for accumulation. Therefore, in this situation, the rate limiting factor was the electron transport to the FTO. Under back-side illumination, charges were generated close to the FTO. Holes needed to migrate over the film and electrons were more easily collected at the FTO side. Thus the hole transport determined the overall performance.

In the current-potential curve (**Figure 5.3**), the photocurrents measured in un-doped BiVO_4 under front and back illumination were undistinguished clearly below $1.0 V_{\text{RHE}}$, but started to differentiate at $>1.0 V_{\text{RHE}}$ with higher photocurrent under back-side illumination. This observation suggested that the hole transport in un-doped BiVO_4 was not limiting the overall performance of PEC water oxidation as the holes generated far from the surface by back-side illumination were still able to migrate towards the surface.

The transient absorption data under front-side and back-side illuminations showed similar decay dynamics on ms-s timescales, in terms of transient absorption

amplitude and the decay lifetime. Previously the initial charge separation of photogenerated holes was observed to be efficient, evidenced by the correlation of long-lived hole yield and the width of the space charge layer (Chapter IV). The space charge layer in the un-doped BiVO₄ has been determined to be large (90 nm at 1.2 V_{RHE}). The transient absorption decays on microseconds (μs) to milliseconds (ms) were assigned to a bimolecular recombination process as discussed in Chapter IV. The transient absorption amplitude on μs-ms timescales under back-side illumination was higher than that under front-side illumination. Because the excitation was corrected to be equal for front and back side illumination, the same amount of charges were generated after laser excitation. For the front side illumination to un-doped BiVO₄, it suggests that the bimolecular recombination process occurred faster and dominant on sub ms timescales than the back-side illumination.

In terms of electron transport, it is apparent that electrons generated from the front-side illumination could not be collected efficiently than by back-side illumination, thus facilitating faster recombination. However, there was only a small time window to observe this effect. In order to clarify this assignment, transient absorption measurements on faster timescales, probably from femtoseconds to nanoseconds, were required.

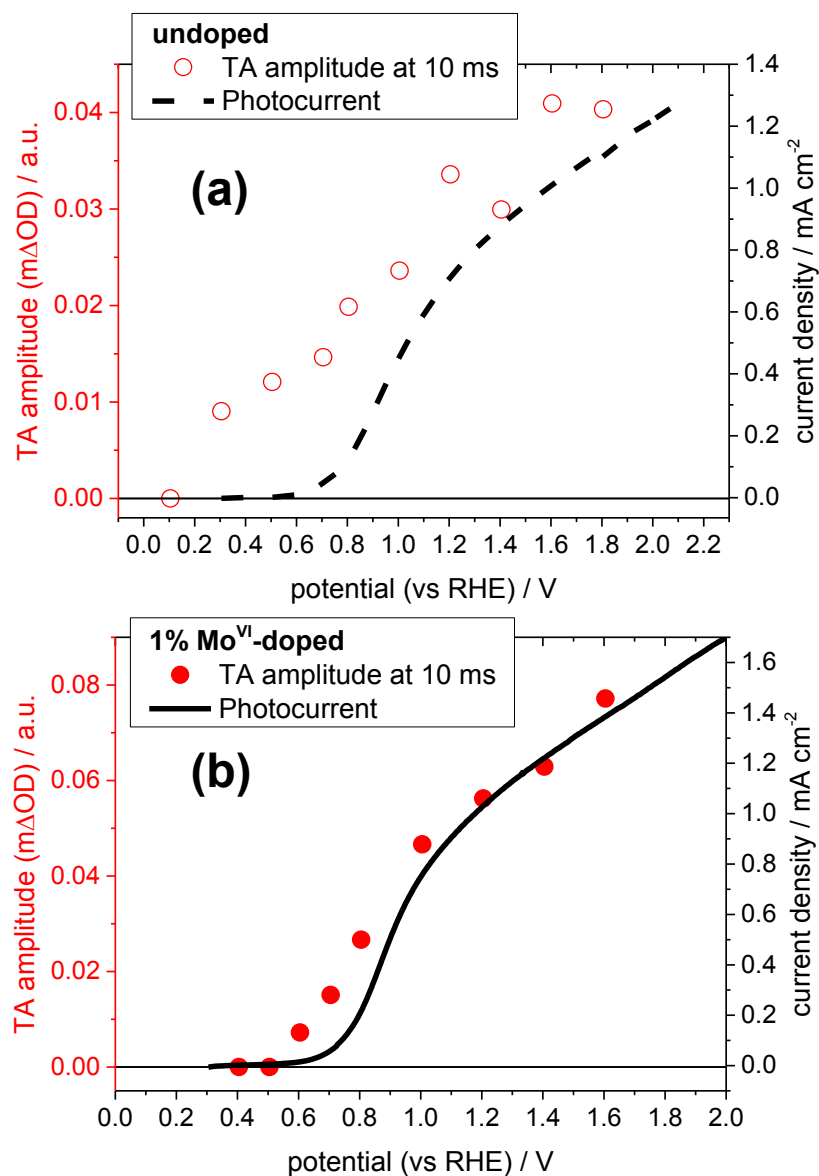


Figure 5.7. Correlation of transient absorption amplitude of long-lived photogenerated holes recorded at 10 ms after photo-excitation (red circles) with photocurrent (lines). (a): un-doped BiVO₄; (b): 1% Mo^{VI}-doped BiVO₄. Excitation direction: front side for both. Scan rate of the photocurrent measurements: 10 mV s⁻¹.

5.4.2 Charge Transport in Mo^{VI} doped BiVO₄

Charge transport in the doped BiVO₄ is now discussed. The photocurrent response (front vs back side illumination) suggests that electron collection in the doped BiVO₄ was efficient. Electron transport in the doped BiVO₄ was more favourable. Electron transport can be defined by mobility or conductivity. The conductivity can be increased by increasing mobility or electron density according to Equation 5.1. DFT calculation suggested that the effective mass of electrons in Mo^{VI}-doped BiVO₄ ($m_e^*/m_0 = 1.16$) was two times higher than the electrons in un-doped BiVO₄ ($m_e^*/m_0 = 0.55$).¹¹ The higher effective mass may decrease the mobility.¹ Therefore, it is likely that the photoelectrochemical improvement was due to enhanced conductivity for electrons in doped BiVO₄. Despite the lower mobility of electrons, it could be compensated by significantly higher electron density in doped BiVO₄.

The transient absorption amplitude shows significant difference between front and back side illumination. In doped BiVO₄, transient absorption signals of long-lived holes on ms–s timescales were not observed under modest applied potential ($< 0.6 V_{RHE}$), although they were observed at $> 0.1 V_{RHE}$ in un-doped BiVO₄. The Mott-Schottky analysis indicated that the space charge layer in doped BiVO₄ was too small to allow charge separation. Therefore, it appears that fast bimolecular recombination was dominant in doped BiVO₄ at applied potentials $< 0.6 V_{RHE}$. When the space charge layer formation was sufficient to separate charges (under higher applied potential, i.e. $> 0.6 V_{RHE}$), the long-lived (ms-s) holes started to accumulate, allowing water oxidation to occur. There was a strong correlation between the yield of long-lived holes and the photocurrent in the doped BiVO₄, which was significantly different from the long-lived hole yield observed for un-doped BiVO₄. The correlation

between long-lived hole amplitude and photocurrent density was shown in **Figure 5.7**. The long-lived amplitude at 10 ms did not correlate with photocurrent in undoped BiVO_4 , which has been determined due to back electron/hole recombination limiting water oxidation efficiency (discussed in Chapter IV). However, doped BiVO_4 exhibited a very strong correlation between the long-lived hole yield and photocurrent across the whole potential range.

The transient absorption amplitude (**Figure 5.4**) directly indicated the change in density of photogenerated holes as a function of time. It is clear that, for doped BiVO_4 , the amplitude of photogenerated holes, on microsecond to seconds timescales, generated via front-side illumination was higher than that generated via back-side illumination, at potentials anodic of the photocurrent onset potential. As has been discussed in the previous section, front-side illumination facilitates hole accumulation at the surface. The greater yield of holes under front side illumination in doped BiVO_4 , and the strong correlation of the yield of long-lived holes and photocurrent density, suggested that the field of the space charge layer was sufficient to prevent recombination of surface-accumulated holes. On the other hand, the lower yield of holes measured on μs -s timescales under back-side illumination indicates that transport of photogenerated holes from the bulk of the photoanode to the BiVO_4 surface was the limiting factor for water oxidation.

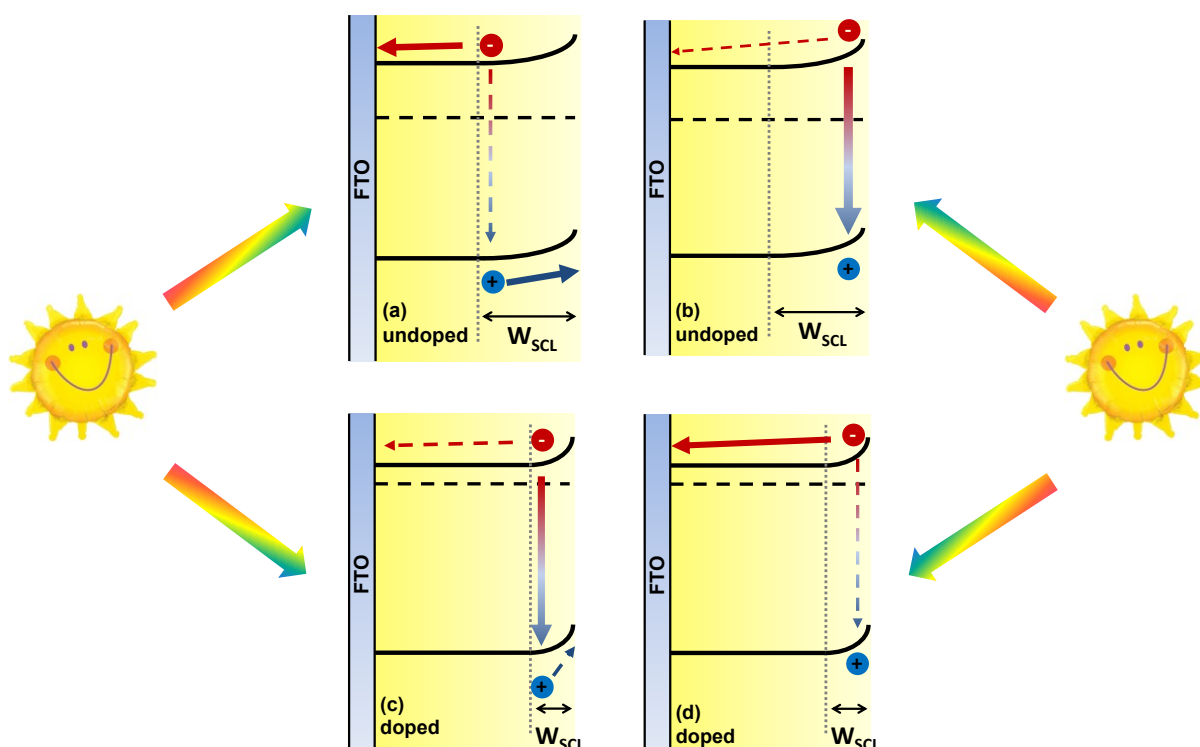
The higher amplitude of photogenerated holes measured under front-side illumination suggested that electron transport did not limit the overall performance in doped BiVO_4 . The results reported herein indicate that electron transport from the surface to the back contact (by front-side illumination) was improved by doping, as evidenced by the photocurrent and transient absorption amplitude of holes, consistent with previous reports of PEC measurements.^{1,10}

The charge transport in un-doped and doped BiVO₄ studied by transient absorption spectroscopy and photoelectrochemical methods was summarised in **Scheme 5.1**. The hole transport in doped BiVO₄ was limited because bulk recombination was dominant in the doped BiVO₄ film. The Mott-Schokkty analysis indicated that the space charge layer was maximum 10 nm in the doped BiVO₄ employed in the studies reported herein. A wide space charge layer helped initial charge separation and hole accumulation at the surface. Such a thin space charge layer suggested that only a small fraction of the BiVO₄ volume was active for efficient charge separation. The back-side illumination lead to a long distance for holes to migrate to reach the surface, compared to the direct hole accumulation under front-side illumination. Since there was no electric field in the bulk to drive holes approaching to the surface, the hole transport was likely to be controlled by diffusion in the bulk. It was apparent that the diffusion was insufficient to drive hole transport in BiVO₄ over long distance (< 500 nm) and only holes generated near the space charge layer could approach to the surface.

In un-doped BiVO₄, the space charge layer is *ca.* 90 nm at the onset potential. The holes generated by back-side illumination could accumulate at the surface more efficiently due to the long space charge layer, which swept holes to the photoanode surface via drift (rather than diffusion through the bulk). However, the electron transport to the back contact was poor, probably due to the poor conductivity as reported by the Mullin's group.⁷

It should be noted that Mullin's group previously reported a significantly lower donor density of Mo^{VI}-doped single crystal BiVO₄ using AC-field Hall effect measurements. The donor density was determined to be *ca.* $5 \times 10^{15} \text{ cm}^{-3}$ by measuring the charge mobility in an AC electric field, which was three orders of

magnitude lower than that measured using impedance spectroscopy.⁷ This difference suggests that the donor density may be overestimated by the impedance measurements as doping could introduce extra trap states in the crystal lattices,⁶ which was measured and interpreted as the space charge capacitance in the Mott-Schottky analyses. In addition, the current-potential results shown in **Figure 5.3** also suggest that the photocurrent generation was still controlled by the depletion region at the surface. If the space charge layer was maximum 10 nm thick in the doped BiVO₄, the electron transport cross the entire film in the front-side illumination should primarily be controlled by a diffusion process, which was independent of applied potential. A plateau of photocurrent should be expected to be observed in the 1% Mo^{VI}-doped BiVO₄, similar to previously reported literature on TiO₂ photoanodes (i.e. charge transport was controlled by diffusion).¹² The photocurrent results of doped BiVO₄ in **Figure 5.3** suggests that the width of the space charge layer may be greater than 10 nm but not wide enough to suppress the bimolecular recombination on sub-ms timescales. The SEM images shown in **Figure 5.2** indicated that the particle size of 1 % Mo^{VI}-doped BiVO₄ was similar to un-doped BiVO₄, around 80-100 nm. Therefore, it is possible that the first layer of the doped BiVO₄ particles was depleted, thus yielding a larger space charge layer than that determined from the impedance data. Nevertheless, all results obtained from transient absorption and photoelectrochemical data indicated that doping of BiVO₄ can change both the charge transport properties of BiVO₄ and charge carrier dynamics. The width of the space charge layer can be determined qualitatively to be narrower in the 1 % Mo^{VI}-doped BiVO₄ than un-doped BiVO₄.



Scheme 5.1. Schematic representations of charge transport in BiVO_4 photoanodes. (a) and (b): electron and hole transport in un-doped BiVO_4 measured under back-side (a) and front-side (b) illumination; (c) and (d): electron and hole transport in 1 % Mo^{VI} -doped BiVO_4 under back-side (c) and front-side (d) illumination.

5.4.3 Impact of the Space Charge Layer for Charge Separation

The width of the space charge layer in doped and un-doped BiVO_4 photoanodes needed to be considered for the water oxidation performance. Doping n-type semiconductors with electron-rich elements resulted in an increased donor density. This increased donor density also lead to a decreased space charge layer width. Since the space charge layer was important for separation of photogenerated charges, it needed to be maintained with a reasonable length in order to allow hole accumulation and retard fast electron/hole recombination on sub-milliseconds timescales.

In the doped BiVO_4 photoanodes, the space charge layer was narrowed by the higher electron density. No long-lived photogenerated holes were detected under modest applied potential in the Mo^{VI} -doped BiVO_4 . Therefore, it may be difficult to shift the onset potential towards the flat band potential. It has been reported that the onset potential in W^{VI} -doped BiVO_4 photoanodes is limited to *ca.* $0.8 V_{\text{RHE}}$ even with cobalt phosphate (CoPi) surface modification.^{3,6} Surface modification with CoPi could significantly reduce the potential required for photocurrent generation,^{3,8-10,13} which will be discussed in Chapters VI and VIII. However, the CoPi modified undoped BiVO_4 exhibited a reported onset potential of $0.3 V_{\text{RHE}}$,⁶ clearly demonstrating the importance of long-lived holes required for such negative shift of onset potential. Since the formation of a long space charge layer was important in BiVO_4 for a high yield of photogenerated holes, it should be important to maintain a reasonable long space charge layer in order to achieve high photocurrent under low applied potential.

5.5 Conclusion

In this chapter, results were reported of the transient absorption study of photogenerated holes in doped and un-doped BiVO_4 photoanodes. The charge transport properties were addressed and linked to the dynamics of the long-lived holes for water oxidation. Doping BiVO_4 can improve the electron transport probably due to enhanced conductivity, but severely limits the space charge layer thickness due to increased donor density. However, the narrowed space charge layer limited the long-lived hole generation under modest applied potential. Therefore, the future modification of such doped BiVO_4 may be difficult in terms of decreasing the onset potential, due to insufficient concentrations of long-lived holes available between flat-band and onset potentials. These results addressed the importance of balancing the electron transport by doping with a sufficient length of space charge layer in the BiVO_4 material design.

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Chapter VI

6. Efficient Suppression of Back Electron/hole Recombination in CoPi-Modified Un-doped BiVO₄ Photoanodes

In this chapter, the dynamics of photogenerated holes in BiVO₄ photoanodes with and without CoPi modification were compared, employing transient absorption and photocurrent measurements on microsecond to second timescales. The impact of CoPi surface modification on BiVO₄ photoanodes was discussed in terms of the cathodic shift of photocurrent onset potential, the catalytic function of CoPi under the experimental conditions employed and the implications for material design.

6.1 Introduction

In Chapter I, the strategy of applying electrocatalysts to modify photoanode surfaces was introduced. Surface modification of BiVO₄ photoanodes with cobalt phosphate (CoPi) and other electrocatalysts has been reported to result in a shift of the onset potential for photocurrent generation from *ca.* 0.6–0.8 V_{RHE} towards the BiVO₄ flat-band potential (0.1 V_{RHE}).^{1–4} These reports clearly demonstrated the importance of surface modification using electrocatalysts if high energy conversion efficiencies were to be achieved at low applied potentials.^{4–6} In the study reported in this chapter, transient absorption and transient photocurrent measurements were employed to investigate the origin of such cathodic shifts of photocurrent onset potential, employing un-doped BiVO₄ photanodes with and without a CoPi surface modification. Details of the CoPi catalyst, including catalytic properties and physical characterisations, have been introduced in Chapter I.

Studies of CoPi functionalised BiVO₄ photoanodes have suggested that water oxidation under illumination occurs via oxidation of the CoPi catalyst by photogenerated holes from the semiconductor.⁷ This CoPi oxidation process also implied a charge separation at the semiconductor surface, which could mitigate back electron/hole recombination.^{4,8} This conclusion has been supported by studies comparing water oxidation photocurrents for BiVO₄ photoanodes with and without CoPi modification in a hole scavenger solution.^{4,7} However, previous transient optical studies of CoPi-modified α -Fe₂O₃ photoanodes have indicated that the most significant effect of CoPi overlayers, at least on α -Fe₂O₃, was to reduce the anodic potential required to retard recombination losses within the α -Fe₂O₃ and thereby reduce the potential required to generate the long-lived holes required for water oxidation.^{9,10} Whilst steady-state CoPi oxidation was observed, it was suggested that

this oxidation was not the primary reason for the cathodic shift of the photocurrent onset potential.¹⁰ A similar conclusion was also obtained from frequency domain photoelectrochemical analyses.¹¹ In addition, previous studies of CoPi deposition on $\alpha\text{-Fe}_2\text{O}_3$ did not distinguish between the impact of CoPi deposition upon bulk recombination losses limiting hole transfer to the surface or upon back electron/hole recombination. This latter (slower) recombination pathway appeared to be particularly important in limiting the onset potential for un-doped BiVO_4 photoanodes.

In the study reported in this chapter, transient absorption spectroscopy (TAS) and transient photocurrent (TPC) measurements were employed to investigate the time-resolved behaviour of photogenerated holes and the water oxidation process on CoPi-modified BiVO_4 photoanodes. The recombination and water oxidation kinetics occurring on CoPi-modified BiVO_4 were studied as a function of potential. The transient absorption and TPC data were correlated and compared to understand the kinetics in such photoanodes. The impact of CoPi treatment on the improvement of photocurrent onset was discussed.

6.2 Results

Flat, 450 nm thick un-doped BiVO₄ films were fabricated by spin-coating using the metal-organic deposition methods previously reported in Chapters II and III.¹² Material characterisation of these films have been reported in Chapter III (XRD, SEM, UV-vis). CoPi was photo-electrodeposited on these un-doped BiVO₄ photoanodes according to methods developed previously, resulting in the deposition of a ca. 100 nm thick overlayers of CoPi.^{4,13,14} **Figure 6.1** compares the chopped light current-potential performance of un-doped BiVO₄ photoanodes before and after CoPi modification measured in potassium phosphate buffer (KPi, pH 6.7). For the unmodified BiVO₄ photoanodes, the onset potentials (*versus* reversible hydrogen electrode, RHE) for water oxidation in light and dark were 0.7 V_{RHE} and 1.9 V_{RHE}, respectively, which was consistent with the results reported in Chapter III and literature data.^{5,7,12,15} A cathodic shift of 200–300 mV for the onset potentials of both dark and light current generation was observed for the CoPi-modified BiVO₄ photoanode, similar to previous reports.^{2,4,16} The more cathodic dark onset obtained with the CoPi overlayer was consistent with its electrocatalytic properties, as reported by Nocera and coworkers.^{13,17,18}

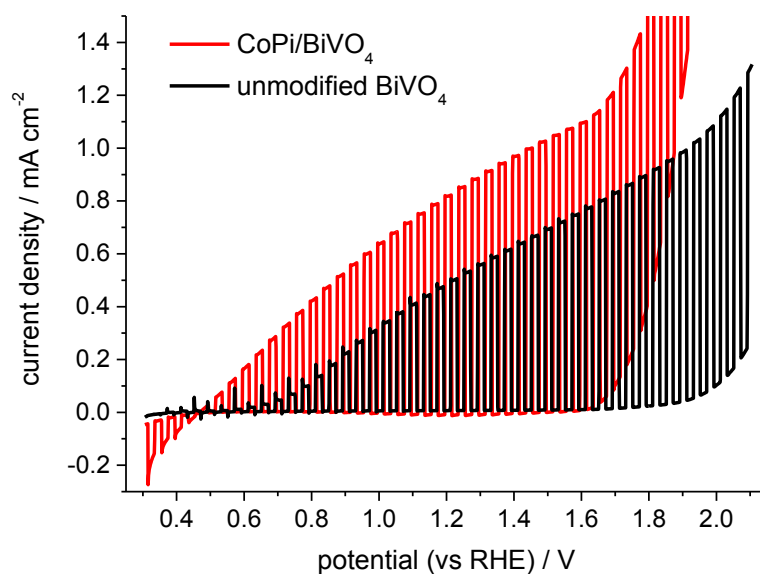


Figure 6.1. Chopped light j-U curve for unmodified (black) and CoPi-modified (red) BiVO_4 photoanodes in 0.1 M Kpi buffer (pH 6.7), under back-side illumination (FTO- BiVO_4); The scan rate is 10 mV s^{-1} and the chopping frequency is 0.2 Hz.

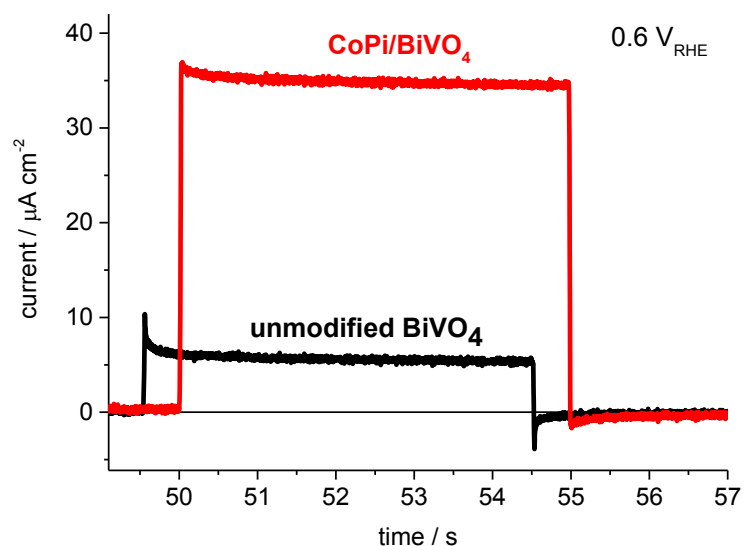


Figure 6.2. Transient photocurrent measured at $0.6 V_{\text{RHE}}$ for unmodified (black) and CoPi-modified (red) BiVO_4 photoanodes under white light bias illumination with 5 s small-perturbation 365 nm pulse. The background currents due to bias light have been corrected to zero.

Transient photocurrent (TPC) measurements (using white light bias and a 5 s small-perturbation 365 nm LED pulse) were conducted as an initial study of charge carrier dynamics. **Figure 6.2** presents typical TPC results for unmodified (black) and CoPi-modified (red) BiVO₄ photoanodes under modest anodic potential (0.6 V_{RHE}), just positive of the photocurrent onset. Particular attention has been paid to the negative transient current peaks observed after light off, which have previously been assigned to back electron/hole recombination (Chapter IV).^{19,20} It is apparent that this negative transient was reduced in amplitude and retarded in recovery time in the presence of the CoPi overlayer, indicative of a suppression of back electron/hole recombination, as is discussed further below.²⁰

Transient absorption spectroscopy was employed to further investigate the dynamics of photogenerated holes in CoPi-modified BiVO₄ water oxidation photoanodes. The transient absorption spectrum of photogenerated holes in unmodified BiVO₄ photoanodes comprised a broad absorption across the visible and near-IR, with a maximum at 550 nm, which was also reported by other groups.^{21,22} Under anodic potential, the decay dynamics of this photo-induced absorption for an unmodified un-doped BiVO₄ photoanode were observed to be biphasic. A ‘fast’ power law phase assigned to back electron/hole recombination competing with hole accumulation on the BiVO₄ surface is observed on μs–ms timescales. This was followed by a ‘slow’ exponential decay phase (10 ms–s) assigned to water oxidation in kinetic competition with back electron/hole recombination, consistent with the results discussed in Chapters III and IV.

We now compare the transient absorption spectra of unmodified BiVO₄ and CoPi-modified BiVO₄, from microsecond (μs) to second (s) timescales under 1.2 V_{RHE} applied potential. **Figure 6.3** showed that CoPi surface modification did not

significantly change the shape or the amplitude of the transient absorption spectra, with both photoanodes exhibiting broad spectra peaking at 550 nm with initial amplitudes of ΔOD $5.5\text{--}6\times 10^{-5}$. It has been noted that CoPi oxidation results in a broad absorption increase in the visible region, particularly noticeable at wavelengths < 550 nm.¹⁰ This was clearly different from the transient absorption spectra (**Figure 6.3**). Therefore we assigned the transient absorption signals for both the CoPi-modified and unmodified BiVO_4 primarily to photogenerated BiVO_4 holes.

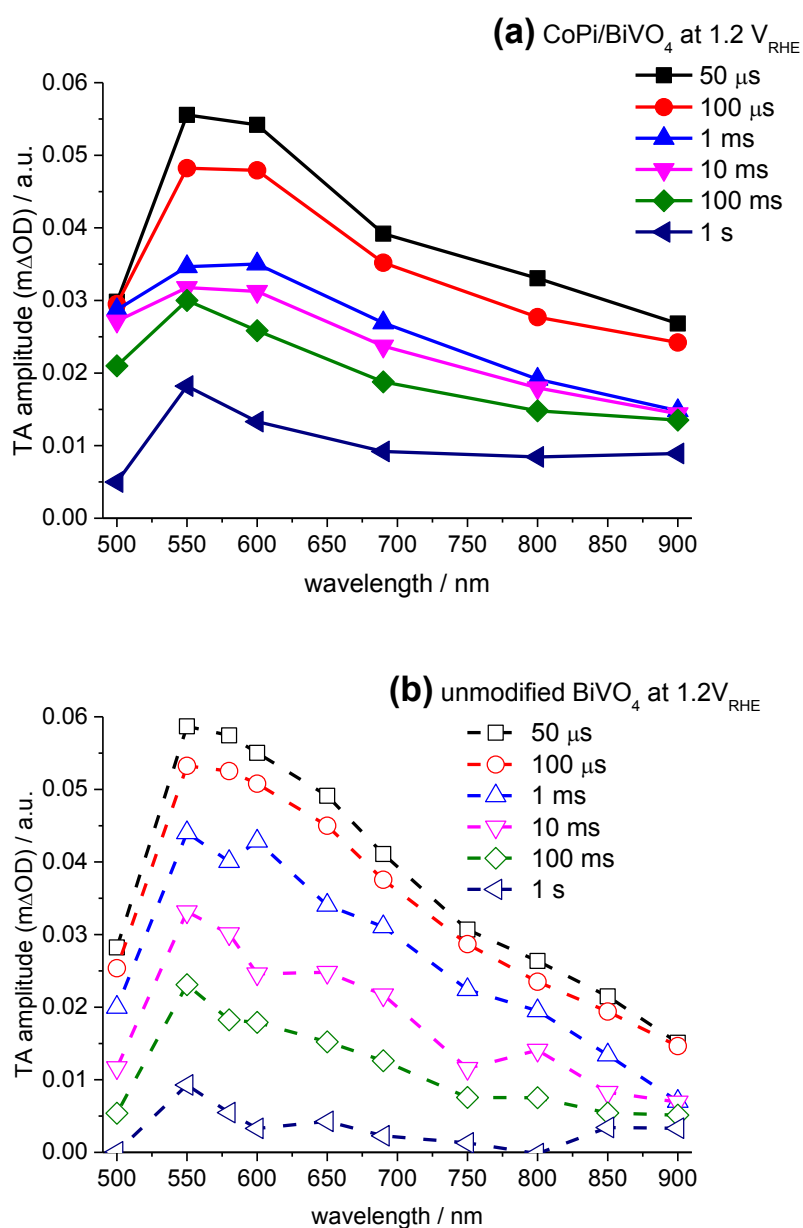


Figure 6.3. Transient absorption spectra of (a) CoPi-modified BiVO₄ (solid lines and full marks) and (b) unmodified BiVO₄ (dashed lines and empty marks) under 1.2 V_{RHE}, recorded from 50 μs to 1 s after laser excitation (355 nm, 100 μJ cm⁻², 0.33 Hz).

Figure 6.4 shows typical transient absorption decay kinetics of photogenerated holes measured at 550 nm for both unmodified and CoPi-modified BiVO₄ photoanodes under modest (0.6 V_{RHE}) and strong (1.4 V_{RHE}) applied potentials. As previously reported in literature and in Chapter III,^{23,24} these decays were fitted by a combination of power law (for the ‘fast’ decay phase) and single exponential (for the ‘slow’ decay phase) functions,

$$\Delta OD = at^b + \phi_{TAS2}e^{-t/\tau_{TAS2}} \quad (6.1)$$

where a and b define the power law function, ϕ_{TAS2} is the amplitude of the exponential slow decay phase and τ_{TAS2} is its decay time constant. All fit results were shown in **Table 6.1**.

Potential (vs RHE) / V	CoPi-modified BiVO ₄				unmodified BiVO ₄			
	a / a.u.	b / a.u.	ϕ_{TAS2}	τ_{TAS2}	a / a.u.	b / a.u.	ϕ_{TAS2}	τ_{TAS2} /
			(mΔOD) /	/ s			(mΔOD)	s
			a.u.				/ a.u.	
1.6	-	-	-	-	3.1E-06	-0.24	0.047	1.4
1.4	3.7E-07	-0.41	0.04	1.6	3.0E-06	-0.23	0.046	1.2
1.2	1.1E-06	-0.32	0.04	1.6	1.1E-06	-0.33	0.042	1.0
1	2.5E-07	-0.44	0.03	1.6	3.6E-06	-0.23	0.036	0.9
0.8	9.0E-07	-0.35	0.03	1.5	2.7E-06	-0.25	0.029	0.8
0.6	9.3E-07	-0.35	0.02	1.3	1.0E-06	-0.35	0.025	0.2
0.4	1.0E-06	-0.31	0.01	0.2	3.5E-06	-0.22	0.017	0.1
0.2	1.9E-	-0.35	0.004	0.02	1.2E-	-0.22	0.007	.01

Table 6.1. Fit results of transient absorption decays of unmodified and CoPi/BiVO₄ photoanodes as a function of applied potential using a combination of power law and single exponential function shown in Equation 6.1.

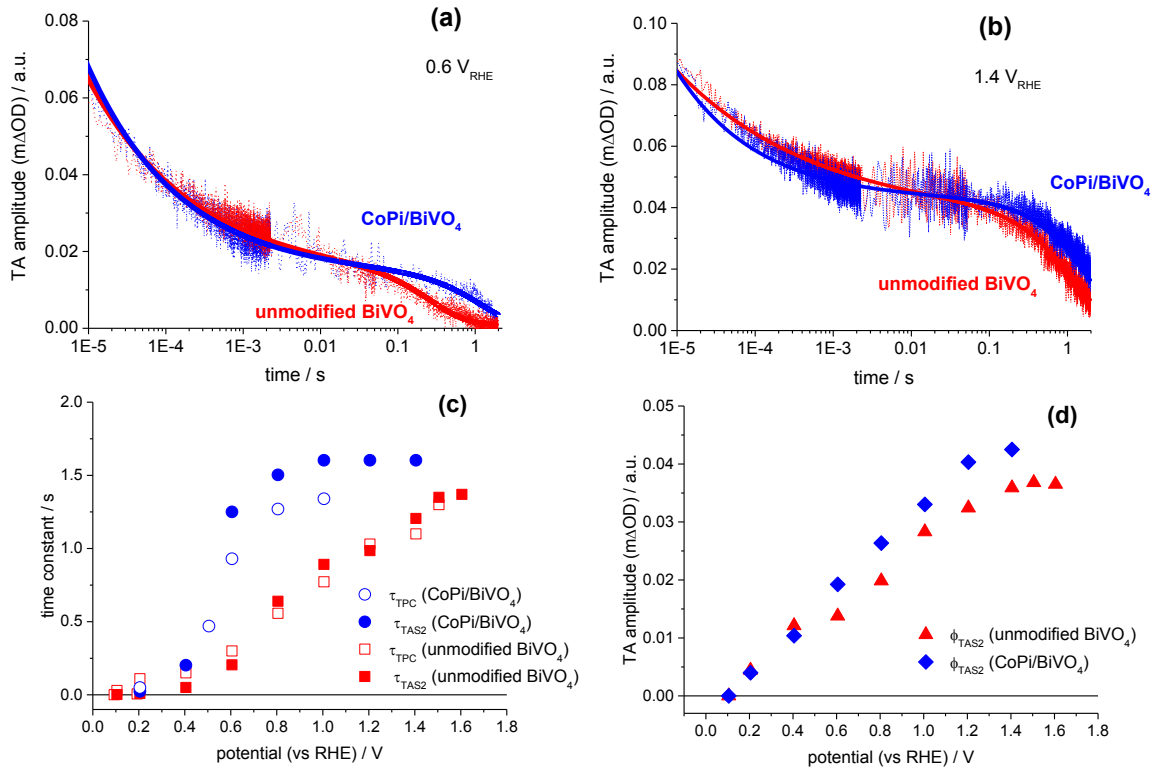


Figure 6.4. (a) and (b) Comparison of transient absorption decays of unmodified BiVO₄ (red dots) and CoPi-modified BiVO₄ (blue dots) photoanodes measured in 0.1 M Kpi buffer under 0.6 V_{RHE} (a) and 1.4 V_{RHE} (b). Fits to the data using Equation 6.1 (blue lines: CoPi-modified BiVO₄; red lines: unmodified BiVO₄) were overlaid with the measured transient absorption data. (c) Time constants from transient absorption and transient photocurrent decays versus applied potential. Solid circles and squares: τ_{TAS2} , time constants from the exponential decay phase (Equation 6.1) for unmodified (red) and CoPi (blue) BiVO₄ photoanodes. Empty circles and squares: τ_{TPC} , the time constants of negative transient current, for unmodified (red) and CoPi-modified (blue) BiVO₄ photoanodes, in the TPC measurements, obtained from fits using Equation 6.2. (d) Amplitude of the slow transient absorption decay phase ϕ_{TAS2} versus applied bias; red triangles: unmodified BiVO₄; blue diamonds: CoPi-modified BiVO₄.

It is apparent from **Figures 6.4 a** and **b** that, under the low applied potential, a significantly retarded exponential decay (approximately one order of magnitude) was observed in a CoPi-modified BiVO₄ photoanode compared to the unmodified BiVO₄. Similar results were obtained from the transient absorption studies of CoPi surface-modified α -Fe₂O₃ photoanodes.^{9,10}

Figures 6.4 c and **d** show the lifetimes and amplitudes of the slow exponential decay phase in unmodified BiVO₄ and CoPi-modified BiVO₄ photoanodes as a function of applied anodic potentials, determined from fits of the data to Equation 6.1. The decay time constants and amplitudes increased with increasing anodic applied potential in both photoanodes. It is apparent that CoPi deposition did not significantly change the amplitude of the exponential decay phase, ϕ_{TAS2} , nor its dependence upon applied potential. In contrast, CoPi deposition had a large impact upon the potential dependence of the lifetime of this decay phase (τ_{TAS2}). For the unmodified BiVO₄ photoanode, τ_{TAS2} increased gradually across the potential range studied from ca. 10 ms at 0.2 V_{RHE} to ca. 1.4 s at 1.6 V_{RHE}. In contrast, for the CoPi-modified photoanode, τ_{TAS2} increased in lifetime much more sharply with applied potential, saturating at 1.6 s for potentials ≥ 1.0 V_{RHE}. The potential dependence of τ_{TAS2} for unmodified BiVO₄ has previously been assigned to retardation of back electron/hole recombination (Chapter IV). The significant increase in lifetime of the ms-s exponential phase under modest applied potentials following CoPi deposition suggested that this back electron/hole recombination was retarded, as is discussed in more detail below.

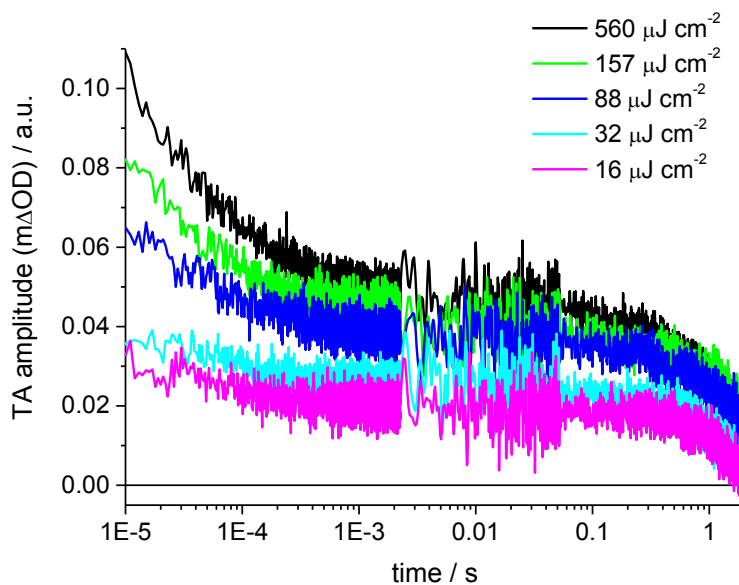


Figure 6.5. Transient absorption decays of a CoPi-modified BiVO₄ photoanode measured as 1.2 V_{RHE} as a function of excitation intensity.

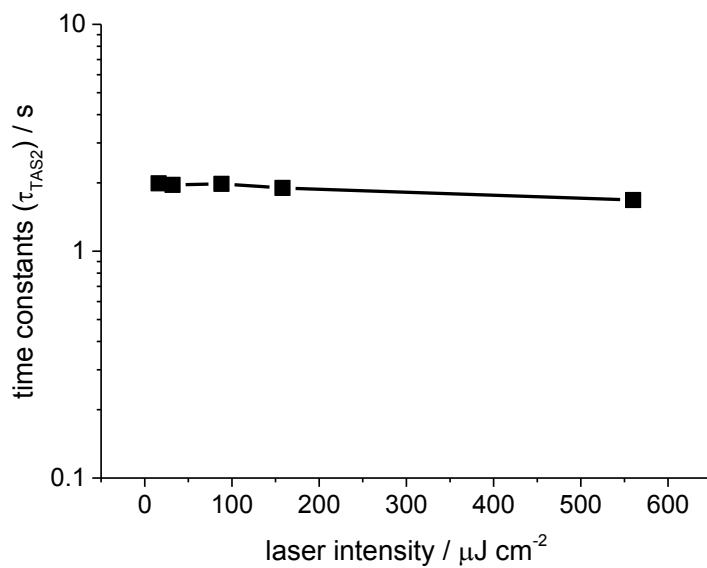


Figure 6.6. Slow phase time constants (τ_{TAS2}) of transient absorption decays at 1.2 V_{RHE} as a function of excitation intensity in a CoPi-modified BiVO₄ photoanode. The time constants were obtained from fitting the transient absorption decays in Figure 6.5 using Equation 6.1.

It is also noted that the slow phase time constants did not change with increasing excitation intensity shown in **Figures 6.5** and **6.6**, suggesting that the kinetics of long-lived holes oxidising water was not changed with the hole density at the BiVO₄ surface also not accelerated by the CoPi overlayers, as is discussed further below. The transient absorption amplitude on faster phase (μs-ms) increased with increasing laser intensity whereas the slow phase (ms-s) amplitude becomes saturated. In Chapter IV, for the unmodified BiVO₄, the faster phase has been assigned to a bimolecular recombination process which was dominant at high laser intensities.

In order to provide further evidence retardation of back electron/hole recombination on BiVO₄ by CoPi deposition, transient photocurrent data were collected as a function of applied potential from 0.1–1.6 V_{RHE}. The background current due to the bias light was subtracted to be zero. The negative transient peaks (after light-off) were fitted by a single exponential function:^{19,20,25}

$$I(t) = I_0 e^{-(t / \tau_{TPC})} \quad (6.2)$$

where $I(t)$ is the transient current measured under applied potential; I_0 is the amplitude of negative transient peak, and τ_{TPC} is the time constant of the negative transient recovery. This negative current transient has been assigned to back electron/hole recombination, in kinetic competition with water oxidation.²⁰ The TPC time constants τ_{TPC} were shown in **Figure 6.4c** as a function of applied potential, overlaid with the transient absorption time constants τ_{TAS2} . There was a good agreement between τ_{TPC} and τ_{TAS2} for both the unmodified and CoPi-modified BiVO₄ photoanodes, indicating that both τ_{TPC} and τ_{TAS2} were monitoring the same process, consistent with the previous results for unmodified BiVO₄ photoanodes in Chapter IV.

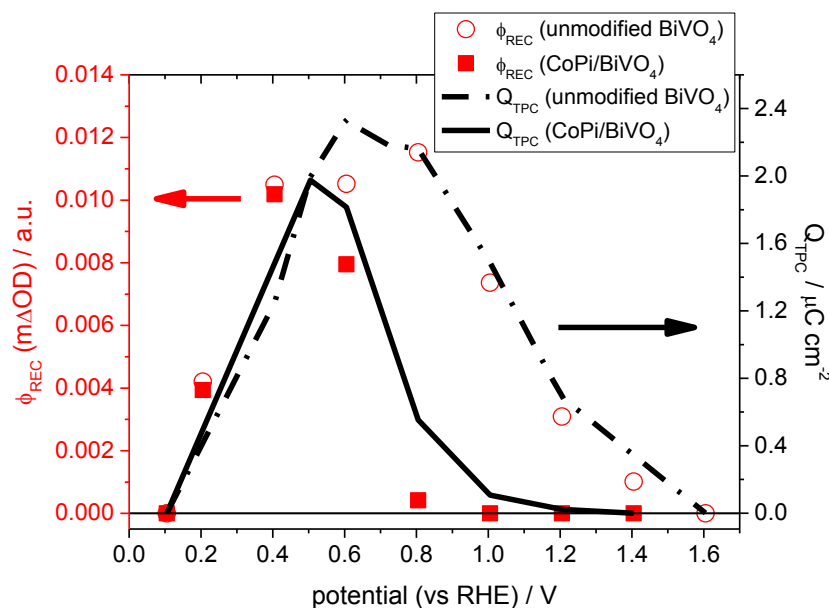


Figure 6.7. Comparison of back electron/hole recombination yield measured by transient absorption spectroscopy (ϕ_{rec}), in unmodified (red empty circles) and CoPi-modified (red filled squares) BiVO_4 photoanodes, and by TPC measurements (Q_{TPC}), in unmodified (black dashed line) and CoPi-modified (black solid line) BiVO_4 photoanodes.

Quantification of the total charge lost to back electron/hole recombination following light-off in the TPC measurement could be obtained by integrating the negative TPC transient. **Figure 6.7** shows this integrated charge (broken and solid lines) as a function of applied potential for unmodified and CoPi-modified BiVO_4 photoanodes. The amount of charge (i.e. surface accumulated holes) lost due to this back electron/hole recombination was strongly potential-dependent, being maximal at 0.5–0.6 V_{RHE} . It is also apparent that deposition of CoPi resulted in a substantial negative shift in the potential which must be applied to turn off these back electron/hole recombination losses. The disappearance of negative current transients in CoPi-modified BiVO_4 has also been reported previously.² This negative shift of the potential required to turn off back electron/hole recombination was also consistent with the transient absorption data, and likely to be the key reason for the

cathodic shift of photocurrent onset potential following CoPi deposition, as is discuss in detail below.

6.3 Discussion

6.3.1 Correlating Long-Lived Holes with Photocurrent Density

Water oxidation on metal oxide photoanodes appeared to be a kinetically rather slow process.²⁶ Rate constants for water oxidation under pulsed laser excitation of 0.7 s^{-1} and 5 s^{-1} for hematite¹⁹ and titania²³ photoanodes respectively have been reported. Similarly slow rate constants have also been reported from electrochemical analyses of hematite photoelectrodes.¹¹ For unmodified BiVO_4 , it has been reported in Chapter IV that a rate constant for water oxidation of *circa* 1 s^{-1} . This rate constant was determined from the decay time constant of the slow decay phase observed by transient absorption under strong anodic potential, where back electron/hole recombination was turned off. This rate constant was consistent with the data reported herein (*ca.* 0.7 s^{-1}) for the unmodified films at $> 1.6 \text{ V}_{\text{RHE}}$. Due to these slow rate constants, long-lived holes accumulated at the photoanode surface. Determining the yields and lifetimes of these surface holes was therefore central to understanding the efficiency of water oxidation by such photoanodes.

Studies herein were focused upon the effect of a photo-electrodeposited surface layer of CoPi electrocatalyst on un-doped BiVO_4 photoanodes. The impact of CoPi surface modification on the yield of long-lived holes were first considered, as assayed by the amplitude ϕ_{TAS2} of the exponential slow phase observed in the transient absorption studies. This yield was a measure of the efficiency of hole transfer to the photoanode surface, and was therefore a measure of the efficiency of charge separation, driven primarily by the space charge layer formed at the semiconductor-electrolyte interface. **Figure 6.8a** (open symbols) shows ϕ_{TAS2} for unmodified and CoPi-modified BiVO_4 photoanodes as a function of applied potential,

overlaid with the photocurrent density. It is apparent that for both photoanodes, there was an offset between the appearances of long-lived photogenerated holes and photocurrent. This difference in the potential dependence of ϕ_{TAS2} and photocurrent was however much smaller following CoPi deposition. For unmodified BiVO₄, this difference in the potential dependence of ϕ_{TAS2} and photocurrent has been assigned to back electron/hole recombination across the space charge barrier on ms–s timescales, in kinetic competition with water oxidation. This loss necessitates the additional application of a 600–700 mV anodic potential for photocurrent (water oxidation) generation (see **Figure 6.8a**). This implied that for unmodified BiVO₄ photoanodes, a strongly anodic potential, resulting in a wide space charge layer and strong band bending, was required to provide a sufficient barrier to prevent back electron/hole recombination. For the CoPi-modified BiVO₄ photoanode, the significantly smaller difference between the potential dependence of ϕ_{TAS2} (i.e. charge separation yield) and photocurrent implied that back electron/hole recombination losses were less severe. It is noted that the potential for the onset of long-lived holes in unmodified and CoPi-modified BiVO₄ were similar (both 0.2 V_{RHE}), suggesting that the flat-band potential was largely unaffected by CoPi deposition, consistent with previously reported studies of cobalt-modified BiVO₄²⁷ and α -Fe₂O₃⁸ photoanodes by other groups. Additionally, the amplitude of the long-lived holes was only slightly increased by CoPi (**Figure 6.4d**), indicative of only minor retardation of sub-ms electron/hole recombination and indicating that the yield of hole transfer to the photoanode surface was largely independent of CoPi surface modification. These results suggest that the main effect of CoPi on BiVO₄ photoanodes was to significantly reduce recombination of bulk electrons with surface accumulated holes in BiVO₄.

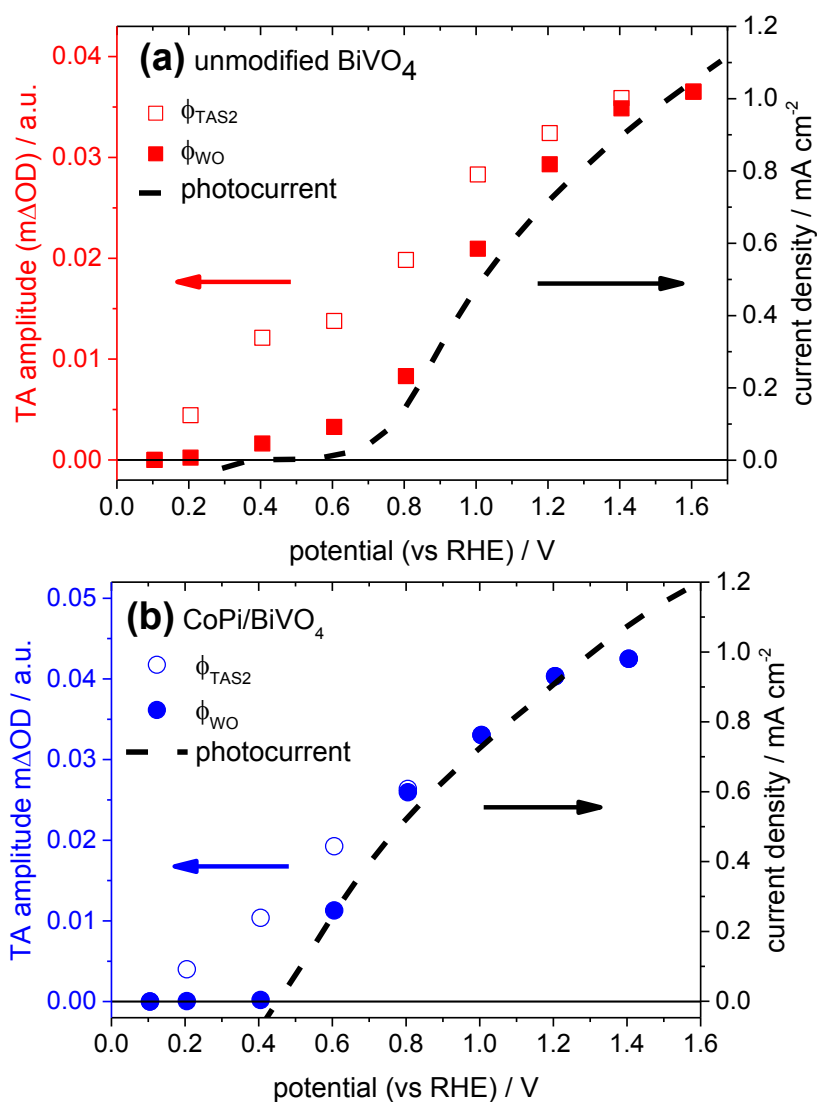


Figure 6.8. Empty red squares and empty blue circles: transient absorption amplitude of long-lived holes (ϕ_{TAS2}) in unmodified (a) and CoPi-modified (b) BiVO₄ photoanodes, obtained from Equation 6.1, as a function of applied anodic potential. Filled red squares and filled blue circles: amplitude of holes that contribute to water oxidation (ϕ_{WO}) in unmodified (a) and CoPi-modified (b) BiVO₄ photoanodes, calculated from Equation 6.3, overlaid with photocurrent (dashed black lines).

6.3.2 Kinetic model for photoanode function

Now a simple kinetic model for water oxidation was considered by focusing on the kinetic competition between water oxidation and back electron/hole recombination, as shown in **Scheme 6.1**. Previously this kinetic model has been applied to

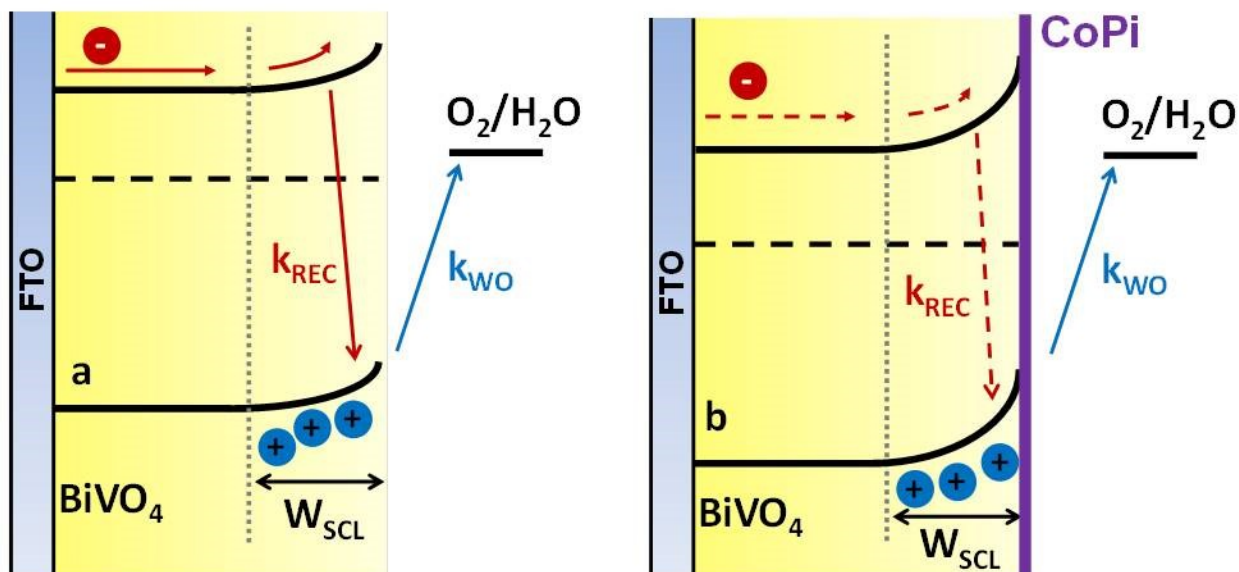
unmodified BiVO₄ (in Chapter IV) and Fe₂O₃ photoanodes.¹⁹ As has been applied in Chapter IV, assuming 100 % Faradaic efficiency of water oxidation during the transient absorption measurements, the relative water oxidation yield, $\phi_{WO}(V)$, and back electron/hole recombination yield, $\phi_{REC}(V)$, can be calculated from:

$$\phi_{WO}(V) = \phi_{TAS2}(V) \times \frac{k_{WO}}{k_{WO} + k_{REC}(V)} \quad (6.3)$$

$$\phi_{REC}(V) = \phi_{TAS2}(V) \times \frac{k_{REC}(V)}{k_{WO} + k_{REC}(V)} \quad (6.4)$$

$$k_{WO} + k_{REC}(V) = \frac{1}{\tau_{TAS2}(V)} \quad (6.5)$$

where $\phi_{TAS2}(V)$ and τ_{TAS2} , were the amplitudes and lifetimes of the slow transient absorption decay phase, and therefore proportional to the yield and lifetimes of holes transferred to the photoanode surface, as shown in **Figure 6.4d**; k_{WO} and $k_{REC}(V)$ were the water oxidation and back electron/hole recombination rate constants, respectively. The water oxidation rate constant is assumed to be potential independent, and is determined directly from τ_{TAS2} in the limit of strong anodic bias, where back electron/hole recombination is suppressed.



Scheme 6.1. Schematic presentation of charge carrier dynamics considered in the kinetic model of water oxidation following photoexcitation of un-doped unmodified (a) and CoPi-modified (b) BiVO_4 photoanodes, illustrating the kinetic competition between water oxidation (k_{WO}) and back electron/hole recombination (k_{REC}). For the CoPi-modified film, these back electron/hole recombination losses were significantly suppressed.

The water oxidation yield $\phi_{\text{WO}}(V)$ calculated from Equation 6.3 using the data shown in **Figure 6.4** is shown in **Figure 6.8** (filled circles/squares). For both the unmodified and CoPi-modified BiVO_4 photoanodes, the water oxidation yield was in excellent agreement with the measured photocurrent density, demonstrating the effectiveness of this simple kinetic model.

The yield of back electron/hole recombination $\phi_{\text{REC}}(V)$, as quantified from Equation 6.4 from the transient absorption data, is shown in **Figure 6.7**, overlaid with the charge lost through this recombination pathway determined from integration of the photocurrent transients. For both photoanodes, there was an excellent agreement between transient absorption and transient photocurrent assays of the yield of back electron/hole recombination, providing further support for the validity of the analyses presented here.

The analysis shows the origin of the cathodic shift of the photocurrent onset potential following CoPi deposition on BiVO₄. It appears that CoPi deposition did not substantially change the potential dependence or efficiency of hole transfer to the BiVO₄ surface. For both photoanodes, the onset potential for the generation of long-lived (ms) holes was *ca.* 0.2 V_{RHE}, close to the flat band potential for BiVO₄. However CoPi deposition did change the potential required to turn off back electron/hole recombination, resulting in the observed cathodic shift in photocurrent generation.

Under sufficiently strong positive potential, back electron/hole recombination was suppressed for both unmodified and CoPi modified photoanodes; under these conditions τ_{TAS2} corresponds directly to the time constant for water oxidation. It is apparent from the data in **Figure 6.4** that this limiting time constants were similar for both photoanodes (1.4 s and 1.6 s without and with CoPi deposition). It could thus be concluded that the rate constant for water oxidation by BiVO₄ holes was independent of CoPi. This time constant was also found to be independent of laser excitation density (see **Figures 6.5** and **6.6**). It is thus apparent that CoPi did not accelerate water oxidation by BiVO₄. This was also consistent with an intensity-modulated photocurrent spectroscopy study which concluded that cobalt species did not increase the reaction rate of water oxidation on a cobalt-treated α -Fe₂O₃ photoanode.¹¹ In fact, CoPi deposition appears to result in a small retardation of water oxidation (see **Figure 6.4b**), most probably due to the reduced accessibility of water to the BiVO₄ surface following CoPi deposition. These data do not mean that CoPi was not oxidised under steady state irradiation at anodic potential (resulting for example from a low quantum yield of hole transfer from BiVO₄ to the CoPi layer). A detailed study of this issue, employing continuous illumination, is ongoing and will be discussed in Chapter VIII. It is also noted that it has been suggested that on α -Fe₂O₃

photoanodes, thicker than optimum CoPi layers may result in a higher proportion of water oxidation proceeding from oxidised CoPi.²⁸ The study herein employs a relative thin (100 nm) CoPi layer, found to give optimum performance as previously reported.² Notwithstanding these caveats, the data reported herein implied that, for the optimised CoPi layer thickness employed, any such oxidised CoPi, if present, did not contribute strongly to the enhanced water oxidation photocurrent. Instead, the improved photocurrent onset potential and higher photocurrent density could be explained by efficient suppression of back electron/hole recombination in a BiVO₄ photoanode modified by CoPi overlayers.

Previously significant retardation of back electron/hole recombination following CoPi-modification of α -Fe₂O₃ photoanodes has been observed.^{9,10} These previous studies did not distinguish between the impact of CoPi deposition on bulk back electron/hole recombination (i.e. the efficiency of hole transfer to the surface) or on back electron/hole recombination. It is also noted that back electron/hole recombination losses were less prominent for these hematite photoelectrodes compared to the BiVO₄ photoanodes studied herein, most probably associated with the higher doping density and faster bulk recombination losses in the hematite photoanodes. Nevertheless they were consistent with the results presented herein, namely that the primary effect of CoPi deposition is the retardation of recombination losses rather than acceleration of water oxidation.

This transient absorption study reported herein suggests that the yield of charge separation (i.e. fraction of holes reaching the BiVO₄ surface) was not improved in the presence of CoPi overlayer, as evidenced by the nearly unchanged initial amplitude of long-lived holes in BiVO₄ photoanodes following CoPi modification. This result was consistent with photoelectrochemical investigations of CoPi-modified and

unmodified BiVO_4 using H_2O_2 hole scavenger.^{4,7} Both the transient absorption studies reported herein and previous PEC studies^{4,7} were in agreement that recombination within the space charge layer was reduced in CoPi-modified BiVO_4 photoanodes. Additionally, the results presented herein from CoPi-modified BiVO_4 indicated that such lower recombination losses result specifically from an inhibition of back electron transfer from the bulk across the space charge layer to recombine with surface holes. Consequently, more holes in the space charge layer were able to contribute to water oxidation under modest applied potentials, thus enhancing the photocurrent.

The mechanism of how CoPi deposition reduced the losses due to back electron/hole recombination was not clear. Previously we suggested that reduced recombination losses in CoPi modified $\alpha\text{-Fe}_2\text{O}_3$ photoanodes may result from enhanced band bending and space charge layer formation by CoPi.^{9,10} We note that the space layer depth in these doped $\alpha\text{-Fe}_2\text{O}_3$ photoanodes (ca. 8 nm at 1.23 V_{RHE}) was substantially narrower than in the un-doped BiVO_4 studied herein (ca. 90 nm at 1.23 V_{RHE}). The very small increase in the long-lived hole amplitude in CoPi-modified BiVO_4 suggested that the width of the space charge layer was not significantly increased in the presence of CoPi overlayers. Instead, the significant reduction of back electron/hole recombination may be caused by increased electric field strength associated with the electrostatics of the $\text{BiVO}_4/\text{CoPi}$ interface, although detailed understanding of this point was beyond the scope of this study.

6.4 Conclusion

In this chapter, transient absorption spectroscopy and photoelectrochemical methods were employed to characterise the photogenerated charge carriers in CoPi surface modified BiVO_4 photoanodes responsible for water oxidation. The photoelectrochemical results confirmed that water oxidation performance of BiVO_4 photoanodes could be improved by CoPi deposition, resulting particularly in a cathodic shift in the photocurrent onset potential. Transient absorption and transient photocurrent studies indicated that this improvement was not primarily due to the catalytic function of CoPi on the BiVO_4 surface under the measurement condition. Rather, it appeared to result from suppression of recombination of surface-accumulated holes with bulk electrons (back electron/hole recombination), therefore more holes contribute to water oxidation. These results emphasised the key role of recombination losses in limiting photoanode performance, and how these losses can be reduced by surface modification.

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Chapter VII

7. Rate Law Analysis of Water Oxidation on Un-doped BiVO₄ Surface

A rate law analysis of water oxidation on the surface of un-doped BiVO₄ photoanodes was described in this chapter. Such analyses could provide insight of the kinetics of water oxidation and the rate-determining step in the catalytic water oxidation circle on the BiVO₄ surface under the photoelectrochemical working condition. A rate law analysis was applied to investigate the reaction order of water oxidation and the corresponding rate constants. The water oxidation kinetics and whether BiVO₄ could drive multi-hole water oxidation were particularly discussed and compared with α -Fe₂O₃ photoanode.

7.1 Introduction

In this chapter, the kinetics of water oxidation on the surface of BiVO_4 under the photoelectrochemical (PEC) working conditions was discussed. The particular concern addressed in this chapter about water oxidation is whether BiVO_4 could drive multi-hole water oxidation under illumination.

Previously the transient absorption study in Chapters III and IV reported a low yield of long-lived surface accumulated holes for water oxidation. Water oxidation by the long-lived surface holes on ms-s timescales was observed to follow first order kinetics under pulsed laser excitation (i.e. single exponential behaviour of photogenerated holes on ms-s timescales). However, the study of excitation intensities indicated that this technique does not allow a substantial amount of long-lived holes to accumulate at the surface due to dominant bimolecular recombination on early (μs -ms) timescales. The understanding of water oxidation by long-lived holes under high accumulation conditions is therefore limited, which is the objective of this chapter.

Oxygen evolution reaction (OER) has been studied intensively in Photosystem II. The oxygen evolution catalyst has been determined to be a CaMn_4O_5 cubane cluster,¹ where oxygen evolution reaction was associated with the transition of oxidation state of Mn between 3+ and 5+ with the turnover rate of 10^3 s^{-1} . One oxygen molecule was released after the step by step storage of four oxidising equivalents in the Mn atoms.^{2,3} The most critical step for the oxygen evolution reaction in Photosystem II is O-O bond formation. The mechanism of this O-O formation, however, is still unclear.^{3,4}

Investigation of the mechanism of water oxidation on metal oxides for artificial photosynthesis has been limited to date.^{5,6} Cobalt oxide as an efficient water oxidation catalyst has attracted particular interest.⁷ Mechanistic studies of Co_3O_4 ⁸ suggest that multi-hole water oxidation was possible at the reaction centre (catalytic cluster) of water oxidation. Zhang *et al.* investigated Co_3O_4 water oxidation using time-resolved FT-IR. They found that an intermediate probed by such technique carries three holes in the catalytic water oxidation circle with the turnover frequency (TOF) of $> 3 \text{ s}^{-1}$.⁸ Ann and Bard recently have reported a kinetic study of CoPi (amorphous CoO_x with phosphate ligand to stabilise the cluster) during water oxidation using scanning electrochemical microscopy. The water oxidation rate determined to be *ca.* 0.19 s^{-1} , indicating a rather slow kinetics of water oxidation of cobalt oxide catalysts. The water oxidation rate constant has also been reported *c.a.* 0.01 s^{-1} based on the turnover frequency,⁹ It was thus agreed that water oxidation on cobalt oxide was a rather slow process on seconds timescales.

Previously water oxidation by sequential single-hole reactions has been observed according to transient absorption spectroscopy measurements under pulsed laser excitation of titania (TiO_2),^{10,11} hematite ($\alpha\text{-Fe}_2\text{O}_3$)¹²⁻¹⁴ and BiVO_4 (Chapter IV). Transient absorption studies as a function of temperature and excitation intensity in hematite ($\alpha\text{-Fe}_2\text{O}_3$) photoanodes indicated that the single-hole reaction was possible due to the deep valence band providing sufficient thermodynamic driving force for holes to oxidise water. The energetics of water oxidation in these materials was discussed in detail in the discussion section. The valence band (VB) of BiVO_4 consists of hybridised Bi_{2s} and O_{2p} orbitals giving the VB edge is 2.5 eV.¹⁵⁻¹⁷ Such deep valence band can provide sufficient driving force for holes to oxidise water, similar to $\alpha\text{-Fe}_2\text{O}_3$. The chemical nature of photogenerated holes in BiVO_4 was not

clear yet to date. It was understood that the presence of $\text{Bi}_{2\text{s}}$ narrows the band gap from 2.9 eV down to 2.5 eV. Therefore, it was reasonable to assume that photo-induced high valence Bi species (from 3+ to 4+) could be responsible for hosting the holes. The current technique, transient absorption spectroscopy, employed to study charge carriers for water oxidation, was based on short laser pulse that did not allow substantial accumulation of photogenerated holes at the BiVO_4 surface, resulting from severe bimolecular recombination at high intensity of laser excitation on μs -ms timescales (see Chapters III and IV). In addition, the photocurrent of BiVO_4 photoanodes under AM 1.5 was observed close to 1 mA cm^{-2} at high applied potential. Such photocurrent corresponded to a hole concentration of 4 m ΔOD required at the surface if water oxidation proceeded with the first order kinetics (reaction rate is 1.3 s^{-1} determined from Chapter IV, and extinction coefficient ($500 \text{ M}^{-1} \text{ cm}^{-1}$) is calculated below). Such calculated hole concentration was two orders of magnitude higher than $5 \times 10^{-2} \text{ m}\Delta\text{OD}$ observed in the transient absorption studies. Therefore, the measurements under pulsed laser excitation did not correspond to hole densities representative of those expected under continuous solar irradiation.

One of the challenges is to accumulate sufficient holes at the surface without other efficiency losing processes, such as back electron/hole recombination which has been discussed in Chapter IV. The study in Chapter IV showed that this can be eliminated by applied significantly high applied potential to the working electrode to allow the formation of a wide and deep space charge layer. Such a large space charge layer can prevent efficiency losses from back electron/hole recombination.

One method to obtain a higher surface hole concentration on the BiVO_4 surface at the semiconductor/electrolyte interface is to illuminate the working electrode using continuous illumination (several seconds compared to a few nanoseconds), also

considered similar to the working condition for PEC water splitting.¹⁸ In this chapter, photo-induced absorption (PIA) spectroscopy was employed to study the long-lived holes of BiVO₄ generated by continuous illumination on the seconds timescale. The long excitation facilitates charge carriers to reach their steady state concentration. The PIA signal represents the concentration of photogenerated holes at the BiVO₄ photoanode surface during 5 s step on/off illumination. In addition, transient photocurrent (TPC) was also recorded at the same time of PIA measurements. The comparison of the hole concentration (PIA signals) and electron flux (photocurrent) during water oxidation reaction provided comprehensive information for PEC water oxidation at the BiVO₄ surface.

The reaction order of photogenerated holes or the dependence of the water oxidation kinetics of photogenerated holes was obtained by two different methods. One considers the relationship between the hole concentration at the surface and the photocurrent, and another directly analysed the hole amplitude decay after light off. The implications for reaction mechanism and comparison with other photoanode materials were considered and discussed.

7.2 Calculation of the LED intensity compared to AM 1.5 radiation

For PIA and TPC measurements, the excitation source was one / two 365 nm LEDs depending on the intensity required. The intensity of the LED illumination has been converted to the ratio compared with AM 1.5 intensity in terms of the number of photons.

The single photon energy is calculated using Equation 7.1:

$$E(\lambda) = h \times \frac{c}{\lambda} \quad (7.1)$$

where $E(\lambda)$ is the photon energy (J), h is the Planck's constant (6.626×10^{-34} J s), C is the speed of light (3×10^8 m s⁻¹) and λ is the photon wavelength (m).

The solar photon flux was then calculated from Equation 7.2:

$$flux(\lambda) = \frac{P(\lambda)}{E(\lambda)} \quad (7.2)$$

where $flux(\lambda)$ is the solar photon flux (m⁻² s⁻¹ nm⁻¹), and $P(\lambda)$ is the solar power flux (W m⁻² nm⁻¹). The AM 1.5 solar power flux data were obtained from NREL.

Integration of the solar photon flux gives the photon flux (m⁻² s⁻¹) across the wavelength selected. For BiVO₄, the absorption edge is 500 nm, therefore, the photon flux under 500 nm is obtained from Equation 7.3:

$$flux(< 500 \text{ nm}) = \int_{280 \text{ nm}}^{500 \text{ nm}} Flux(\lambda) d\lambda = 4 \times 10^{20} \text{ m}^{-2} \text{ s}^{-1} \quad (7.3)$$

where 500 nm is the BiVO₄ absorption edge; 280 nm is the lower limit of AM 1.5 spectrum. The integration yields the photon flux of 4×10^{20} m⁻² s⁻¹ at the BiVO₄ surface under AM 1.5 condition.

The light power was measured by an optical power meter (PM 100, Thorlabs) with a power sensor (S120UV, Thorlabs) at 365 nm, and then converted to the photon flux using Equation 7.4:

$$flux(365\text{ nm}, LED) = \frac{P(365\text{ nm})}{E(365\text{ nm})} \quad (7.4)$$

The rate of LED light vs AM 1.5 (*rate (%)*) is obtained by measuring the power at 365 nm and converted using Equation 7.5,

$$rate(\%) = \frac{flux(365nm, LED)}{4 \times 10^{20} \text{ m}^{-2} \text{ s}^{-1}} \times 100\% \quad (7.5)$$

The setup of photo-induced absorption spectroscopy has been described in Chapter II, developed from the setup of transient absorption spectroscopy. The optical signal acquired by a photodetector was sent to a DAQ card and then processed and saved by a home-programmed software based on LabView™. The light pulse frequency was 0.2 Hz except for the PIA measurement to determine the extinction coefficient (0.4 Hz).

7.3 Results

In this chapter, the main techniques employed were photo-induced absorption spectroscopy and transient photocurrent. The sample was placed in a PEC cell under strong anodic applied potential. The PIA and TPC signals were compared to study the water oxidation kinetics (see below). **Figure 7.1** represents the PIA results of the BiVO_4 photoanodes and the photocurrent, measured as a function of light intensity of 365 nm LED. Within 5 s of illumination, the current and optical signals reached a steady state. The time resolution for PIA measurements herein is on milliseconds timescales, which was only associated with the kinetics of water oxidation when back electron/hole recombination has been fully suppressed. The bimolecular recombination (see Chapter IV) was not monitored due to its faster kinetics typically on sub-milliseconds timescales. The photocurrent transients observed within 1 s were associated with reduced band bending due to hole accumulation at the surface during excitation, which reduced the charge separation efficiency. However, there was no negative current transient observed, indicating that the surface recombination was suppressed under 1.7 V_{RHE} applied potential. After the light-off the current returned to zero instantly whereas the optical signal's decays were kinetically slower, which is very similar to what we have observed in the PIA study of $\alpha\text{-Fe}_2\text{O}_3$ photoanodes.¹⁸ The rise of PIA signals were dominated by the process of hole accumulation, which was associated with the hole flux towards the surface. Water oxidation was driven by the surface holes. On the other hand, the decay of the PIA signals suggested that the surface accumulated holes were consumed by the process of water oxidation following light turned off.

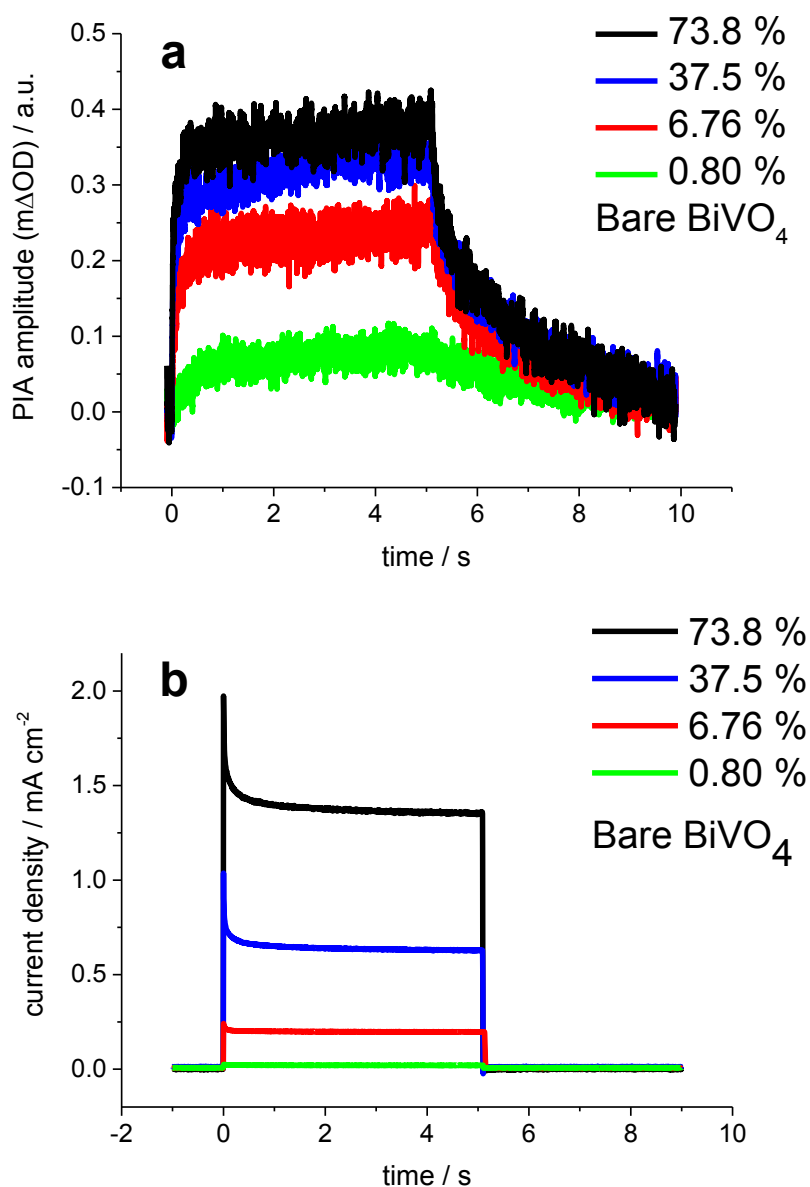


Figure 7.1. (a) PIA measurements of an un-doped BiVO₄ photoanode under 1.7 V_{RHE} applied potential. The PIA signals were recorded as a function of light intensity from a 365 nm LED. The intensities were calculated to compare with AM 1.5 intensity. (b) Photocurrent density measured simultaneously with the PIA signals.

In order to study the photogenerated holes oxidising water, it is necessary to identify the photogenerated hole signal in the PIA measurements. In a previous chapter (Chapter III), the transient absorption spectra of photogenerated holes have been identified using electron/hole scavengers and applied potential. In addition, the

PIA spectrum measured at 5 s, at a steady state, before the light pulse was turned off under 1.7 V_{RHE} . The photogenerated holes of BiVO_4 had a broad spectrum between 500 nm and 900 nm, peaking at 550 nm. The PIA amplitude was much higher than the transient absorption amplitude. The long pulse of illumination used in the PIA measurements generated much more long-live photogenerated holes. The PIA spectrum is shown in **Figure 7.2 (a)** under different light intensities. The normalised PIA spectra exhibited similar shapes, suggesting that the same species were probed during PIA measurements. The shape of PIA spectra were very similar to the transient absorption spectrum shown previously for long-lived photogenerated holes for water oxidation. This strongly suggests that long-lived photogenerated holes in BiVO_4 were probed in the PIA measurements ranging from 500 nm to 900 nm, with the signal maximal at 550 nm.

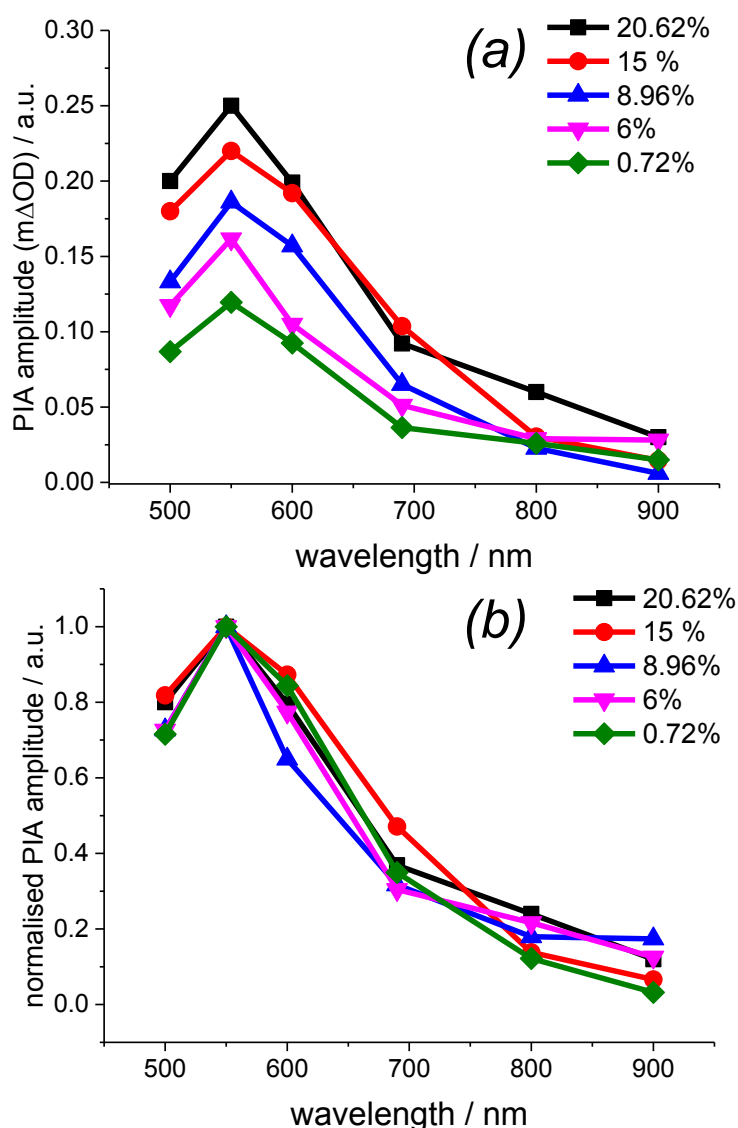


Figure 7.2. (a) The PIA spectra of the un-doped BiVO_4 measured at 5 s after light-on under 1.7 V_{RHE} . The spectra were measured under different light intensities. **(b)** Normalised PIA spectra at 550 nm.

The steady-state PIA and photocurrent signals measured at 5 s behaved differently as a function of light intensity, as shown in **Figure 7.3**. It is apparent that the photocurrent increased linearly with increasing the light intensity, whereas the amplitude of photogenerated holes clearly increased sub-linearly.

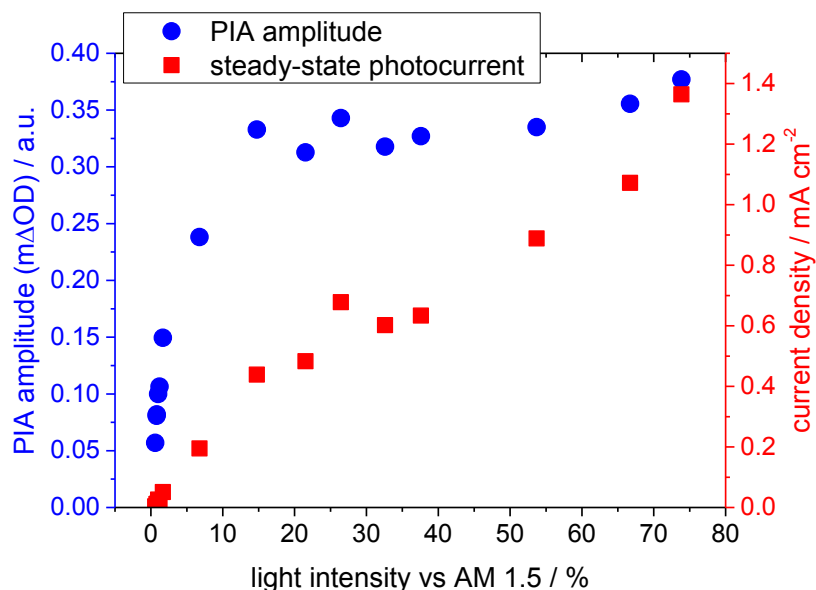


Figure 7.3. Blue: the PIA amplitude of the un-doped BiVO₄ photoanode. Red: the photocurrent of the BiVO₄. Both PIA and photocurrent amplitude were recorded at 5s under 1.7 V_{RHE}, as a function of light intensity, in percentage of AM 1.5 photons.

The PIA signal was the optical absorbance of long-lived photogenerated holes for water oxidation. It was useful to obtain an extinction coefficient for this hole absorbance and thereby, using the Beer Lambert equation, the surface hole concentration. The kinetics of water oxidation could be addressed in terms of the relationship between hole concentration (e.g. holes nm²) and photocurrent density (e.g. mA cm⁻² for geometric surface and mA nm⁻² for real surface). The extinction coefficient of photogenerated holes therefore needed to be calculated from the PIA measurements in this chapter. One method was to measure the PIA and photocurrent transients under bias conditions in which back electron/hole recombination dominates without significant water oxidation. This was realised by fixing the applied potential to 0.6 V_{RHE}, which is *ca.* 100 mV negative of the onset potential of photocurrent. Previous transient absorption and transient photocurrent studies (Chapter IV) indicated that at this potential almost all holes transferred to the

photoanode surface underwent back electron/hole recombination. The PIA signal recorded under 0.6 V_{RHE} was therefore assigned to surface accumulated holes undergoing this back electron/hole recombination. TPC negative transient under this condition was assigned to the corresponding electrons flowing back into the photoanode due to this back electron/hole recombination. Integration of this transient therefore gave the number of charges involved in this process. The PIA amplitude could be then used to determine the surface charge concentration according to the Beer-Lambert law (Equation 7.6).

$$\Delta OD = \varepsilon_{hole} \times p_s \quad (7.6)$$

Where ΔOD was the PIA amplitude of surface accumulated holes; ε_{hole} was the extinction coefficient of surface accumulated holes ($M^{-1} cm^{-1}$); p_s was the concentration of surface holes (holes nm^{-2}) determined from integration of negative current transient after light-off; therefore, ε could be calculated according to Equation 7.7.

$$\varepsilon = \frac{\Delta OD}{p_s} \quad (7.7)$$

By applying different light intensities, it is apparent that the PIA amplitude (ΔOD) increased linearly with increasing the concentration of surface charge, as shown in **Figure 7.4**. The extinction coefficient of photogenerated holes in BiVO₄ was therefore calculated to be ca. 500 $M^{-1} cm^{-1}$ (corresponding to $1.2 \times 10^{15} cm^{-2} m\Delta OD^{-1}$). This extinction coefficient is close to that measured for photogenerated holes in α -Fe₂O₃ (640 $M^{-1} cm^{-1}$).¹⁸

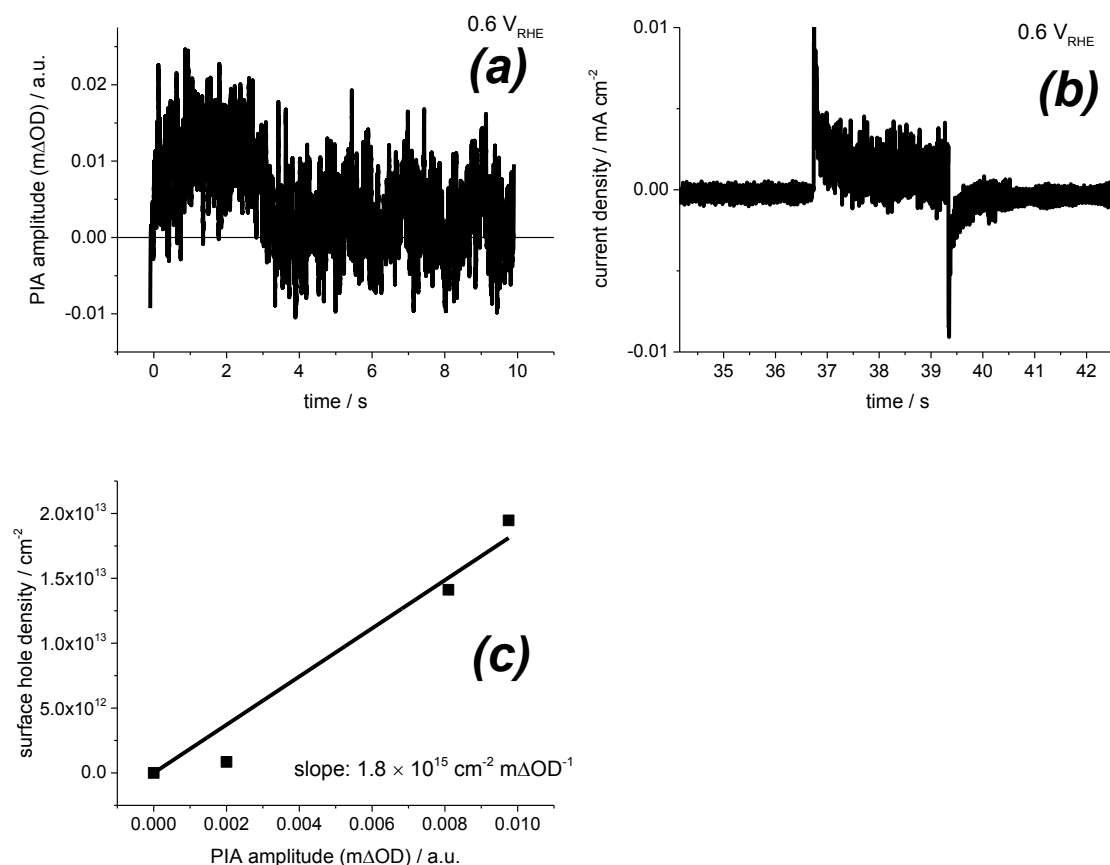


Figure 7.4. (a) The representative PIA amplitude measured under $0.6 V_{\text{RHE}}$ with 38 % of AM 1.5 intensity. (b) The current transient response due to back electron/hole recombination. (c) Determination of the extinction coefficient of photogenerated holes in BiVO₄ photoanodes. The slope yields an extinction coefficient of 500 M⁻¹ cm⁻¹ ($1.2 \times 10^{15} \text{ cm}^{-2} \text{ m}\Delta\text{OD}^{-1}$). The PIA data were recorded where there is only back electron/hole recombination occurring. The charge was obtained by integration of the negative transient after light off in the TPC measurements. Light pulse frequency: 0.4 Hz.

7.4 Discussion

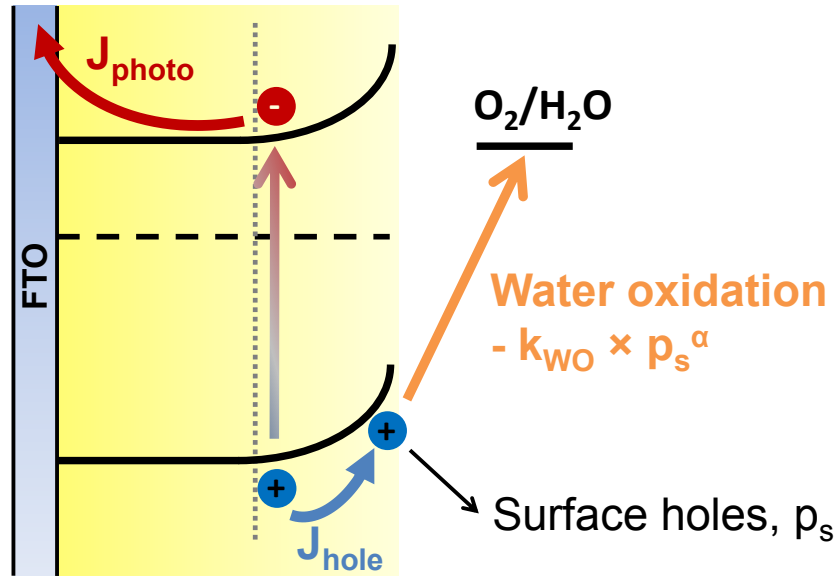
7.4.1 Rate Law Analysis of Water Oxidation on the BiVO₄ Surface

The PIA measurements reported above demonstrate that the relationship between the photocurrent and the surface concentration of accumulated holes was not linear. Previous transient absorption studies of BiVO₄ photoanodes indicated that the water oxidation reaction after the laser pulse was first order, with a rate constant approximately 1 s⁻¹. Other photoanode materials also exhibit a first order behaviour in transient absorption spectroscopic studies.^{11,19} Such a slow process has been determined as a rate-limiting factor for the water oxidation performance. However, there has been no study of water oxidation reaction under continuous illumination conditions, i.e. working condition for PEC water oxidation by BiVO₄ photoanodes.

A rate law analysis was applied to elucidate kinetics of water oxidation by photogenerated holes in BiVO₄, particularly focusing on the dependence of water oxidation rate upon the concentration of surface-accumulated holes. The BiVO₄ photoanode employed in this study is dense and flat with a thickness of *ca.* 500 nm. Analyses in Chapter IV indicated that the space charge layer in such photoanode is *ca.* 100 nm wide, determined from Mott-Schottky analysis. Transient absorption data have already suggested that the photogenerated holes accumulated at the surface did not undergo back electron/hole recombination at 1.7 V_{RHE}. Therefore under this bias condition, the surface-accumulated holes were consumed only by the water oxidation reaction. At the semiconductor-electrolyte interface under continuous illumination, the rate of hole concentration change (dp_s/dt) under this condition was described in Equation 7.8,

$$\frac{dp_s}{dt} = j_{hole} - k_{wo} \times p_s^\alpha \quad (7.8)$$

where j_{hole} describes the hole flux approaching to the surface and accumulate; k_{WO} is the rate constant of water oxidation by BiVO_4 holes; p_s is the hole concentration at the surface; α is the reaction order of water oxidation. This process was visualised in **Scheme 7.1**.



Scheme 7.1. Schematic of the water oxidation process on a BiVO_4 photoanode surface. This process is used to determine the reaction order on the BiVO_4 surface.

In Equation 7.8, the water oxidation kinetics were described by the $-k_{WO} \times p_s^\alpha$ term. The photocurrent, j_{photo} , was the electron flux towards the FTO back contact after charge separation. It was equal to j_{photo} due to the fact that there is no back electron/hole recombination under the 5 s LED pulse. To simplify the condition for water oxidation, the hole concentration at the steady state was considered, i.e. PIA amplitude recorded at 5 s. Under steady state conditions, the hole population did not vary ($dp_s/dt = 0$). Equation 7.8 can therefore be considered as:

$$\frac{dp_s}{dt} = 0 = j_{hole} - k_{WO} \times p_s^\alpha \quad (7.9)$$

$$j_{photo} = j_{hole} = k_{WO} \times p_s^\alpha \quad (7.10)$$

$$\log(j_{photo}) = \log(k_{WO}) + \alpha \times \log(p_s) \quad (7.11)$$

Equation 7.11 shows a log-log plot of the photocurrent versus the surface hole concentration, both measured at the steady state. In this plot, the reaction order α is given by the gradient of **Figure 7.5**. It was indicative of two regions with $\alpha = 1.2 \pm 0.2$ for $p_s < 1 \text{ nm}^{-2}$ and $\alpha = 3.3 \pm 0.2$ for $p_s > 1 \text{ nm}^{-2}$. The rate law analysis of $\alpha\text{-Fe}_2\text{O}_3$ also showed a similar behaviour with first order reaction at low hole concentration and third order reaction at high hole concentration.

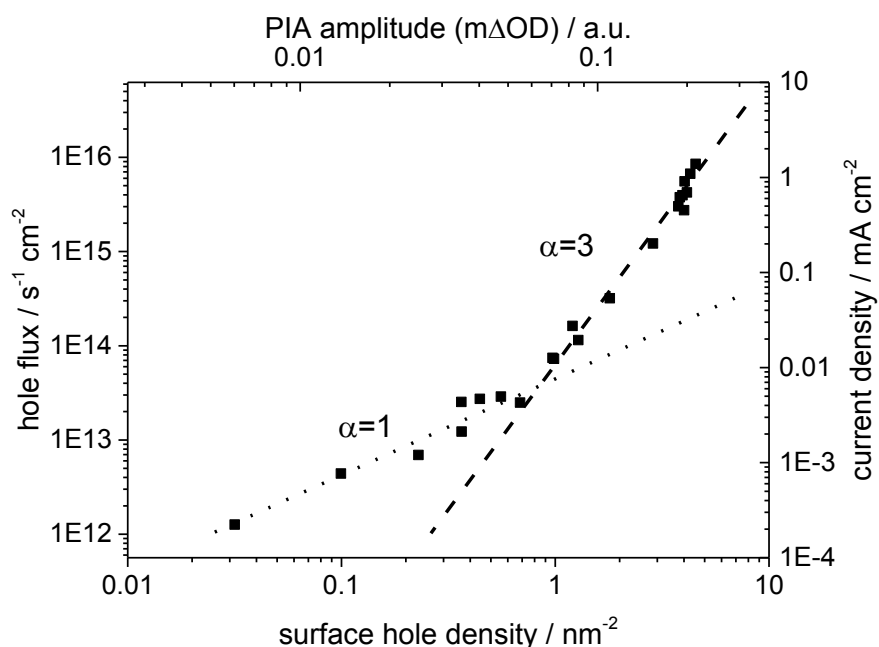


Figure 7.5. Rate law analysis of water oxidation on a BiVO_4 surface according to Equation 7.11. The hole flux calculated from the steady-state photocurrent is shown as a function of surface hole concentration, giving a reaction order of one under $p_s < 1 \text{ hole nm}^{-2}$ and three for $p_s > 1 \text{ hole nm}^{-2}$. The surface hole concentration is determined using the extinction coefficient of photogenerated holes ($500 \text{ M}^{-2} \text{ cm}^{-1}$) according to Equation 7.7.

The reaction order of water oxidation could also be determined from the decay of PIA data after the light pulse was switched off. Holes accumulated on the surface were still consumed by the water oxidation reaction whereas there was no hole flux

towards the surface. Therefore, the rate law in Equation 7.8 was written as Equation 7.12,

$$\frac{dp_s}{dt} = -k_{WO} \times p_s^\alpha \quad (7.12)$$

$$\log\left(-\frac{dp_s}{dt}\right) = \log(k_{WO}) + \alpha \times \log(p_s) \quad (7.13)$$

the reaction order was determined from Equation 7.13 and shown in **Figure 7.6**, independent of the photocurrent data.

The third method for the analysis of reaction order was to monitor the initial slope after light off for PIA decays recorded under several LED intensities (i.e. α in Equation 7.13 for several PIA decays). The reaction order may depend on the surface hole concentration at the moment of light off, which could be controlled using different light intensities.

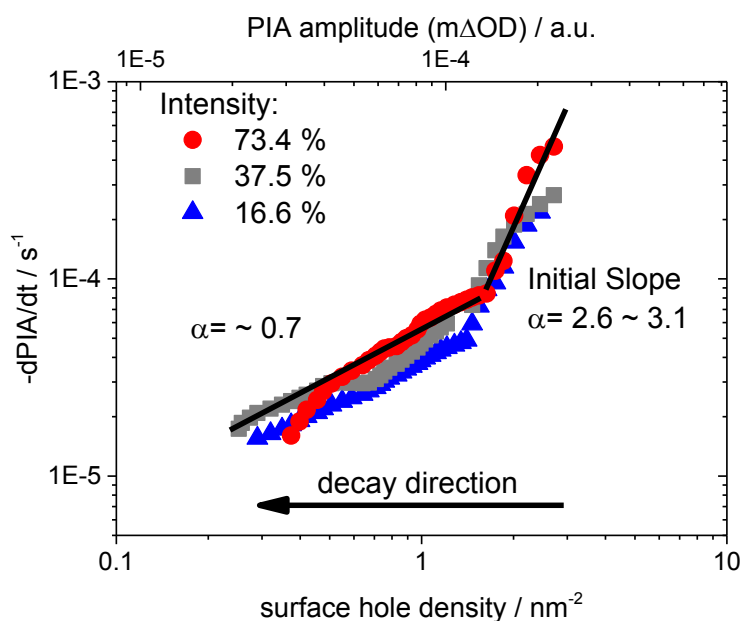


Figure 7.6. Rate law analysis of three PIA decays after light off according to Equation 7.13. Excitation intensity: 73.4 % (red), 37.5 % (grey) and 16.6 % (blue). The slopes were close to 3 at high PIA amplitude, and 1 at low PIA amplitude.

The rate constant in the first order region is ca. 0.5 s^{-1} , consistent with previous transient absorption results in Chapter IV (0.8 s^{-1}). The third order rate constant was determined to be ca. $1 \text{ s}^{-1} \text{ hole}^{-2} \text{ nm}^4$.

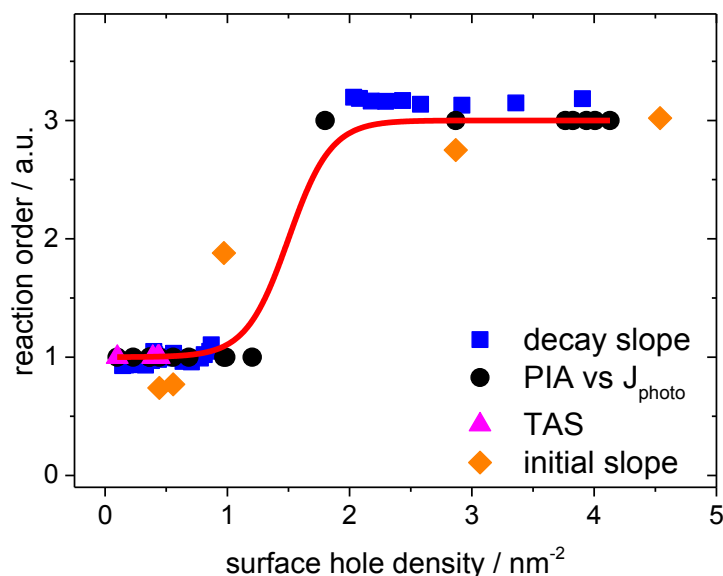


Figure 7.7. Reaction order of water oxidation determined from four techniques. Blue squares: rate law analysis by monitoring the PIA decay of 73.8 % light intensity; Black circle: rate law analysis concerning the relationship between photocurrent and the surface hole concentration; Pink triangles: slow (ms – s) phase transient absorption decays in Chapter IV; Orange diamonds: rate law analysis by monitoring the initial slope of each PIA decay after light off. The red line is to guide eyes.

The mechanism of water oxidation on BiVO_4 surface was not clear. It is striking that the third order of water oxidation was unexpected because the oxygen evolution reaction involves four holes to synthesise one oxygen molecule. The conditions in which PIA was performed were similar to the working condition for PEC water splitting. The light intensity has been determined close to AM 1.5 condition and oxygen was detected according to reports under such conditions.²⁰ It has been proposed that the rate determining step may be associated with the formation of

intermediates with three holes.^{8,21} Our group previously investigated $\alpha\text{-Fe}_2\text{O}_3$ photoanodes using photo-induced absorption spectroscopy.¹⁸ The rate law analyses were also applied to reveal the water oxidation mechanism and kinetics. Similarly, the water oxidation reaction order was determined to be three under high surface hole concentration and one under low surface concentration on the $\alpha\text{-Fe}_2\text{O}_3$ surface. It was proposed that two possible reaction mechanisms for multi-hole water oxidation: a) water oxidation involved two adjacent holes on two high valence Fe ions and the rate-determining step was the third hole for the formation of O-O bond between the two Fe sites; b) water oxidation was via a nucleophilic attack of a bridging surface oxygen atom, forming a peroxide precursor with three holes for O_2 evolution. Both mechanisms suggested that the third hole needed to migrate over a longer distance across the surface. In the rate law analyses of water oxidation on the BiVO_4 surface herein, it was plausible to propose the same mechanisms as for $\alpha\text{-Fe}_2\text{O}_3$ photoanodes. The surface exposed Bi atoms were proposed to be responsible for water oxidation with either mechanism. The kinetics of water oxidation on BiVO_4 however is different from $\alpha\text{-Fe}_2\text{O}_3$, which was discussed below. It should also be noted that surface accumulated holes may repulse the holes generated inside the bulk approaching to the surface. However, such a consideration can be ruled out by the fact that, in $\alpha\text{-Fe}_2\text{O}_3$ for example, the surface hole concentration was still less than the concentration of surface-exposed Fe atoms ($4\text{-}12\text{ atoms nm}^{-2}$).¹⁸ PIA measurements showed that there were $3\text{ Fe atoms nm}^{-2}$ oxidised by photogenerated holes under AM 1.5 illumination. Therefore, there were sites available for holes to accumulate at the surface. In addition, if columbic repulsion were to occur, a decreased surface hole concentration should be expected to be detected. The photocurrent should also decrease proportionally to the decrease in surface hole

concentration. As the result, the decreases in surface hole concentration and photocurrent would be cancel each other out, giving effectively no change in the water oxidation kinetics shown in Equation 7.11.

7.4.2 Comparison of Multi-Hole Catalytic Water Oxidation with $\alpha\text{-Fe}_2\text{O}_3$

The PIA studies of BiVO_4 and $\alpha\text{-Fe}_2\text{O}_3$ showed a similar water oxidation behaviour in terms of reaction order. It was also noted that the amplitude of PIA signals measured for $\alpha\text{-Fe}_2\text{O}_3$ was 10-times greater than that for BiVO_4 . Given the similar extinction coefficient of photogenerated holes determined in these two materials and similar photocurrent observed, it was very unlikely that $\alpha\text{-Fe}_2\text{O}_3$ requires >10 times greater hole concentration than BiVO_4 to achieve the same photocurrent. **Figure 7.8** shows the rate law analyses for both photoanodes under similar condition (although the electrolyte pH employed was different: pH 13 for $\alpha\text{-Fe}_2\text{O}_3$ and 6.8 for BiVO_4 ; $\alpha\text{-Fe}_2\text{O}_3$ PIA data were collected by Dr Florian Le Formal, Department of Chemistry, Imperial College London). The roughness factor for both samples has been taken into consideration (i.e. 21 for $\alpha\text{-Fe}_2\text{O}_3$ ²¹ and assuming 1 for BiVO_4). It indicates that under simulated AM 1.5 condition, $\alpha\text{-Fe}_2\text{O}_3$ generated ca. 20 times more holes which accumulates at the surface, however the current generated by $\alpha\text{-Fe}_2\text{O}_3$ was only higher by three times than BiVO_4 . The rate constant for the first and third order reaction was compared herein by considering the real surface area (taking into account the roughness). The results were shown in **Table 7.1**.

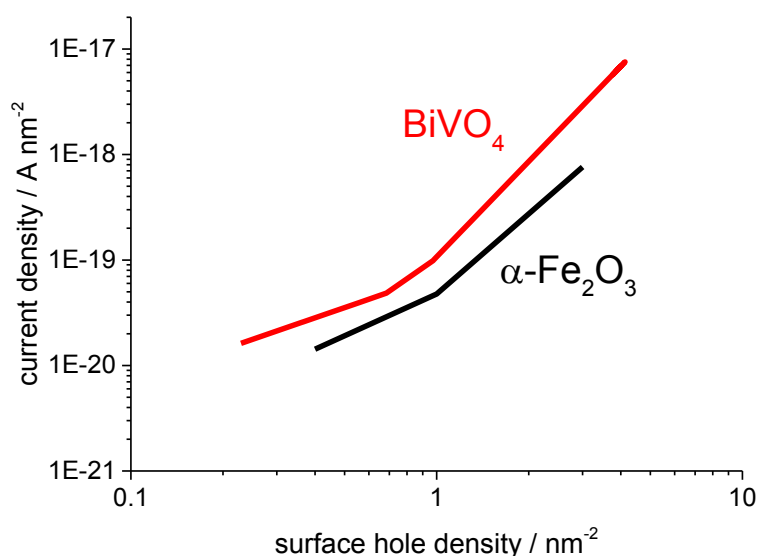


Figure 7.8. Comparison of rate law analyses in BiVO_4 and $\alpha\text{-Fe}_2\text{O}_3$ photoanodes. The roughness factors for BiVO_4 (1) and $\alpha\text{-Fe}_2\text{O}_3$ (21) were considered for calculation of surface hole concentration and current density.

Table 7.1. Rate constants determined from rate law analyses for BiVO_4 and $\alpha\text{-Fe}_2\text{O}_3$ photoanodes using photo-induced absorption spectroscopy.

Rate constants	BiVO_4	$\alpha\text{-Fe}_2\text{O}_3$
1 st order / s^{-1}	0.5	0.25
3 rd order / $\text{s}^{-1} \text{ hole}^{-2} \text{ nm}^4$	1	0.2

Table 7.1 shows that for the first order reaction, the rate constant was 0.5 s^{-1} for BiVO_4 and 0.25 s^{-1} for $\alpha\text{-Fe}_2\text{O}_3$; for the third order reaction, the rate constant in BiVO_4 was ca. $1 \text{ s}^{-1} \text{ hole}^{-2} \text{ nm}^4$ and k_{WO} in $\alpha\text{-Fe}_2\text{O}_3$ was ca. $0.2 \text{ s}^{-1} \text{ hole}^{-2} \text{ nm}^4$. Water oxidation appeared to occur faster on BiVO_4 than $\alpha\text{-Fe}_2\text{O}_3$ for both mechanisms. For the first order water oxidation, the reaction was independent of surface hole concentration. Both PIA and transient absorption studies indicated that sequential

one-hole water oxidation was possible on BiVO₄ and α-Fe₂O₃. Previous temperature-dependent transient absorption study indicated that α-Fe₂O₃ required *ca.* 0.45 eV of activation energy¹⁴ to initiate the single-hole water oxidation. The valence band edge of α-Fe₂O₃ is reported to be 2.5 V_{RHE}.²² It was likely that the single-hole water oxidation was to form hydroxyl radicals which required one hole from the oxide surface ($H_2O + h^+ \rightarrow OH^\cdot + H^+$). The standard redox potential is *ca.* 2.8 V_{SHE} (pH=0).²³ When BiVO₄ oxidised water with first order kinetics, the valence band edge was *ca.* 100 mV (2.6 V_{RHE}) higher than α-Fe₂O₃, which may reduce the activation energy required for the reaction. In contrast, TiO₂ did not require activation energy to initiate first order water oxidation¹⁴ and the reaction rate was faster¹¹ than BiVO₄ and α-Fe₂O₃ determined from transient absorption results, probably due to the deepest valence band edge (*ca.* 3.1 V_{RHE}) among these three materials. The kinetics of first order water oxidation may be associated mainly with the valence band edge of the materials.

For the third order mechanism determined in α-Fe₂O₃, the rate-determining step was the third hole approaching to the intermediate. This suggested that the third hole may have to migrate over a longer distance than the distance between two adjacent Fe sites for α-Fe₂O₃. In BiVO₄, the 5-times faster kinetics suggested that the third hole travelled either shorter distance or was faster to reach the intermediate site. This could be related to the higher Bi density per nm², which reduced the distance, or higher hole mobility across the BiVO₄ surface. Alternatively, the faster kinetics may be associated with a reduced activation energy due to the deeper valence band energy. Studies and analyses of water oxidation rate law to other metal oxides are on-going and will be reported elsewhere.

7.5 Conclusions

In this chapter, a rate law analysis of water oxidation on a surface of BiVO_4 photoanodes was reported. The reaction order was dependent on the surface hole concentration; first and third order reactions were determined with surface hole concentrations $< 1 \text{ nm}^{-2}$ and $> 2 \text{ nm}^{-2}$, respectively. The third order reaction suggested that the rate determining intermediate formed during water oxidation under strong light irradiation required three holes to come together. Compared with the behaviour of $\alpha\text{-Fe}_2\text{O}_3$ photoanodes, BiVO_4 exhibited a faster water oxidation rate constant than $\alpha\text{-Fe}_2\text{O}_3$ which may be related to hole mobility across the surface for the third order reaction and / or its deeper valence band edge.

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Chapter VIII

8. Photo-Induced Absorption Study of CoPi-modified BiVO₄ Photoanodes to Identify the Catalytic Function of CoPi during Water Oxidation

In this chapter, results were reported using photo-induced absorption spectroscopy to study water oxidation in a CoPi-modified BiVO₄ photoanode. The results showed that BiVO₄ holes could oxidise CoPi under continuous illumination, but the concentration of oxidised CoPi was not enough to drive water oxidation efficiently. This was supported by spectroelectrochemical measurements on CoPi/FTO electrodes; water oxidation still occurred mainly via BiVO₄ surfaces even in the presence of CoPi overlayers. CoPi appeared not to act as an efficient catalyst on BiVO₄ during PEC water oxidation.

8.1 Introduction

In Chapter VI, the CoPi surface modified BiVO₄ photoanodes were studied using transient absorption spectroscopy and photoelectrochemical methods. The transient absorption signals observed in CoPi-modified BiVO₄ were dominated by the signals of BiVO₄ photogenerated holes. This observation suggests that the photogenerated holes did not transfer to the CoPi catalysts, suggesting that water oxidation was not catalysed by CoPi, at least under pulsed laser experimental conditions. The pulsed laser (6 ns) condition leads to a low yield of surface accumulated holes due to dominating bimolecular recombination on sub-μs timescales. In Chapter VII, the rate law analysis of water oxidation on un-doped and unmodified BiVO₄ photoanodes was carried out using photo-induced absorption (PIA) spectroscopy. This technique measures the absorption response of photo-induced charge carriers under long pulse (5 s) illumination. The PIA signal represents the long-lived photogenerated holes accumulating at the BiVO₄ surface. Such experimental conditions were close to the working condition of PEC water oxidation. PIA measurements allowed the photogenerated holes to accumulate at the semiconductor/electrolyte interface with a high yield and to be probed during the water oxidation behaviour. The photocurrent response could be measured simultaneously, giving insights on both the electron flux by measuring steady-state photocurrent and the density of surface-accumulated hole.

In this chapter, an investigation was reported of BiVO₄ photoanodes with CoPi surface modification for photo-assisted water oxidation using photo-induced absorption spectroscopy. It was especially focused on whether CoPi deposited on n-type photoanodes could catalyse water oxidation under continuous illumination, as previously reported using impedance spectroscopy¹ and photoelectrochemical methods.^{2,3} Spectroelectrochemical (SEC) measurements of CoPi deposited on FTO

electrodes were also conducted to compare the electrocatalytic role of CoPi alone. The function of CoPi as an electrocatalyst in the dark and as a catalyst on BiVO₄ for photo-assisted water oxidation was discussed.

8.2 Experimental

Electrodeposition of CoPi on FTO substrates was carried out using the same method without illumination. The FTO was immersed in the electrolyte containing $\text{Co}(\text{NO}_3)_2$ under 1.9 V_{RHE} applied potential for 10 minutes. For CoPi deposition on BiVO_4 and FTO, the deposition charge passing through the substrates was controlled to be 2.4 C cm^{-2} for both BiVO_4 and FTO. Therefore the amount of CoPi deposited should be similar on both substrates. The thickness of CoPi was measured by SEM

Spectroelectrochemical (SEC) measurements were conducted to measure the UV-Vis absorption spectra of CoPi/FTO in a PEC cell under applied potential, using a UV-Vis spectrometer (Lambda 25, Perkin Elmer). Potentials were applied with an Autolab potentiostat (PGSTAT 12 equipped with FRA2 module). All SEC spectra were measured under steady-state condition, in which the CoPi electrode was stabilised under each applied potential for 60 s before SEC (UV-Vis) measurements started. SEC spectra were obtained by subtracting all UV-Vis spectra under applied potential with the UV-Vis spectrum at the open-circuit condition (i.e. isolated CoPi/FTO film in the electrolyte without connection to the potentiostat). The steady-state currents were recorded at the same time during the SEC measurements. The SEC amplitude is obtained:

$$\Delta OD_{\text{SEC}}(V) = OD(V) - OD_{\text{OC}} \quad (8.1)$$

Where $\Delta OD_{\text{SEC}}(V)$ is the SEC amplitude; $OD(V)$ is the measured absorption signal from 500 nm to 900 nm under a given applied potential; OD_{OC} is the absorption signal from the same wavelength range measured at open circuit without connection to the potentiostat.

8.3 Results

8.3.1 Physical and Photoelectrochemical Characterisations

Figure 8.1a-f show the SEM images of unmodified BiVO₄, CoPi-modified BiVO₄ and CoPi/FTO electrodes employed for the studies reported in this chapter. The thickness of CoPi overlayer on both BiVO₄ and FTO was *ca.* 100 nm, determined from the cross-sectional SEM images.

Figure 8.1g compares the XRD results of unmodified BiVO₄, CoPi-modified BiVO₄ and CoPi/FTO electrodes. CoPi deposited on both BiVO₄ and FTO was amorphous as there was no XRD feature indicating crystalline CoPi, consistent with literature reporting on CoPi using (photo-)electrochemical deposition.³⁻⁷

Figure 8.1h shows the photocurrent density change as a function of CoPi thickness which controlled by deposition time. Depositing CoPi over 600 s provided the best photocurrent density. The CoPi overlayer, which gave the highest photocurrent density, on BiVO₄ was thicker than 30 nm of porous BiVO₄ reported by van de Krol's group.⁸ This was similar to a previous report of CoPi surface modification of porous/dense α -Fe₂O₃ photoanodes, in which the dense α -Fe₂O₃ required thicker CoPi to achieve the premium photocurrent density.²

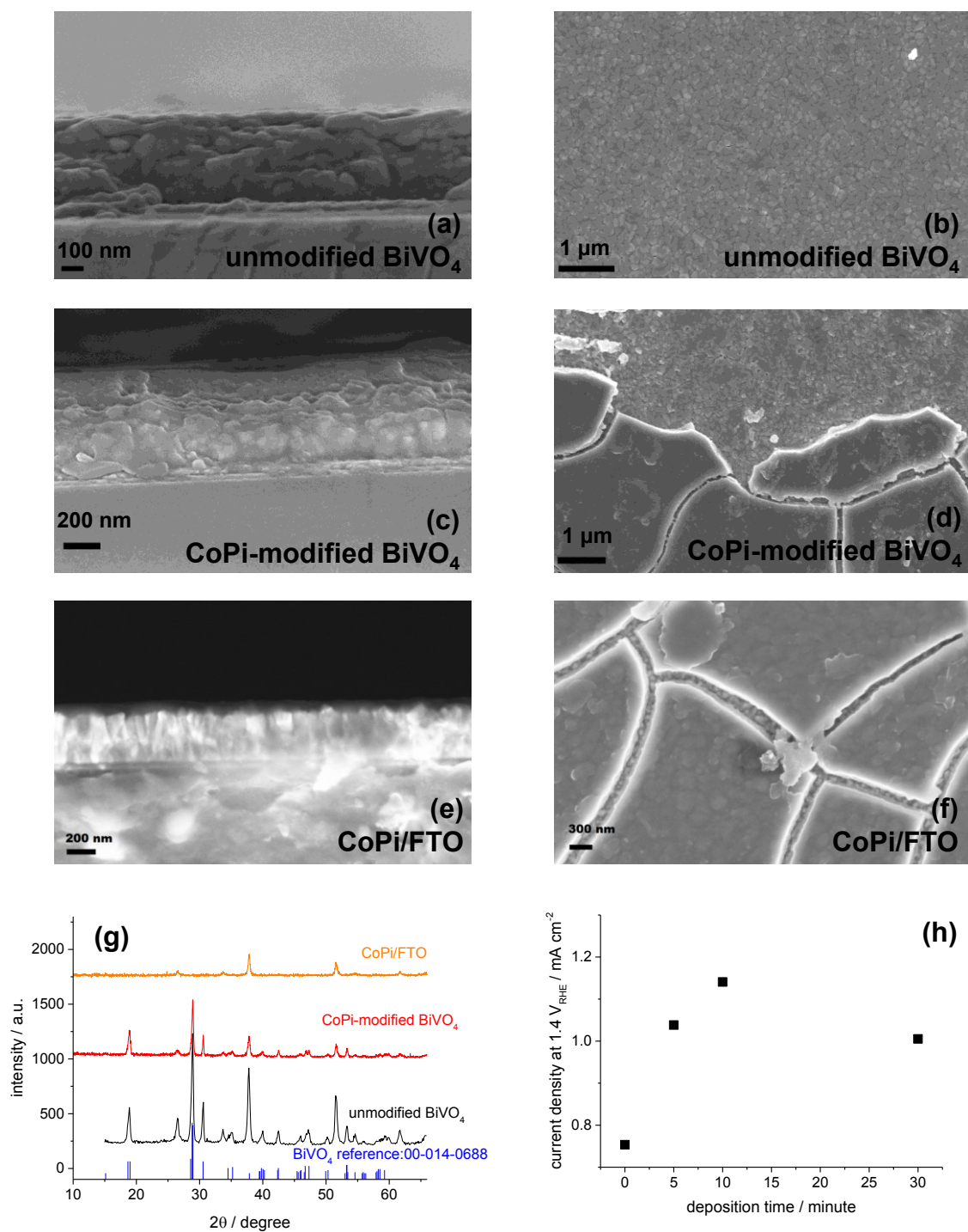


Figure 8.1. (a)-(f): SEM images of unmodified BiVO₄, CoPi-modified BiVO₄, CoPi/FTO electrodes used in this chapter, including top view and cross-sectional images. (g): XRD comparison of unmodified BiVO₄ (black), CoPi-modified BiVO₄ (red) and CoPi/FTO (orange) electrodes; (f): photocurrent density as a function of CoPi deposition time (CoPi thickness).

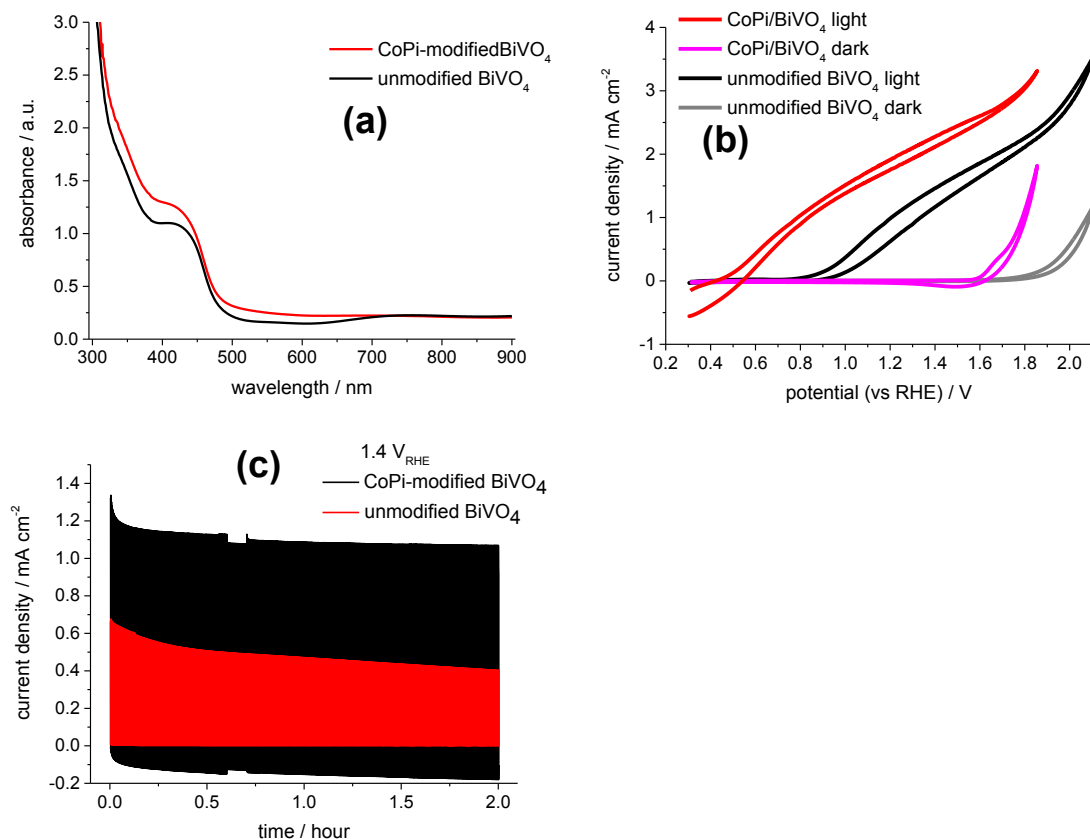


Figure 8.2. (a) UV-Vis absorption spectra of CoPi-modified BiVO₄ (red) and unmodified (black) BiVO₄ photoanodes. (b) Cyclic voltammetry measurements of CoPi-modified BiVO₄ (red) and unmodified BiVO₄ (black) measured under 365 nm illumination and the cyclic voltammetry of CoPi-modified BiVO₄ in dark is magenta and cyclic voltammetry of unmodified BiVO₄ in dark is grey; (c): Stability test of CoPi-modified BiVO₄ photoanodes at 1.4 VRHE under LED illumination. Light intensity: 100 % AM 1.5.

Figure 8.2a shows the UV-vis absorption spectra of BiVO₄ samples before/after CoPi deposition. The increased absorption in the CoPi-modified BiVO₄ was due to the broad absorption of CoPi, consistent with our previous reports on CoPi-modified α -Fe₂O₃ photoanodes.^{9,10} A wide background absorption before the absorption edge (> 500 nm) was due to the scattering of light by the BiVO₄ particles.

Figure 8.2b shows the cyclic voltammetry results of these two systems under dark or 365 nm LED continuous illumination. CoPi overlays enhanced BiVO₄ PEC

performances in terms of onset potential and amplitude of photocurrent, consistent with previous reports^{3,11} and the results presented in Chapter VI. In addition, the dark onset potential was also negatively shifted in the presence of CoPi overlayers. The current shoulder at 1.7 V_{RHE} observed in the CoPi-modified BiVO₄ in dark was associated with the electrochemical properties of CoPi. Previously Kanan and Nocera reported a cyclic voltammetry measurements of ITO electrodes in Co²⁺ containing KPi electrolyte at pH 7. A distinctive current peak was observed at 1.6 V_{RHE}, indicating that the cyclic voltammetry peak was associated with an oxidation process of Co²⁺ to Co³⁺.⁴ **Figure 8.2c** shows that CoPi enhanced the stability of BiVO₄ stability under LED illumination over 2 hours of testing conditions, consistent with the literature reports.^{12,13}

The cyclic voltammetry result of CoPi/FTO electrodes for electrochemical oxidation is shown in **Figure 8.3**. The CoPi/FTO exhibited a current shoulder between 1.4 V_{RHE} and 1.7 V_{RHE}, then the current increased rapidly with increasing applied potential. However, the amplitude of the current of the shoulder decreased with decreasing the scan rate (**Figure 8.3a**), and becomes zero under the steady state. The shoulder was associated with CoPi oxidation. XPS analyses have indicated that the oxidation state of cobalt in CoPi is 2+. The cyclic voltammetry measurements reported by Kanan and Nocera indicated that the anodic current peak was associated with Co²⁺ to Co³⁺.^{4,14} CoPi did not have any photoactivity during PEC measurements (**Figure 8.3b**).

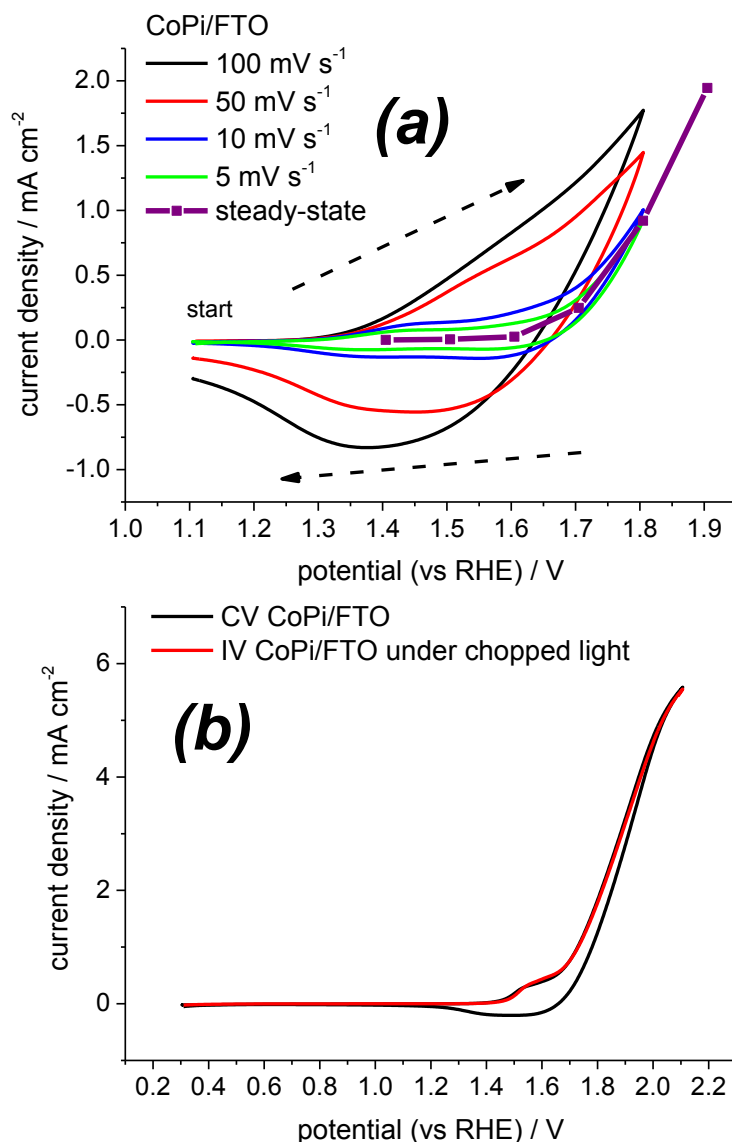


Figure 8.3. (a) Cyclic voltammetry measurements of CoPi/FTO electrodes at different scan rate. Purple: steady-state current of CoPi/FTO; (b) Current response of CoPi/FTO electrodes in dark (black) and under illumination (red). Scan rate for both measurements: 10 mV s^{-1} .

8.3.2 Photo-Induced Absorption Spectroscopic Study

Figure 8.4 shows the PIA response **(a)** and the simultaneously recorded current response **(b)** of unmodified and CoPi-modified BiVO_4 probed at 550 nm to a 5 s (for unmodified BiVO_4) or 8 s (for CoPi-modified BiVO_4) light pulse at 20 % of AM 1.5 in terms of photon numbers, and the PIA spectra **(c)**. The sample was held at $1.7 \text{ V}_{\text{RHE}}$

(unmodified) and 1.4 V_{RHE} (CoPi-modified) applied potentials, selected to be just before the dark water oxidation onset.

The PIA amplitude measured for the two samples was considered first. For the unmodified BiVO_4 , the maximum absorbance at 550 nm probing wavelength was about 0.33 m ΔOD under excitation of LED (red line in **Figure 8.4a**). In Chapter VII, the PIA amplitude of unmodified BiVO_4 photoanodes was assigned to the surface accumulated holes for water oxidation. The PIA results of a CoPi-modified BiVO_4 photoanode at applied potential of 1.4 V_{RHE} was compared in **Figure 8.4** with the PIA signal measured for unmodified BiVO_4 . The PIA signal of BiVO_4 in the presence of CoPi overlayers was approximately two orders of magnitude greater than that measured with the unmodified BiVO_4 electrode (e.g. 0.33 m ΔOD versus 27 m ΔOD at 550 nm). The greater amplitude of the PIA signal in CoPi-modified BiVO_4 were not likely to have originated from the photogenerated holes in BiVO_4 as the photocurrent measured were improved only by three times, as shown in **Figure 8.4b**. The photocurrent of CoPi-modified BiVO_4 shown in **Figure 8.4b** suggests that there was an electron back transfer process after light off. However, such a process was not observed in unmodified BiVO_4 . The PIA spectrum of CoPi-modified BiVO_4 was significant broader compared to the unmodified BiVO_4 (**Figure 8.4c**). Previously, the spectroelectrochemical study of CoPi-modified $\alpha\text{-Fe}_2\text{O}_3$ photoanodes showed a broad absorption spectrum in the visible range due to the electrochemical oxidised CoPi species, similar to the PIA spectrum of CoPi-modified BiVO_4 photoanodes.^{9,10,15} An absorption spectral study compared CoPi-modified TiO_2 before and after excitation. The absorption spectrum was similar to the PIA spectrum of CoPi-modified BiVO_4 .¹⁶ Therefore, it is suggested that the PIA signal observed in CoPi-

modified BiVO_4 is another photo-induced species rather than photogenerated holes in BiVO_4 , most likely to be the oxidised CoPi species, as discussed further below.

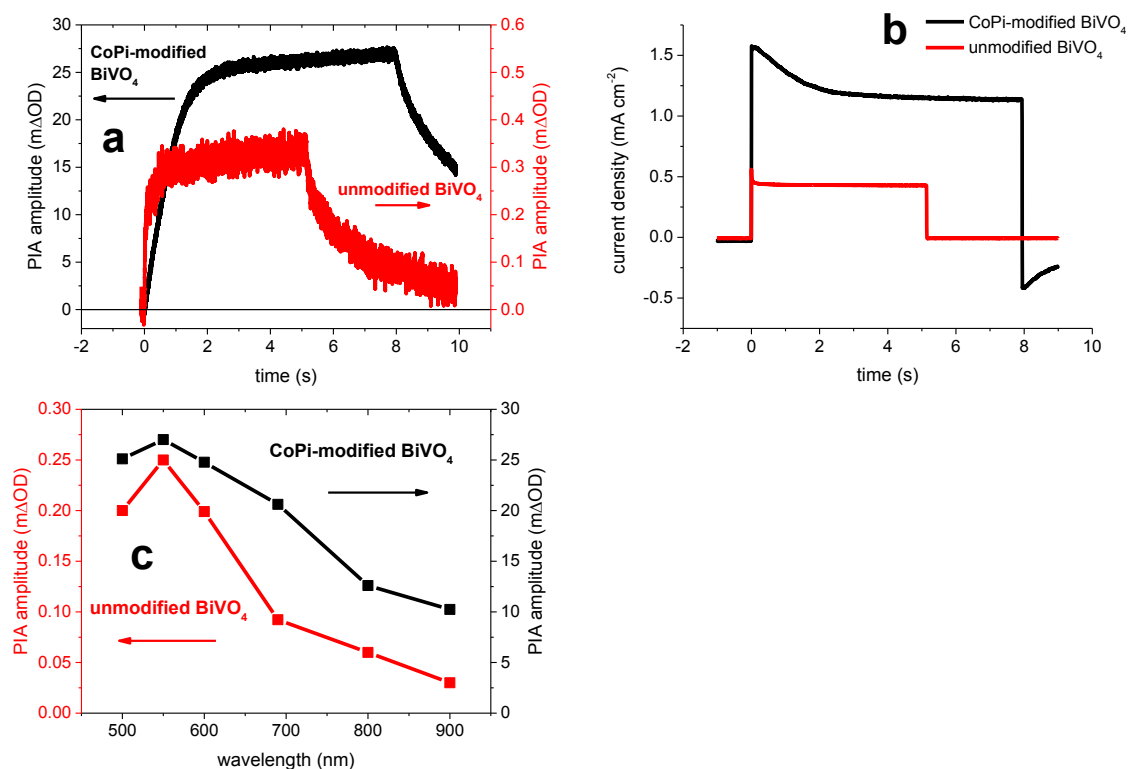


Figure 8.4. (a) PIA response of the unmodified (red, under 1.7 V_{RHE}) and CoPi-modified (black, under 1.4 V_{RHE}) BiVO_4 photoanodes under different light intensities. The probed wavelength is 550 nm. (b) Photocurrents of unmodified (red) and CoPi-modified (black) BiVO_4 measured at the same time with PIA measurements. (c) PIA spectra of the unmodified BiVO_4 . Light intensity: 20% of AM 1.5.

8.3.3 Spectroelectrochemical Measurements of CoPi on FTO for Water Oxidation.

In the PIA measurements of CoPi-modified BiVO_4 , although the greater amplitude of PIA signal was likely to be the oxidised CoPi by photogenerated holes from BiVO_4 , it was not clear whether the improvement of photocurrent in the CoPi-modified BiVO_4 was due to the catalytic property of CoPi. Therefore, the electrocatalytic property of CoPi needed to be quantified under comparable conditions of CoPi oxidation.

Electrocatalytic properties of CoPi deposited on FTO substrates were studied using spectroelectrochemical (SEC) measurements. The SEC signals were obtained by subtracting the steady-state absorption signals under different applied potentials by the steady-state absorption signal measured without applied potential (open circuit). **Figure 8.5a** presents the SEC results of a CoPi electrode as a function of anodic potential from 1.4 V_{RHE} to 2.4 V_{RHE} , where water oxidation current started to appear (according to **Figure 8.3a**). The spectra obtained from 500 nm to 900 nm at different applied potential showed very similar spectral shape, characterised by a broad absorption decreasing mildly towards longer wavelengths. It suggests that the same oxidised species across the range of applied potentials were monitored during SEC experiments on CoPi/FTO. In addition, the SEC spectral shape was similar to the PIA spectrum of CoPi-modified BiVO_4 , suggesting that for both measurements, the same oxidised CoPi species were monitored, in agreement with our assignment above. The absorption amplitude recorded at 550 nm increased with increasing applied potential with onset at 1.4 V_{RHE} (black squares shown in **Figure 8.5b**). The amplitude of SEC spectra was much higher than the PIA amplitude by one order of magnitude. The steady-state current (red line and squares) measured during SEC measurements was also recorded at each applied potential and shown in **Figure 8.5b**, also compared with the current measured by cyclic voltammetry. The SEC signals measured below 1.6 V_{RHE} were like to be the Co^{2+} to Co^{3+} charging current, which did not contribute to steady-state water oxidation current. The saturated currents measured beyond 2.0 V_{RHE} were likely to be limited by the diffusion of O_2 from the film surface to the electrolyte due to active O_2 formation by CoPi electrocatalysis of water.

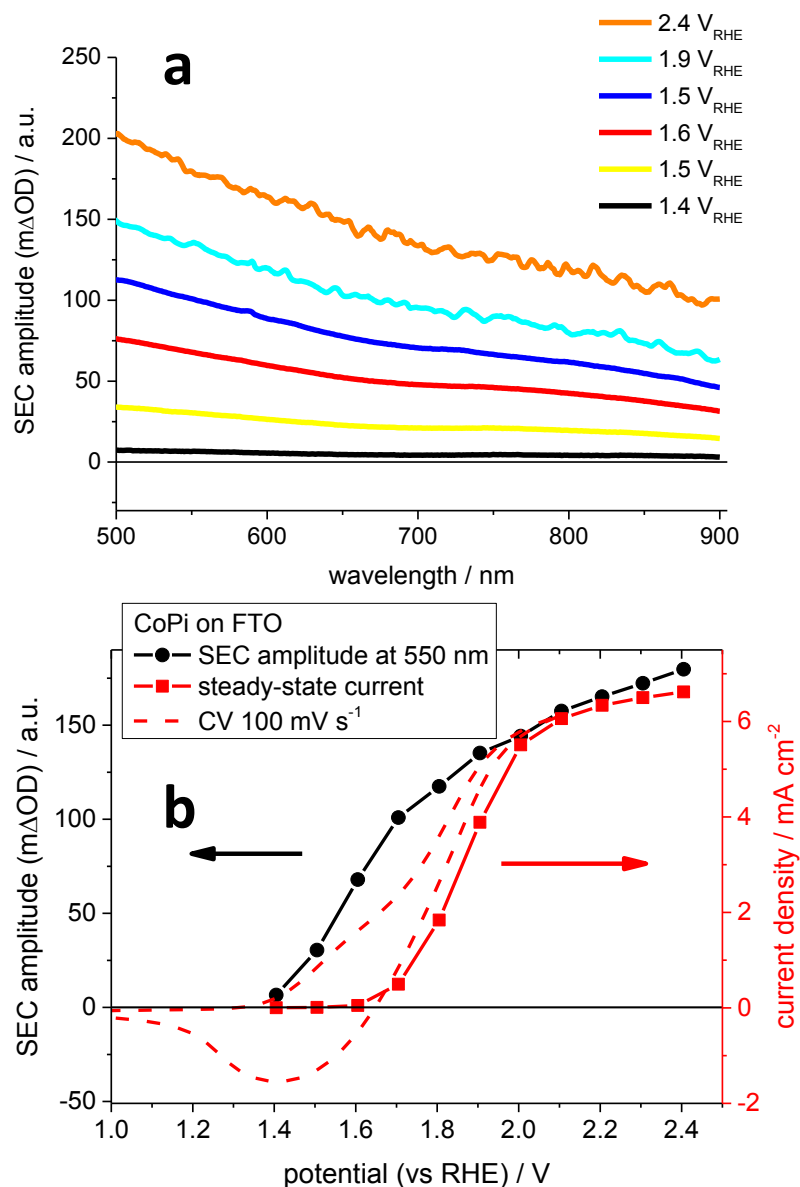


Figure 8.5. (a) SEC spectra of the CoPi/FTO electrode measured as a function of applied potential from 1.4 V_{RHE} to 2.4 V_{RHE}. All spectra were subtracted by the spectrum measured at open-circuit condition. (b) The SEC amplitude of CoPi/FTO at 550 nm as a function of applied potential (black line and circles); the steady-state current recorded during SEC measurement of CoPi/FTO (red line and squares); the cyclic voltammetry result (red, dashed line) of CoPi/FTO scanned at 100 mV s⁻¹.

8.4 Discussion

Photo-induced absorption spectroscopy allowed probing photogenerated charge carriers under working condition of PEC water oxidation. The PIA spectra of unmodified BiVO₄ photoanodes has been assigned to the long-lived photogenerated hole signal for water oxidation by comparing PIA spectra with different excitation intensities (Chapter VII) and the transient absorption spectra (Chapter III). Compared to the optical amplitude of photogenerated holes in transient absorption studies, an enhancement of nearly one order of magnitude in the optical signal was observed in PIA measurements in the unmodified BiVO₄ due to larger hole accumulation. For CoPi-modified BiVO₄ photoanodes, the PIA amplitude was further increased by two orders of magnitude under the similar excitation intensity. However, the photocurrent measured did not increase proportionally with the PIA increase. The different PIA spectral shape in these two systems also suggests that there was another photo-induced species rather than BiVO₄ photogenerated holes in CoPi-modified BiVO₄. It was likely that photo-oxidised CoPi species were probed.

The oxidation state of the CoPi overlayer (on BiVO₄ or FTO) before/after being (photo-/electro-) oxidised was then considered. The cyclic voltammetry current density of the CoPi/FTO electrode for electrocatalytic water oxidation indicated that the current wave at 1.6 V_{RHE} was dependent on the scan rate. This current decreased to zero at steady-state condition (**Figures 8.3a and 8.5b**), indicating that currents at these potentials did not contribute to water oxidation. Electrocatalytic water oxidation on CoPi/FTO electrodes initiated from *ca.* 1.7 V_{RHE}. The current wave between 1.4 V_{RHE} and 1.7 V_{RHE} was due to oxidation of CoPi (CoPi charging) without further oxidation of water (i.e. a non-Faradaic process). X-ray photoelectron spectroscopic analyses have indicated that Co²⁺ in isolated CoPi-modified α -Fe₂O₃⁶

and CoPi/FTO.⁴ Therefore, it was possible that this non-Faradaic process of CoPi oxidation was due to Co^{2+} being oxidised to Co^{3+} . In the CoPi-modified BiVO_4 , the cyclic voltammetry current in the dark also showed a current wave around 1.7 V_{RHE}, consistent with its electrocatalytic nature, similarly to CoPi/FTO system. The slight positive shift by 100 mV was probably due to the poor conductivity of BiVO_4 causing additional potential drop as compared to FTO. Nevertheless, in general, the composite of CoPi on BiVO_4 was consistent with the CoPi deposited on FTO.

The PIA spectra shown in **Figure 8.4c** suggests that CoPi was oxidised by BiVO_4 holes after photo-excitation. This assignment is supported by comparing the PIA amplitude of CoPi-modified BiVO_4 under illumination with the SEC spectra of electro-oxidised species in a CoPi/FTO electrode. The PIA signal of CoPi-modified BiVO_4 indicated a hole transfer process from BiVO_4 to CoPi.

The comparison of these absorption signals and the currents was then considered. Water oxidation required the accumulation of positive charges in natural and artificial photosynthesis.¹⁷ In unmodified BiVO_4 , long-lived hole accumulation at the surface for water oxidation has been observed in the transient absorption study and the PIA measurements. A higher amplitude of PIA signal (i.e. surface accumulated holes) than transient absorption signals was the result of efficient charge separation but slow water oxidation kinetics, and lead to high photocurrent generation in unmodified BiVO_4 photoanodes.

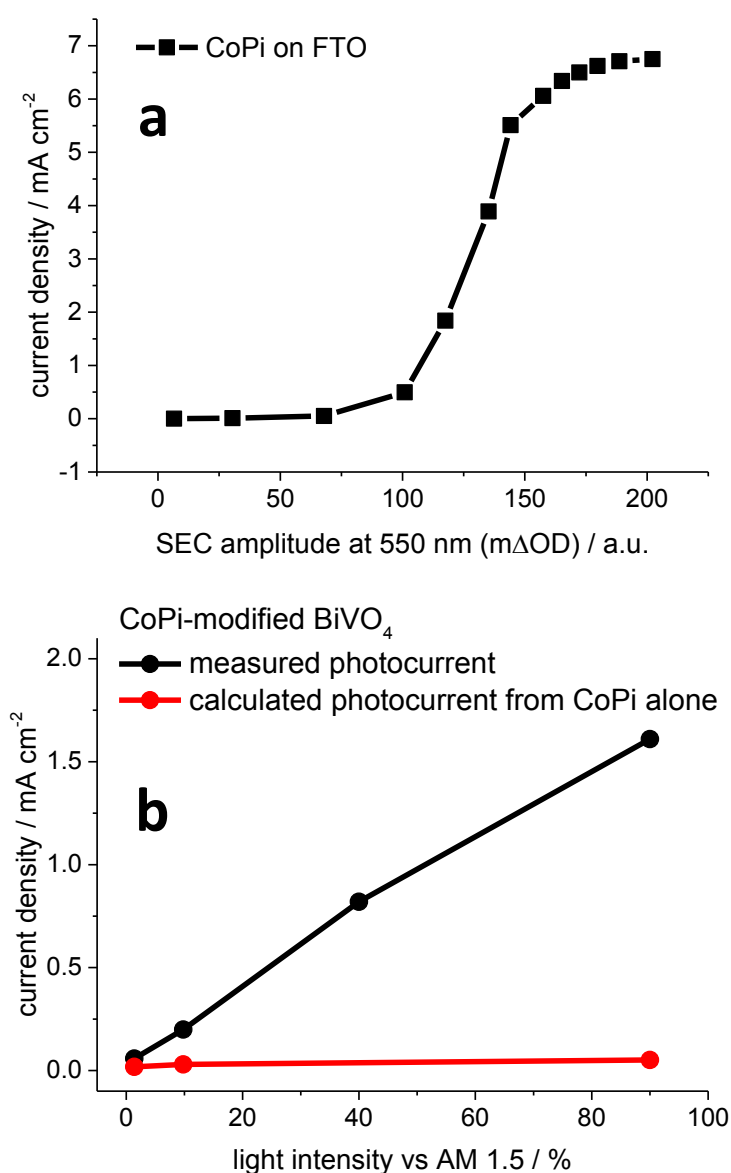
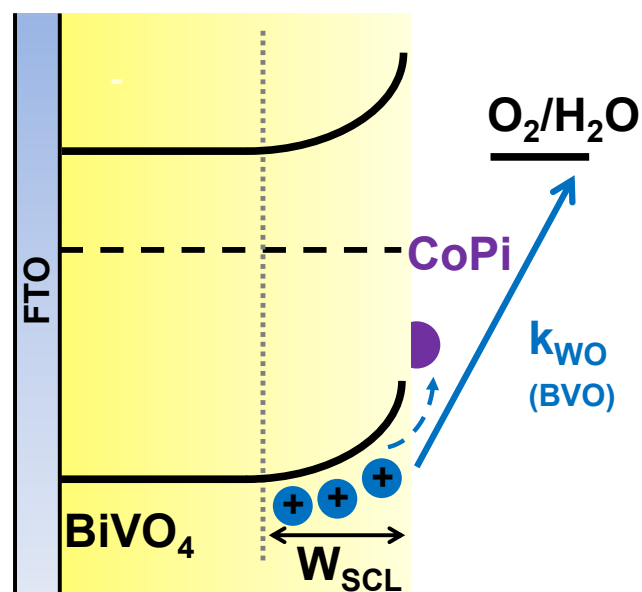


Figure 8.6. (a) Steady-state electrochemical water oxidation current measured in a CoPi/FTO electrode as a function of concentration of oxidised CoPi species (SEC amplitude at 550 nm from Figure 8.5(a); (b) Black: photocurrent of CoPi-modified BiVO₄ during PIA measurements as a function of light intensity; Red: calculated photocurrent of CoPi-modified BiVO₄, assuming water oxidation only proceeds from CoPi, and the PIA amplitude observed is photo-oxidised CoPi species by BiVO₄ holes ready for water oxidation.

In the CoPi-modified BiVO₄ system, the greater absorption signal was assigned to the accumulation of oxidised CoPi on the surface. It is unclear whether these

oxidised CoPi could oxidise water. To address this, we used the SEC data on CoPi / FTO to quantify the expected density of water oxidation from CoPi on BiVO₄. The optical signals of oxidised CoPi measured in PIA and SEC measurements were compared herein assuming that: (a) water was oxidised by CoPi in CoPi-modified BiVO₄ and CoPi/FTO; (b) CoPi had the same process of water oxidation on FTO electrochemically as on BiVO₄ photoelectrochemically. The oxidised CoPi was essential for both oxidation processes. **Figure 8.6a** plotted the steady-state water oxidation current in CoPi/FTO as a function of SEC amplitude. The relationship shown in **Figure 8.6a** indicated that the water oxidation current by CoPi correlated with the optical density ($m\Delta OD$) of oxidised CoPi. **Figure 8.6b** shows the photocurrent amplitude of CoPi-modified BiVO₄ as a function of light intensity (black line and circles) during PIA measurements. If water oxidation in CoPi-modified BiVO₄ proceeded primarily from CoPi, the PIA amplitude of CoPi-modified BiVO₄ should correspond to the density of oxidised CoPi ready for water oxidation. Therefore, a calculated current could be obtained from **Figure 8.6a**. This was obtained by putting the PIA amplitude in the curve of **Figure 8.6a** and then reading the current accordingly. The calculated current by CoPi alone in a CoPi-modified BiVO₄ photoanode was shown in **Figure 8.6b** red line and circles. It was clear that the calculated current for water oxidation through CoPi overlayer on BiVO₄ photoanodes was negligible compared to the measured ones during PIA measurements. This demonstrated that the photocurrent observed in CoPi-modified BiVO₄ did not result primarily from the CoPi catalytic water oxidation process. Therefore, the results presented in this chapter suggested that hole transfer from BiVO₄ to CoPi could occur but the amount of oxidised CoPi was not enough to drive efficient water oxidation.



Scheme 8.1. Schematic presentation of the function of CoPi deposition on un-doped BiVO₄ for water oxidation. Part of surface accumulated holes can transfer to CoPi (by oxidising CoPi) but these oxidised CoPi cannot further oxidise water efficiently. The water oxidation reaction is performed by the remaining BiVO₄ surface holes.

Dau's group carried out electrochemical experiments to determine the relationship between the CoPi water oxidation current density and the CoPi thickness. They found that the water oxidation current density increased proportionally with increasing CoPi thickness at applied potentials between 1.6 V_{RHE} and 1.8 V_{RHE}, and water oxidation reaction could occur in the bulk of the CoPi layer, suggesting that water could penetrate inside the CoPi layer.¹⁸ In CoPi-modified BiVO₄, if the photocurrent density (1.2 mA cm⁻² shown in **Figure 8.4b**) was attributed to CoPi water oxidation, the amplitude of PIA signals (ca. 25 mΔOD) should indicate the concentration of photo-oxidised CoPi responsible for water oxidation. Compared with the spectroelectrochemical results of CoPi/FTO water oxidation current density in **Figure 8.5b**, at 1.2 mA cm⁻², the concentration of oxidised CoPi was ca. 120 mΔOD in a 100 nm thick CoPi layer. This condition also corresponded to the electrochemical water oxidation under 1.8 V_{RHE} shown in **Figure 8.5b**. Therefore, ca.

20% of CoPi was photo-oxidised in CoPi-modified BiVO₄. Due to the linear relationship between the CoPi thickness and water oxidation current density in CoPi/FTO electrodes, 20 nm CoPi (20 % thick of 100 nm CoPi/FTO) water oxidation under 1.8 V_{RHE} should produce a current density of 0.24 mA cm⁻². Comparing this to 1.2 mA cm⁻² measured in PIA measurements of CoPi-modified BiVO₄, it is clear that CoPi did not result in significant water oxidation.

Previous transient absorption studies in Chapter VI have shown that there was no significant evidence to support the assignment of hole transfer to CoPi overlayers, whereas PIA measurements indicated that part of photogenerated holes transferred to CoPi overlayers under continuous illumination. These different results could be explained by the amount of hole accumulation at the BiVO₄ surface. In the transient absorption measurements, the maximum hole amplitude was *ca.* 5×10^{-2} mΔOD due to low quantum yields of long-lived holes. The results presented herein were summarised and visualised in **Scheme 8.1**, suggesting that the process of hole transfer was a competitive process against water oxidation. Only a part of holes could transfer to CoPi and the remaining holes oxidised water from the BiVO₄ surface. Therefore, in the transient absorption measurements, the low quantum yield of hole transfer did not enable measurements of such small amount of oxidised CoPi species, as the result of BiVO₄ photogenerated holes dominating the optical signals probed between 500 nm and 900 nm. In PIA measurements, the hole amplitude was larger by two orders of magnitude due to the continuous illumination, which facilitated more CoPi to be oxidised and therefore observed. Such photo-oxidised CoPi could not further oxidise water, therefore these species needed to be consumed after light off. The negative current transient in **Figure 8.4b** suggested that back electron transfer to recombine with the oxidised species was possible. In

Chapter VI, transient absorption and small-perturbation TPC studies that there was no back electron transfer to recombine with BiVO₄ holes in CoPi-modified BiVO₄ photoanodes. The PIA study herein suggests that after a small portion of photogenerated holes transferred to CoPi, the BiVO₄-CoPi interface could efficiently suppress back electron/hole recombination.

Hole transfer from the photoanode to CoPi has been reported previously using impedance spectroscopy and photoelectrochemical methods.¹⁻³ The function of CoPi has been debated over the past few years between optical and electrical measurements.¹⁹ It has been discussed that different characterisation techniques may cause different understandings in terms of the function of CoPi on photoanodes. In this PIA study of CoPi-modified BiVO₄, hole transfer from BiVO₄ to CoPi appeared to occur under continuous illumination, consistent with the photoelectrochemical results.^{2,3} However, the oxidised CoPi did not contribute to efficient catalytic water oxidation, which was the key observation in this study. CoPi catalytic water oxidation was limited probably by further oxidation of Co³⁺ to Co⁴⁺, which may require overcoming a higher energetic barrier. Additionally, the water oxidation kinetics of CoPi and Co₃O₄ has been reported to be a rather slow process, slower than oxidation by BiVO₄ holes by one-two orders of magnitude (i.e. *ca.* 0.5 s⁻¹ in BiVO₄ compared to 0.01-0.1 s⁻¹ in CoPi).^{20,21} As a result, most photogenerated holes in BiVO₄ could oxidise water without needing to transfer to CoPi due to the faster kinetics. Previously, it has been reported in Chapter VI that CoPi could efficiently suppress back electron/hole recombination, which was thought to be the most important function of CoPi contributing to efficient photo-assisted water oxidation in CoPi-modified BiVO₄ photoanodes.

8.5 Conclusion

In this chapter, understanding if water oxidation could be catalysed by CoPi when deposited on BiVO₄ photoanodes was considered. Using photo-induced absorption spectroscopy and spectroelectrochemical methods, it was found that photogenerated holes generated in BiVO₄ could oxidise CoPi based on the enhanced PIA amplitude. However, these oxidised species could not further oxidise water and the water oxidation was caused by holes from BiVO₄. Therefore, under continuous illumination, the CoPi did not catalyse water oxidation when deposited on BiVO₄ photoanodes.

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Chapter IX

9. Conclusions

These are summarised below for each of the five objectives of the thesis.

- a) Identification of transient absorption signals of photogenerated holes in BiVO_4 .
- b) Understanding of charge carrier dynamics in un-doped BiVO_4 photoanodes for photo-assisted water oxidation.
- c) Understanding of the effects of doping on the properties and kinetic behaviour of BiVO_4 photoanodes.
- d) Understanding the effects of surface modification on BiVO_4 photoanodes.
- e) Understanding the reaction kinetics of water oxidation on BiVO_4 photoanodes under simulated working conditions.

In this thesis, results of functional studies of the charge carrier dynamics of BiVO₄ for solar water oxidation were described. The techniques were based on time-resolved spectroscopies and photoelectrochemical measurements, including electrochemical impedance spectroscopy and transient photocurrents. The un-doped and unmodified BiVO₄ photoanodes employed in these experiments showed only modest photocurrents (ca. 1 mA cm⁻² at 1.2 V_{RHE}) and water oxidation efficiencies (10 % IPCE at 1.2 V_{RHE}). These results were not comparable with the outstanding performance (4 mA cm⁻² at 1.2 V_{RHE}) reported in literature.¹ This difference was also attributed to the morphology and surface modification of BiVO₄ used in these experiments. The flat and dense film enabled the space charge model to apply for interpretation of the behaviour and properties of semiconductor-electrolyte interfaces. The central aim of this thesis was to understand the charge carrier dynamics of recombination and reaction with water using time-resolved absorption spectroscopies. Knowing such parameters could help determine the bottleneck against highly efficient water oxidation on the BiVO₄ surface, thus directing the design strategies to overcome the bottleneck.

Achievements of this PhD project have been listed below, referring to the Project Objectives shown in Chapter I.

1. In Chapter III, the optical spectrum of photogenerated holes in BiVO₄ was successfully identified using transient absorption spectroscopy. A broad absorption spectrum between 500 nm and 900 nm, peaking at 550 nm, assigned to photogenerated holes was observed using electron and hole scavengers. This assignment of photogenerated holes was also supported by the transient absorption measurements with applied potentials. No transient

absorption signal of electrons was observed, probably due to the absorption in the IR region (> 1000 nm).

2. In Chapter IV, the dynamics of photogenerated holes in un-doped BiVO_4 was reported. Long-lived photogenerated holes were found to correlate with the width of the space charge layer, but not to correlate with the photocurrent density. A recombination process which kinetically competed with water oxidation was founded, due to back electron transfer to recombine with the long-lived holes, supported by transient photocurrent data. These results suggested that photocurrent could be improved by blocking this electron back transfer.
3. In Chapter V, the dynamics of photogenerated holes in Mo^{VI} doped BiVO_4 was reported. Compared with front and back side illumination in PEC and transient absorption measurements, it was found that Mo^{VI} dopants could improve charge transport in BiVO_4 . However, the formation of space charge layer in Mo^{VI} doped BiVO_4 was limited due to increased donor density by Mo^{VI} doping. Therefore, charge recombination was dominant and the generation of long-lived photogenerated holes was no longer efficient in doped BiVO_4 .
4. In Chapters VI and VIII, the dynamics of charge carriers in CoPi-modified BiVO_4 were reported, using transient absorption spectroscopy (Chapter VI) and photo-induced absorption spectroscopy (Chapter VIII). Chapter VI described that CoPi did not help to catalyse water oxidation. Rather, CoPi could efficiently reduce the slow recombination of electron back transfer, competing with water oxidation on the same timescales. The negative shift of onset potential was due to more long-lived holes contributing to water oxidation without recombination. Chapter VIII described that under continuous

illumination by LED, a small part of holes in BiVO_4 could transfer (oxidise) to CoPi. However, such oxidised CoPi could not further catalyse water oxidation. Therefore, it confirmed that the function of CoPi on BiVO_4 was mainly associated with retardation of recombination without the catalytic function for water oxidation.

5. Chapter VII described the water oxidation mechanism and kinetics by undoped BiVO_4 under continuous illumination. Water oxidation reaction order was found to be first under low surface hole density and third under high surface hole density. Comparing with $\alpha\text{-Fe}_2\text{O}_3$ photoanodes, the water oxidation rate was found to be faster in BiVO_4 , probably due to lower activation energy and higher mobility of surface holes.

Future work

Despite the fact that the primary objectives of this thesis have been achieved, there were still unresolved questions that need to be answered to advance further understanding of charge carrier dynamics in BiVO_4 .

Temperature-dependent transient absorption/photocurrent studies: Transient absorption studies as a function of temperature have been reported previously by our group on TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$ photoanodes.⁴ The activation energy in $\alpha\text{-Fe}_2\text{O}_3$ for single-hole water oxidation was determined using the Arrhenius equation. However, TiO_2 does not require activation energy for water oxidation due to the deep valence band. It has been not clear whether BiVO_4 requires activation to initiate the water oxidation reaction or not. Therefore, temperature-dependent transient absorption studies of BiVO_4 under high potentials (to turn off back electron/hole recombination) should be carried out. More importantly, back electron/hole recombination has been determined to be a thermally activated process. Therefore, it would be important to support this assignment by carrying out transient absorption / photocurrent studies under conditions where back electron/hole recombination is dominant on ms-s timescales.

Temperature-dependent photo-induced absorption studies: Third order water oxidation kinetics using photo-induced absorption spectroscopy has been described in Chapter VII. The activation energy under such condition (working condition) is unclear. Therefore, it is necessary to determine the activation energy, if required, for water oxidation under working condition of water oxidation.

Ultra-fast transient absorption studies of BiVO_4 : The timescales from microseconds to seconds for transient absorption studies reported in this thesis is

the focus to understand the charge carrier dynamics in BiVO₄, because those are the timescales on which water oxidation occurs. However, its behaviour at sub- μ s timescales is not discussed in this thesis. Although there were several transient absorption studies on BiVO₄ focusing on the ultra-fast timescales,^{5,6} the kinetics were still unclear, especially under applied potentials.

Protection layers on BiVO₄ surfaces: Although it has been reported that BiVO₄ is a promising photoanode material, its further development has been limited by its poor photo-stability, which has been reported not only for PEC water oxidation,⁷ but also for transient absorption studies under intensity laser excitation.⁵ In this thesis, the BiVO₄ exhibited a reasonably good stability due to the weak laser pulsed applied. However, under long-term simulated illumination, photocurrent densities decreased over time. Therefore, all the PEC measurements were carried out in a short illumination duration to avoid photocorrosion. In order to functionalise BiVO₄ for future solar fuels devices, it is crucial to improve its long-term stability. It has been reported, and observed in our group, that CoPi overlayers can prevent BiVO₄ from photocorrosion.⁷ However, other strategies have not been attempted, for example Al₂O₃ overlayers by atomic layer deposition. Such a strategy has been applied to α -Fe₂O₃ successfully⁸ and it would be interesting for BiVO₄.

Morphological study of BiVO₄ photoanodes: The studies of charge carrier dynamics in BiVO₄ photoanodes focused on flat and dense films. The properties and kinetic behaviour of its semiconductor-electrolyte interface has been understood by the space charge model. However, photocurrent densities reported in this thesis were still modest even with CoPi surface modification, compared to the reported best performing BiVO₄ photoanodes.¹ One distinction is considered to be their morphology. High surface area is thought to facilitate more photogenerated holes to

accumulate. If such high concentrations of surface holes can be stabilised due to suppression of back electron/hole recombination, higher photocurrent densities could be achieved. In addition, different morphologies would also impact on the charge transport kinetics, which could be clarified by transient absorption studies.

Surface modification with electrocatalysts on BiVO₄: Attaching electrocatalysts on the surface of BiVO₄ photoanodes has been reported to result in significant improvements in water oxidation performance. However, the behaviour of CoPi reported in this thesis did not act as an electrocatalyst on the BiVO₄ surface due to its slower kinetics of water oxidation than BiVO₄ holes. Therefore, other electrocatalysts with high rate constants (i.e. $>> 1 \text{ s}^{-1}$) would be suitable to further improve the water oxidation efficiency in BiVO₄. For example, FeOOH and NiOOH have shown promising results in enhancing water oxidation kinetics when attached on BiVO₄ surfaces. Therefore, studies of the interaction of FeOOH and NiOOH with photogenerated holes in BiVO₄ using transient absorption spectroscopy would further advance the understanding of charge carriers dynamics and water oxidation reaction.

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