

**SPECTROELECTROCHEMICAL
STUDIES OF OXIDATION REACTIONS
ON HEMATITE PHOTOELECTRODES**

Camilo Arturo Mesa Zamora

Department of Chemistry

Imperial College London

Thesis submitted for the Degree of Doctor in Philosophy

October 2018

To my parents and sister

I hereby declare that except when specific reference is made, the material presented in this thesis is the result of my own work. This manuscript does not exceed 100 000 words in length.

Camilo A. Mesa

October 2018

The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform or build upon it. For any reuse or redistribution, researchers must make clear to others the licence terms of this work.

October 2018

ABSTRACT

The abstract for this thesis has been written in English and Spanish

English

In this thesis, the key factors governing the solar fuels catalytic process, *i.e.* photoelectrochemical water splitting, are studied by means of different spectroelectrochemical techniques. Photo-induced absorption spectroscopy together with transient photocurrent measurements are employed to study the catalytic function of different metal oxide photoanodes, focusing particularly on hematite, by the construction of rate law analyses. An introduction to the field is given in *Chapter 1* followed by a description of the methods used herein in *Chapter 2*.

Chapter 3, the first results chapter, focuses on the kinetics of water oxidation on hematite photoanodes at conditions of suppressed surface recombination. This chapter provides evidence of 2 different water oxidation mechanisms, with different activation energies, upon increasing the irradiation intensity. These mechanisms show faster kinetics upon surface deprotonation of the photoanode and a secondary kinetic isotope effect. In this chapter, a detailed water oxidation mechanism at a molecular level for hematite photoanodes is proposed and compared with biological systems such photosystem II. Further comparisons with other metal oxides such titania, bismuth vanadate and tungsten oxide indicate similar mechanisms whose kinetics are sensitive to the valence band edge of the materials.

Chapter 4 explores the use of methanol oxidation on hematite, as a model organic substrate reaction, to improve the hydrogen production rate. This is proposed to be done concomitant with either, the degradation of organic pollutants or the synthesis of high value-added products when these reactions are selective. This chapter shows the selective oxidation of methanol to formaldehyde with kinetics faster than those for water oxidation and sensitive to the valence band edge when the reaction was performed on titania. The data collected allow the proposal of a detailed mechanism of reaction for the selective oxidation of methanol to formaldehyde.

Finally, *Chapter 5* focuses on the decay kinetics of the photogenerated holes in state-of-the-art thin, flat hematite films. This chapter discusses the recombination, accumulation and reaction dynamics of photogenerated holes upon laser excitation. Upon hole accumulation at the photoanode surface, this chapter provides evidence of a kinetic competition between surface recombination and trapping and hole extraction by the electrolyte.

Español

En esta tesis se estudian los elementos clave que rigen los procesos catalíticos en el almacenamiento de energía solar produciendo combustibles solares, a través de la electrólisis de agua, haciendo uso de técnicas espectro-electroquímicas. En esta tesis se utilizan principalmente técnicas resueltas en el tiempo, espectroscópicas y electroquímicas, para la construcción de leyes de velocidad. De esta manera se estudia la función catalítica de diferentes óxidos metálicos, en particular hematita, actuando como fotoánodos.

En el *Capítulo 3*, se estudia la cinética de la reacción de oxidación de agua en la superficie de fotoánodos de hematita, en condiciones de ausencia de recombinación en la superficie. En este capítulo se evidencian 2 mecanismos diferentes, con energías de activación diferentes y efecto isotópico cinético secundario, para dicha reacción en función de la intensidad de luz irradiada. La cinética de estos dos mecanismos aumenta cuando la superficie del fotoánodo está desprotonada. Para la oxidación de en condiciones de operación normales, a intensidad de un sol, se propone un mecanismo de reacción desde un punto de vista molecular y se compara con mecanismos de reacción similares en algunos sistemas biológicos, como en el fotosistema II en la fotosíntesis, y se generaliza esta propuesta de mecanismo a diferentes óxidos metálicos.

La lenta cinética de producción de hidrógeno, a causa de la lenta oxidación de agua en hematita, se puede mejorar cambiando la molécula donadora de electrones de agua a algún sustrato orgánico fácil de oxidarse. Así, en el *Capítulo 4*, se investiga la cinética y se propone un mecanismo para la oxidación de metanol, como sustrato de referencia, en hematita. Este concepto se puede extrapolar a la degradación de materia orgánica en agua o a la síntesis de productos con valor agregado. En este capítulo se concluye que la cinética de la oxidación de metanol es más rápida que la del agua y que dicha cinética no cambia con el potencial aplicado sino con la posición de la banda de valencia del óxido metálico utilizado.

Finalmente, en el *Capítulo 5*, se comparan dos métodos de síntesis de hematita y se estudian las dinámicas de los procesos que induce la iluminación tales como recombinación, acumulación de cargas y su reacción. En este capítulo se evidencia la competencia cinética de las cargas entre procesos de recombinación y reacción. Se concluye que la cinética de la reacción es la misma sin importar el método de síntesis de la hematita.

LIST OF PUBLICATIONS

- “Rate law analysis of water oxidation on a hematite surface”, Le Formal, F., Pastor, E., Tilley, S. D., **Mesa, C. A.**, Pendlebury, S. R., Grätzel, M. and Durrant, J. R., *J. Am. Chem. Soc.*, **2015**, 137, 6629 – 6637.
- “Rate law analysis of water oxidation and hole scavenging on a BiVO₄ photoanode”, Ma, Y., **Mesa, C. A.**, Pastor, E., Kafizas, A., Francàs, L., Le Formal, F., Pendlebury, S. R. and Durrant, J. R., *ACS Energy Lett.*, **2016**, 1, 618 – 623.
- “Kinetics of photoelectrochemical oxidation of methanol on hematite photoanodes”, **Mesa, C. A.**, Kafizas, A., Francàs, L., Pendlebury, S. R. Pastor, E., Ma, Y., Le Formal, F., Mayer, M., Grätzel, M and Durrant, J. R., *J. Am. Chem. Soc.*, **2017**, 139, 11537 – 11543.
- “Spectroelectrochemical analysis of the mechanism of (photo)electrochemical hydrogen evolution at a catalytic interface”, Pastor, E, Le Formal, F., Mayer, M., Tilley, S. D., Francàs, L., **Mesa, C. A.**, Grätzel, M. and Durrant, J. R., *Nat. Commun.*, **2017**, 8, 14280.
- “Membrane-less photoelectrochemical cells: product separation by hydrodynamic control”, Holmes-Gentle, I., Hoffmann, F., **Mesa, C. A.**, and Hellgardt, K., *Sustainable Energy Fuels*, **2017**, 1, 1184 – 1198.
- “Water oxidation kinetics of accumulated holes on the surface of a TiO₂ photoanode: a rate law analysis”, Kafizas, A., Ma, Y., Pastor, E., Pendlebury, S. R., **Mesa, C. A.**, Francàs, L., Le Formal, F., Nuruzzaman, N., Ling, M., Sotelo-Vasquez, C., Carmalt, C., Parking, I. and Durrant, J. R., *ACS Catal.*, **2017**, 7, 4896 – 4903.
- “Rate law analysis of water splitting photoelectrodes”, Francàs, L., **Mesa, C. A.**, Pastor, E., Le Formal, F., and Durrant, J. R., in: *Advances in photoelectrochemical water splitting: Theory, experiment and systems analysis*. Ed: Royal Society of Chemistry **2018**.

- “Ultra-thin Al_2O_3 coatings on BiVO_4 photoanodes: Impact on performance and charge carrier dynamics”, Kafizas, A., Xing, X., Selim, S., **Mesa, C. A.**, Ma, Y., Burgess, C., McLachlan, M. and Durrant, J. R., *Catalysis Today*, **2019**, 321-322, 59-66.
- “Multihole catalysis of water oxidation on hematite photoanodes: Insights from in operando spectroelectrochemistry and density functional theory”, **Mesa, C. A.**, Francàs, L., Yang, Ke., Garrido, P., Pastor, E., Ma, Y., Kafizas, A., Rosser, T., Mayer, M., Reisner, E., Grätzel, M., Batista, V. S., and Durrant, J. R., *Nat. Chem.*, under revision.
- “Spectroelectrochemical study of water oxidation on nickel and iron oxyhydroxide electrocatalysts”, Francàs, L., Corby, S., Selim, S., Lee, D., **Mesa, C. A.**, Godin, R., Stephens, I., Choi, K., and Durrant, J. R., *Nat. Catalysis.*, under revision.
- “Analysis of the kinetics determining the function of nickel/iron oxyhydroxides as electrocatalysts and as co-catalysts on BiVO_4 photoanodes for water oxidation”, Francàs, L., Selim, S., Corby, S., Lee, D., **Mesa, C. A.**, Pastor, E., Choi, K., and Durrant, J. R., *manuscript in preparation*.
- “Towards a general water oxidation mechanism of reaction on hematite photoanodes”, **Mesa, C. A.**, Steier, L., Francàs, L., Mayer, M., Grätzel, M., and Durrant, J. R., *manuscript in preparation*.
- “The role of surface states on the water oxidation catalysis on planar hematite photoanodes”, Steier, L., **Mesa, C. A.**, and Durrant, J. R., *manuscript in preparation*.

ACKNOWLEDGEMENTS

First of all, I thank my supervisor, Professor James R. Durrant for giving me the opportunity to carry out this project, for his guidance and for teaching me to think scientifically. I greatly acknowledge his support as an academic and, sometimes more importantly, as a person throughout my PhD.

This PhD has been a long journey full of scientific discussions but also full of personal growth. I would like to thank all of those who have always supported me, no matter what: Laia, Ernest Mike, Lorenzo, Omar, Araceli, Saritah, Lucho and Edu in the Europe (UK mostly) and Mike, Lana and Kate in Colombia.

Thanks to the Departamento Administrativo de Ciencia, Tecnología e Innovación (COLCIENCIAS) for the scholarship (Convocatoria 568) for funding. Thanks also to the Engineering and Physical Sciences Research Council (EPSRC) for project funding and also to the Royal Society of Chemistry for conferences funding.

Thanks to the past and present post-docs of the Durrant group, Laia, Ernest, Robert, Andreas, Luzi, Yimeng and Steph for all the fruitful discussions. Special thanks to Pabs and Li during the lab work and writing.

Thanks to all the Durrant group for the endless hours of fun, sometimes around a pint, and for their friendship, Laia, Ernest, Hyojung, Mike, Ben, Sacha, Luzi, Shabs, Seb, Yifang, Jiaying, Weidong, YuHan and past members, Elisa and Yimeng.

Thanks to the organisations that allowed me to explore different leadership activities, Latin-American Society at Imperial College and ABeCol. Thanks also to Clubes de Ciencia Colombia and Fundacio la Pedrera for giving me the opportunity to do outreach with the support of the Durrant group, with special thanks to Li.

Thanks to the sports community, Scot for teaching me some squash and became almost unbeatable for Mike, and the P&W football team, specially Dennis, Jorge and Miguel.

Finally, I would like to thank my family. Thanks to Nubis and Dino for their invaluable support and love. Thanks to Vivi for her unconditional love and support, and thanks to the person I admire the most, mi viejo. Muchas gracias familia por su maravilloso e incondicional apoyo.

Table of Contents

ABSTRACT	v
<i>English</i>	vi
<i>Español</i>	vii
LIST OF PUBLICATIONS	viii
ACKNOWLEDGEMENTS	x
LIST OF FIGURES AND TABLES	xv
Chapter 1.Introduction.....	26
1.1. Nature and environment	27
1.2. Example of Colombia.....	29
1.3. Solar energy	30
1.4. From natural to artificial photosynthesis	32
1.5. PEC water splitting.....	34
1.5.1. Semiconductor electrochemistry	36
1.5.2. Metal-oxide photoanodes.....	38
1.5.3. α -Fe ₂ O ₃	40
1.5.3.1. Crystalline and electronic properties	40
1.5.3.2. Doping and vacancies	42
1.5.3.3. Increasing hematite photoanodes performance	43
1.5.3.4. Charge carriers kinetics in hematite.....	45
1.6. Rate law analysis.....	47
1.7. In the next chapters.....	48
1.8. References	50
Chapter 2.Experimental methods	58
2.1. Sample preparation	59
2.1.1. α -Fe ₂ O ₃	59

2.1.2.	TiO ₂	61
2.1.3.	BiVO ₄	61
2.1.4.	WO ₃	62
2.2.	Photoelectrochemical (PEC) set-up	62
2.3.	Transient Absorption Spectroscopy (TAS)	64
2.3.1.	TAS Set-up	64
2.3.2.	Signal conversion to $\Delta O.D.$	65
2.3.3.	Contributions to the observed $\Delta O.D.$	66
2.4.	Light-Induced Spectroelectrochemistry (LI-SEC)	66
2.5.	Transient Photocurrent (TPC)	68
2.6.	Rate law kinetic model	69
2.7.	Kinetic isotope effect	70
2.8.	Heating device	72
2.9.	UV-Vis	72
2.10.	References	74
Chapter 3. Kinetic and mechanistic study of water oxidation on metal-oxide photoanodes		76
3.1.	Introduction	78
3.2.	Experimental	81
3.2.1.	(Photo)electrochemical response	82
3.2.2.	Rate law analysis	82
3.2.3.	pH dependency and kinetic isotope effect analysis	83
3.2.4.	Temperature dependence studies	83
3.2.5.	Density functional theory (DFT) calculations	83
3.3.	Results	84
3.3.1.	(Photo)electrochemical response	84

3.3.2.	Spectral features of long-lived holes in $\alpha\text{-Fe}_2\text{O}_3$	84
3.3.3.	Calculation of surface hole extinction coefficient	85
3.3.4.	Rate law analysis of water oxidation on $\alpha\text{-Fe}_2\text{O}_3$	86
3.3.5.	Temperature dependence study (LI-SEC measurements)	88
3.3.6.	pH dependence and isotopic labelling studies	89
3.4.	Discussion	93
3.4.1.	Temperature and pH dependence and isotopic labelling studies	93
3.4.2.	Mechanistic implications.....	97
3.5.	Conclusions.....	106
3.6.	References.....	107
Chapter 4. Kinetic and mechanistic study of methanol oxidation on $\alpha\text{-Fe}_2\text{O}_3$ and TiO_2 photoanodes.....		113
4.1.	Introduction	115
4.2.	Experimental.....	117
4.2.1.	(Photo)electrochemical (PEC) response.....	117
4.2.2.	Rate law analysis	118
4.2.3.	Formaldehyde quantification.....	118
4.3.	Results.....	119
4.3.1.	(Photo)electrochemical response	119
4.3.2.	Formaldehyde quantification.....	120
4.3.3.	Rate law analysis	122
4.3.4.	Comparison with TiO_2 photoanodes	124
4.4.	Discussion	126
4.4.1.	(Photo)electrochemical response	126
4.4.2.	Rate law analysis	128
4.4.3.	Comparison with TiO_2 photoanodes	132

4.4.4. Mechanistic implications.....	133
4.5. Conclusions.....	136
4.6. References.....	138
Chapter 5. Photogenerated holes surface recombination and trapping vs. reaction: kinetic competition in α-Fe₂O₃ photoanodes.....	142
5.1. Introduction.....	144
5.2. Experimental.....	147
5.2.1. Samples	147
5.2.2. (Photo)electrochemical response	148
5.2.3. Transient absorption spectroscopy and transient photocurrent	148
5.2.4. Rate law analysis	148
5.3. Results.....	148
5.3.1. (Photo)electrochemical response	148
5.3.2. Transient absorption spectroscopy and transient photocurrent	150
5.3.3. Rate law analysis	156
5.4. Discussion	159
5.4.1. Evidence of trap states competing with hole accumulation	159
5.4.2. Rate law analyses and mechanistic implications	162
5.5. Conclusions.....	166
5.6. References.....	167
Chapter 6. Concluding remarks and future work.....	171
6.1. Concluding remarks.....	171
6.2. Future work	172
Appendix	173

LIST OF FIGURES AND TABLES

Figure 1-1. Anthropogenic greenhouse gas (GHG) estimated emissions in 2014. Data taken from the CO₂ emissions from fuel combustion: Overview report by the International Energy Agency.⁶ *Others include N₂O from non-agricultural emissions, waste, biomass burning and post-burn decay, among others.....28

Figure 1-2. Yearly potential of the most common renewable energy sources, i.e. tidal, biomass, wind and solar expressed in terawatts of energy that could be utilised in average in a year in a logarithmic scale (left box), data from the International Energy Agency.²² The ~18 TW of primary energy consumed in 2017 are represented by the Earth globe in the figure and the proven fossil fuels reserves are displayed in the right box, data from BP Statistical Review of World Energy.³ Note that the fossil fuels potential is calculated with the base of one year. 31

Figure 1-3. Schematic representation of electricity demand in the household sector (brown) compared to the solar potential (yellow) in a typical summer day in Texas, U.S.A. For reference.⁴² 32

Figure 1-4. a) Schematic representation of the Z-scheme in natural photosynthesis, where light is absorbed in photosystems I and II, PS I and PS II respectively. Electrons are donated from water at the oxygen evolution centre (OEC) and are finally transferred to produce NADPH, which participates in the Calvin cycle (CO₂ fixation process). b) Artificial photosynthesis scheme, where light excites electrons in a photoabsorber (P for ground state and P* for its excited state), which are transferred to an electron acceptor species (EA) through a reduction catalyst. An electron donor (ED) acts as source of electrons to complete the chain. 34

Figure 1-5. Schematic representation of a PEC water splitting system. Water, as electrons source, is oxidised in the photoanode, releasing 4 H⁺, which are subsequently reduced in the photocathode, producing H₂. 35

Figure 1-6. Energy band diagrams for an electrode (n-type semiconductor) / electrolyte interface, a) before equilibrium in dark (flat band conditions), b) once equilibrium is reached in dark and c) under illumination. E_{CB} and E_{VB} correspond to the conduction and valence band edges, respectively and E_F and E_{Redox} to the fermi level and the electrolyte redox potential,

respectively. $E_{F,P}$ refers to the fermi level of holes under illumination. V_{bi} and V_{ph} correspond to the built-in potential and photovoltage respectively.....37

Figure 1-7. Schematic illustration of a current / potential (J-V) curve. The redox potentials for proton reduction and water oxidation are indicated by the dashed lines, separated by the 1.23 V required to split water. The ideal J-V curves in dark (light blue) and under illumination (dark blue) conditions for a photoanode with a flat band ~ 0.3 V, resembling a hematite photoanode. The red curve exhibits a schematic illustration of the actual J-V behaviour of a hematite photoanode. η_{OER} corresponds to the overpotential required by the photoanode to start driving water oxidation and V_{ph} corresponds to the photovoltage. 38

Figure 1-8. Band positions for some of the most common metal-oxide semiconductors used in water oxidation, compared to the redox potential for hydrogen and oxygen evolution at their best performing pH conditions. pH 13 for $\alpha\text{-Fe}_2\text{O}_3$ and TiO_2 , pH 7 for BiVO_4 and pH 1 for WO_3 . E_g : $\alpha\text{-Fe}_2\text{O}_3$ (2.1 eV), BiVO_4 (2.4 eV), TiO_2 (3.1 eV) and WO_3 (2.8 eV).....39

Figure 1-9. Crystalline structure of $\alpha\text{-Fe}_2\text{O}_3$. The octahedral structure forming pairs of $\text{Fe}(\text{O})_6$ units along the [001] direction is shown. This figure is from the reference ⁸⁶.....40

Figure 1-10. Progress on hematite photoanodes performance to date, based on photocurrent density (J^{ph}) measurements at 1.23 V vs RHE at one sun illumination conditions. The incident photon to current efficiency (IPCE) is shown in green and the catalytic onset potentials for such photoanodes are shown in blue. This includes nanostructuring and doping as well as surface modification, all indicated next to the corresponding J^{ph} value. USP: Ultrasonic spray pyrolysis, APCVD: Atmospheric pressure chemical vapour deposition, H-treated: annealing under a hydrogen flow and Co-Pi: Cobalt-phosphate overlayer.^{84,121–126} 44

Figure 1-11. A general scheme of light-induced and catalytic events taking place in an $\alpha\text{-Fe}_2\text{O}_3$ photoanode, including the two discussed kinetic models a) charge transfer to the electrolyte (and also recombination) through ‘surface states’ and b) charge transfer to the electrolyte from valence band holes. 45

Figure 1-12. A more detailed scheme of light-induced and catalytic events taking place in an $\alpha\text{-Fe}_2\text{O}_3$ photoanode, proposed in Durrant group. The timescales are a general picture as geminate and non-geminate recombination as well as charge carrier separation, transport and reaction are different hematite. 46

Figure 2-1. Si-doped $\alpha\text{-Fe}_2\text{O}_3$ photoanode characterisation, a) SEM image (cross-section) showing the cauliflower-like nanostructure typical of these films, and b) XRD spectrum

showing the preferential crystal face (110). These images were taken from Cornuz, M., et. al.²
60

Figure 2-2. a) HR-TEM images of the $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ interface. I note here that these images were taken on TiO_2 nanowires with a thin ALD deposited $\alpha\text{-Fe}_2\text{O}_3$ layer, and b) Raman spectra of the $\alpha\text{-Fe}_2\text{O}_3$ photoanodes compared to a reference hematite spectrum and the FTO/ TiO_2 substrate. These images were taken from Steier, L., et. al.⁵ 60

Figure 2-3. TiO_2 anatase films characterisation by a) SEM images and b) XRD spectroscopy (black line, experimental data and red line, fitted data. These images were taken from Wang, X., et. al.⁸ 61

Figure 2-4. BiVO_4 films characterisation by a) cross section SEM images, the bar corresponds to 200 nm in length and b) XRD spectroscopy (black line, experimental data and red lines, BiVO_4 reference), the arrows indicate peaks of SnO_2 and FTO substrate. These images were taken from Ma, Y., et. al.⁹ 61

Figure 2-5. WO_3 films characterisation by a) SEM images, the bar corresponds to 2 μm in length and b) XRD spectroscopy, where F indicates peaks of the FTO substrate. These images were taken from Lai, Y., et. al.¹⁰ 62

Figure 2-6. Schematic representation of the photoelectrochemical (PEC) set-up. 1) Xe lamp, 2) filters and focusing lenses, 3) PEEK 3-electrode cell and 4) potentiostat. 62

Figure 2-7. Schematic representation of the home-built TAS system.....64

Figure 2-8. Schematic representation of the simultaneous PIA (optical system) and TPC (electrochemical system) spectrometer. 67

Figure 2-9. Schematic representation of the kinetic model shown in Equation 2-8. The photogenerated holes flux to the surface (J_{holes}) is equivalent to the photocurrent whereas the hole consuming process (i.e. water oxidation reaction) is equal to $(-k_{\text{WO}} \cdot p_s^\beta)$, with β as the reaction order and k_{WO} as the water oxidation rate constant. 69

Figure 2-10. UV-Vis spectra of $\alpha\text{-Fe}_2\text{O}_3$ (red), BiVO_4 (purple), TiO_2 (blue) acquired in transmittance mode and WO_3 (green) acquired in diffuse reflectance mode.....73

Figure 3-1. Schematic representation of water oxidation during natural photosynthesis. a) S-state cycle for the oxygen evolution reaction in the photosystem II, blue S_4^+ refers to an oxyl-oxo radical coupling as rds and orange S_4^+ to a water nucleophilic attack as rds and b) structure of the PSII (left) and the OEC cluster (right), image taken from Askerka et. al.⁹.....78

Figure 3-2. Two of the most discussed pathways for the O-O bond formation as rate determining step in the water oxidation catalytic cycle in metal oxide catalysts, a) water nucleophilic attack (WNA) and b) interaction between two M-O species (I2M). 80

Figure 3-3. Current/potential (J-V) response of the APCVD α -Fe₂O₃ photoanode, under dark (black) and ~ 1 sun, front illumination (electrode/electrolyte) conditions (red) measured in 1 M NaOH. The star indicates the applied potential at which the photo-induced absorption spectroscopy studies were carried out. 84

Figure 3-4. Spectra fingerprints upon illumination of the APCVD α -Fe₂O₃ photoanode. Light grey: spectrum measured at 100 ms after 355 nm laser pulse in the TAS system. Dark grey: spectrum measured after 5 s 365 nm continuous LED illumination. The arrow indicates the accumulation of photogenerated holes at the surface of the photoanode at high applied potential (1.5 V vs RHE) i.e. in absence of surface recombination, evidence provided by the absence of cathodic spikes in the TPC measurements shown in Figure 3-5.b. 85

Figure 3-5. Photogenerated hole optical absorption calibration. a) PIA signal of the accumulated holes at the α -Fe₂O₃ surface monitored at 650 nm during the 5 s ON/5 s OFF pulsed LED illumination at 0.9 V vs RHE, b) transient photocurrent density and c) correlation between the recombined charges and the steady-state optical absorption measured at 650 nm and 0.9 V vs RHE as a function of light intensity, leading to a hole extinction coefficient of 640 M⁻¹ cm⁻¹. These data were modified from Le Formal et. al.⁴⁶ 86

Figure 3-6. Light-induced spectroelectrochemistry (LI-SEC) data of water oxidation on α -Fe₂O₃ as a function of 5 s on/5 s off pulsed 365 nm illumination (~ 4 to ~ 34 mW cm⁻²) under 1.5 V vs RHE applied potential, a) PIA signal of surface valence band hole density (p_s) probed at 650 nm, b) simultaneously assay of TPC and c) steady-state rate law analysis, rate of reaction (J^{ph}) vs surface hole density (p_s), the dashed lines represent the fitted functions for first and third order regimes. These data were modified from Francas et. al.²⁸ 87

Figure 3-7. Temperature dependence of the water oxidation kinetics. a) PIA signal decay dynamics, normalised at ~ 7 mW cm⁻² and b) steady-state rate law analysis, rate of reaction (J^{ph}) vs surface hole density (p_s) of water oxidation on α -Fe₂O₃ as a function of 5 s on/5 s off pulsed 365 nm illumination (~ 1 to ~ 35 mW cm⁻²) under 1.5 V vs RHE applied potential and as a function of temperature from 21 to 50 °C. The dashed line represents approximately the transition point from 1st to 3rd order. 89

Figure 3-8. Photocurrent/potential (J^{ph} -V) response of the APCVD $\alpha\text{-Fe}_2\text{O}_3$ photoanode, under ~ 1 sun chopped illumination (electrode/electrolyte) conditions measured in a range of electrolyte pH values from 6.5 to 13.7. The star indicates the applied potential at which the photo-induced absorption spectroscopy studies were carried out. 90

Figure 3-9. Spectra fingerprints of the APCVD $\alpha\text{-Fe}_2\text{O}_3$ photoanode measured at two different pH electrolytes, neutral (yellow) and alkaline (purple, same data as Figure 3-4) upon 5 s 365 nm continuous LED illumination at high applied potential (1.5 V vs RHE). 91

Figure 3-10. Rate law analysis for the water oxidation reaction on the APCVD $\alpha\text{-Fe}_2\text{O}_3$ photoanode, measured at 650 nm under 1.5 V vs RHE in a range of a) electrolyte pH values from 6.5 to 13.7 and b) electrolyte pD values from 7.2 to 13.7, as a function of 5 s on/5 s off pulsed 365 nm illumination (~ 1 to $\sim 35 \text{ mW cm}^{-2}$). 92

Figure 3-11. Arrhenius plot of the water oxidation reaction, on the APCVD $\alpha\text{-Fe}_2\text{O}_3$ photoanode, a) plotting the rate constants for the observed 1st and 3rd reaction order providing the activation energies for both regimes. The rate constants were calculated from the intercept of the steady-state rate law analyses at a range of temperatures from 21 to 50 °C shown in Figure 3-7, measured at 1.5 V vs RHE. The dashed lines indicate the fitting to extract the activation energy values and b) using the photocurrent density values (J^{ph}) at a fixed surface hole density for the 3rd order of reaction using Equation 3-5. 94

Figure 3-12. Kinetic analysis for the oxidation of water on the APCVD $\alpha\text{-Fe}_2\text{O}_3$ photoanode, under 1.5 V vs RHE in a range of pH values between 6.5 to 13.7. a) pH and pD (inset) dependence of the water oxidation rate constants for the 1st (blue) and 3rd (red) order regimes and b) the corresponding and comparative kinetic isotope effect for the 1st (blue) and 3rd (red) order regimes. 95

Figure 3-13. Comparative pH dependence between the photocurrent onsets and the 3rd order rate constants for the oxidation of water on the APCVD $\alpha\text{-Fe}_2\text{O}_3$ photoanode, under 1.5 V vs RHE. The photocurrents onsets were calculated from the J^{ph} -V curves in Figure 3-8. The dotted line corresponds to the reported point of zero charge (pzc) for $\alpha\text{-Fe}_2\text{O}_3$ 97

Figure 3-14. Representation of the proposed possible water oxidation mechanism on the APCVD $\alpha\text{-Fe}_2\text{O}_3$ photoanode, under ~ 1 sun illumination at 1.5 V vs RHE conditions, suggested by DFT calculations. (Relative free energies are given in green in the unit of kcal/mol and free energy changes are given in blue in the unit of eV; rate-determining steps are shown in red).

Dash lines indicate hydrogen bonds and dotted lines indicate partially formed bonds at transition states. This is a modified figure from the submitted manuscript “Multihole catalysis of water oxidation on hematite photoanodes: Insights from in operando spectroelectrochemistry and density functional theory”, with DFT calculations undertaken by Dr. Ke Yang, Pablo Garrido and Professor Victor Batista at Yale University. 98

Figure 3-15. Comparative analysis of water oxidation on four of the most studied metal-oxide photoanodes, α -Fe₂O₃ (red), BiVO₄ (green), TiO₂ (blue) and WO₃ (purple). a) Photocurrent/potential (J^{ph} -V) response of the four studied photoanodes, ~1 sun illumination conditions. The star indicates the applied potential at which the rate law analyses were carried out. Inset: J^{ph} achieved for each held photoanode at 1.5 V vs RHE and b) UV-Vis spectra of the four photoanodes. Measurement conditions: WO₃, diffuse reflectance system, pH 3; BiVO₄, transmittance system, pH 7; α -Fe₂O₃, transmittance system, pH 13; TiO₂, transmittance system pH 13.....100

Figure 3-16. Comparative kinetic analysis of water oxidation on four of the most studied metal-oxide photoanodes, α -Fe₂O₃ (red), BiVO₄ (green), TiO₂ (blue) and WO₃ (purple). a) Rate law analyses for the water oxidation reaction on the four studied photoanodes, the suns indicate ~1 sun illumination conditions. Inset: Conduction and valence band edges for the four photoanodes studied herein with respect to the water oxidation redox potential and compared to the equivalent redox potentials for PSII and b) turn-over frequencies (TOF), calculated from the data presented in a), for water oxidation as a function of the irradiation intensity. Measurement conditions: WO₃, diffuse reflectance system, pH 3, applied potential 1.4 V vs RHE; BiVO₄, transmittance system, pH 7 at 1.7 V vs RHE; α -Fe₂O₃, transmittance system, pH 13 at 1.5 V vs RHE; TiO₂, transmittance system pH 13 at 1.5 V vs RHE. In all cases 365 nm LED irradiation was used from 0.5% to 300% one sun and measurements were performed at 25 °C 102

Figure 3-17. Schematic general representation of the water oxidation catalytic cycle in a metal-oxide photoanode, where 3 photogenerated surface holes, 3h⁺ (green dots) accumulate in the reaction cluster. Subsequently they equilibrate with the triply oxidised cluster (blue dots) followed by a water nucleophilic attack (WNA). The rate determining step (rds) is reached and the O-O bond formation takes place (violet dots) followed by the 4th hole transfer and oxygen molecule release.....104

Figure 4-1. A common proposed mechanism in literature for methanol oxidation on metal oxide surfaces, within photocurrent doubling conditions.	116
Figure 4-2. Current/potential (J-V) response of the α -Fe ₂ O ₃ photoanode under dark (black line) and ~1 sun front illumination (electrode/electrolyte) conditions measured in 0.1 M NaOH with varying concentration of methanol by volume as follows: 0% (red), 25% (orange), 85% (light green), 90% (dark green), 95% (blue) and 98% (purple). The vertical arrow indicates the increasing plateau photocurrent densities achieved by the increasing concentration of methanol in the electrolyte. The horizontal arrow indicates the decrease in the required applied potential to obtain catalytic currents.	120
Figure 4-3. a) Current/time (chronoamperometric) response of the α -Fe ₂ O ₃ photoanode in 95% CH ₃ OH in 0.1 M NaOH under continuous ~1 sun front illumination conditions at 0.55 V vs Ag/AgCl (inset: charge extracted calculated from the area under the chronoamperometric curve vs time) and b) calibration curve for the spectrophotometric detection of CH ₂ O. Absorbance measured at 549 nm as a function of the CH ₂ O concentration prepared by dilution from a standard (200 ppm) solution.....	121
Figure 4-4. Formaldehyde evolution, calculated with 100% Faradaic efficiency (line) and measured (triangles), following the described spectrophotometric titration	122
Figure 4-5. Oxidation of 95% CH ₃ OH in 0.1 M NaOH on α -Fe ₂ O ₃ as a function of 5 s on/5 s off pulsed 356 nm illumination (~1 to ~35 mW cm ⁻²). PIA signal of surface valence band hole density (p _s) probed at 650 nm under a) 0.55 V and b) 0.00 V vs Ag/AgCl and simultaneous assay of TPC under c) 0.55 V and d) 0.00 V vs Ag/AgCl.	122
Figure 4-6. Oxidation of 95% CH ₃ OH in 0.1 M NaOH on α -Fe ₂ O ₃ . Optical signal decays (when light was turned off) under 0.00 V (light grey) and 0.55 V (dark grey) vs Ag/AgCl. Qualitative indication of surface hole recombination participating in the consumption of holes at low applied potentials. The signals chosen for normalisation were the closest to ~0.5 mΔOD, 5 mW cm ⁻² (light orange) in Figure 4-5.a and 26.4 mW cm ⁻² (dark blue) in Figure 4-5.b.	124
Figure 4-7. Current/potential (J-V) response of the TiO ₂ photoanode under chopped ~1 sun front illumination (electrode/electrolyte) conditions measured in 0.1 M NaOH with varying concentration of methanol as follows: 0% (red), 4% (pruple), 25% (orange) and 50% (green).	125

Figure 4-8. Current/potential (J-V) response of the α -Fe₂O₃ (blue) and TiO₂ (green) photoanodes in 95% and 4% CH₃OH in 0.1 M NaOH respectively, under chopped ~ 1 sun front illumination conditions. The stars indicate the applied potentials at which the photo-induced absorption spectroscopy studies were carried out. 125

Figure 4-9. Rate of methanol oxidation measured at 0.55 V for α -Fe₂O₃ and -0.80 V vs Ag/AgCl for TiO₂ (inset) as a function of methanol concentration in 0.1 M NaOH. 127

Figure 4-10. Kinetic comparison between water – 0.1 M NaOH – (red) and methanol – 95% CH₃OH in 0.1 M NaOH – (blue) oxidation kinetics of reaction on α -Fe₂O₃, a) Normalised PIA decay at $\sim 1.5 m\Delta OD$ measured at 650 nm under 0.55 V vs Ag/AgCl and b) rate law analysis for water and methanol oxidation measured at 650 nm under 0.55 V and 0.00 V vs Ag/AgCl..129

Figure 4-11. Methanol oxidation on α -Fe₂O₃ at 0.55 V vs Ag/AgCl kinetic analysis based uniquely on the optical signal, a) Initial rates law analysis, negative gradient of PIA signal (dp/dt) within the first 30 ms as a function of the surface hole density (p_s) and b) surface hole density decay when light was turned off for a steady-state (p_s) of 0.23 $h^+ nm^{-2}$ (black) and its corresponding fitting to second order kinetics (red).....131

Figure 4-12. Rate law analysis, J^{ph} vs p_s for the oxidation of CD₃OD in aqueous (D₂O) 0.1 M NaOD on α -Fe₂O₃ at 0.55 V (orange) compared to the rate law for the oxidation of CH₃OH on α -Fe₂O₃ at 0.00 V (light blue) and 0.55 V (dark blue). 132

Figure 4-13. Rate law analysis, J^{ph} vs p_s for the oxidation of CH₃OH on α -Fe₂O₃ at 0.00 V (light blue) and 0.55 V (dark blue) vs Ag/AgCl and on TiO₂ at -0.80 V (green) vs Ag/AgCl applied potentials. The dotted lines represent a linear fitting with gradient 2. 133

Figure 4-14. Plausible methanol oxidation mechanism on α -Fe₂O₃, in which the cooperative function of two surface holes ($hs +$) results in a C-H bond breaking during the rate determining step with carbon rehybridization.⁴¹ The surface and valence band (VB) of the α -Fe₂O₃ photoanode are also represented. 135

Figure 5-1. Schematic representation of the processes involving photogenerated charge carriers taking place in a hematite photoanode where a) holes are transferred to the electrolyte from the valence band and b) holes are transferred to ‘surface states’ which participate in the reaction as intermediates. 145

Figure 5-2. Characterisation of the hematite photoanodes employed herein, a) UV-Vis absorption spectra of the as-prepared (blue) and annealed (red) α -Fe₂O₃ photoanodes in 1 M

NaOH and b) raman spectra of both, the AP (red) and AN (blue), α -Fe₂O₃ photoanodes compared to a reference hematite spectrum and the FTO/TiO₂ substrate. This image is from the reference.¹⁰ 147

Figure 5-3. Current/potential (J-V) response of the planar α -Fe₂O₃ photoanodes, AN (red) and AP (blue), under dark (dashed lines) and chopped $\sim$ 1 sun front illumination (electrode/electrolyte) conditions (solid lines) measured in 1 M NaOH electrolyte. The arrow indicates the $\sim$ 200 mV shift in both, dark current and photocurrent potentials after annealing. 149

Figure 5-4. Photocurrent/potential (J^{ph} -V) response of the planar α -Fe₂O₃ photoanodes under $\sim$ 1 sun front illumination (electrode/electrolyte) conditions measured in 1 M NaOH (solid lines) and with a hole scavenger, 95% CH₃OH in 1 M NaOH (dashed lines). a) AP (blue) and b) AN (red) samples. 150

Figure 5-5. Transient absorption spectral response measured 100 μ s (squares and dashed lines) and 100 ms (triangles and solid lines) after a 130 μ J cm⁻² 355 nm laser pulse, of the planar, AP (blue) and AN (red), α -Fe₂O₃ photoanodes at a) 0.76 V and b) 1.50 V vs RHE, respectively in 1 M NaOH electrolyte. 151

Figure 5-6. Transient absorption decays probed at 650 nm after a 130 μ J cm⁻² 355 nm laser pulse, of the planar α -Fe₂O₃ photoanodes in 1 M NaOH electrolyte as a function of a positive applied potential, 0.76, 1.16 and 1.51 V vs RHE (increasing grey scale). a) AP and b) AN samples respectively. The solid lines (increasing colour scale) indicate the single exponential fit. ...152

Figure 5-7. Transient absorption decays probed at 580 nm after a 130 μ J cm⁻² 355 nm laser pulse, of the planar α -Fe₂O₃ photoanodes in 1 M NaOH electrolyte as a function of a positive applied potential, 0.76, 1.16 and 1.51 V vs RHE (increasing colour scale). a) AP (blue) and b) AN (red) samples respectively. 153

Figure 5-8. Transient photocurrent measurement after a 130 μ J cm⁻² 355 nm laser pulse, of the planar α -Fe₂O₃ photoanodes in 1 M NaOH electrolyte as a function of a positive applied potential, from 0.76 to 1.51 V (colour scale) vs RHE for the a) AP (blue) and b) AN (red) samples respectively. 154

Figure 5-9. Normalised steady-state spectral response, measured $\sim$ 5 s after a 16 mW cm⁻² 365 nm LED continuous illumination pulse. a) α -Fe₂O₃ photoanodes held at 1.50 V vs RHE of the planar, AP (blue) and AN (red), b) AP (blue) and c) AN (red) spectral response as a function

of the applied potential from 0.8 to 1.5 (colour scale) V vs RHE, respectively in 1 M NaOH electrolyte. 155

Figure 5-10. Photogenerated hole optical absorption calibration. a) PIA signal of the accumulated holes at the α -Fe₂O₃ surface monitored at 650 nm during the 5 s ON/5 s OFF pulsed 365 nm LED illumination at 0.85 V vs RHE, b) transient photocurrent density produced by the initial extraction and subsequent surface electron-hole recombination of the extracted charges and c) correlation between the recombined charges and the steady-state optical absorption measured at 650 nm and 0.85 V vs RHE as a function of light intensity, leading to a hole extinction coefficient of 700 M⁻¹cm⁻¹. 157

Figure 5-11. Photocurrent density (J^{ph}) vs. photoinduced absorption signal, probed at 650 nm, as a function of irradiation intensity at steady-state conditions for the water oxidation reaction on the AP (blue triangles) and AN (red squares) flat α -Fe₂O₃ photoanodes at different applied potentials. The dotted lines correspond the fitting for the 1st and 3rd reaction orders discussed in Chapter 3. The arrow indicates the increasing irradiation intensity needed to produce the same photocurrent upon decreasing the applied potential as more states are filled available to trap holes. 158

Figure 5-12. Correlation between the photocurrent-potential (J^{ph} -V) behaviour, in 1 M NaOH electrolyte, with the optical amplitude, measured at 100 μ s, of the photogenerated holes measured at 650 nm of both, a) AP (blue) and b) AN (red) α -Fe₂O₃ photoanodes. Additionally, for the AP (blue) photoanode it is shown the differential absorption ($\Delta \Delta \text{OD}$), measured at 30 μ s, corresponding to the trapped charges observed optically at 580 nm shown in Figure 5-7.a and electrically in Figure 5-8. 160

Figure 5-13. Schematic illustration of possible band structure and light induced processes upon increasing the applied potential (from left to right) in both, a) AP and b) AN ALD α -Fe₂O₃ photoanodes respectively. The dashed arrows indicate trapping and recombination processes and the dashes and empty circles represent full and empty mid-band gap states, respectively. 161

Figure 5-14. Comparison between the a) measured photocurrent density with the corresponding b) optical absorption probed at 650 nm of both, a) AP (blue) and b) AN (red) α -Fe₂O₃ photoanodes held, for this example, at 1.5 V vs RHE in 1M NaOH. 163

Figure 5-15. Comparative kinetic analysis, in ‘turn-over frequencies’ of water oxidation the AP (blue) and AN (red) $\alpha\text{-Fe}_2\text{O}_3$ photoanodes at different applied potentials probed at 650 nm in 1M NaOH electrolyte. For comparison, equivalent data for an APCVD film (discussed in Chapter 3) is also shown. The rate law data is presented as ‘turn-over frequencies’ vs surface hole density.....164

Figure 5-16. Schematic representation of the rate determining step in an ALD planar undoped compared to a Si-doped nanostructured $\alpha\text{-Fe}_2\text{O}_3$ photoanodes. Upon hole accumulation, water oxidation reaction proceseds via the mechanism of reaction discussed in Chapter 3 (herein only the rds, the O-O bond formation, of the reaction is represented). 165

Chapter 1. Introduction



Word cloud of this Chapter

'I have no doubt that we will be successful in harnessing the Sun's energy. ... If sunbeams were weapons of war, we would have had solar energy centuries ago'

Sir George Porter

1.1. Nature and environment

Although currently world population is not increasing exponentially, as many people believe, but rather linearly, the number of inhabitants in our planet is still growing, which therefore increases the energy and food demand. When the industrial revolution took place about two centuries ago, the world population started growing exponentially with fertility rates plateauing for a few decades, leading to ~7.5 billion inhabitants by 2017.¹ Current estimations project a stabilisation in the population between 9.6 and 13.2 billion people by the end of this century. While fertility rates have been decreasing in Asia, Europe and America, they are still increasing in Africa, which essentially means that there is a migration effect of new-borns towards poverty and inequality.²

A growing and migrating population requires more equalitarian access to an increasing demand of natural resources, such energy, which historically have been associated with issues of political nature. Currently, the annual world primary energy consumption is about 5.7×10^{20} J, which is equivalent to ~18 TW,³ with carbon-based sources, *i.e.* coal, oil and natural gas, accounting for the 82% (14.8 TW) of such production. This primary energy requirement, according to the U. S. Energy Information Administration, is projected to rise 28% by 2040 based on the current economic growth, with the highest share from non-OECD* countries,⁴ which is associated partly with their still increasing fertility rates. Therefore, finding, controlling and exploiting natural resources such as oil, coal, natural gas and water will be key for these countries to develop their emergent economies.

The Intergovernmental Panel on Climate Change (IPCC) in its *fifth assessment report* concluded that mankind has 'very likely' promoted climate change.⁵ As such, the past, current and projected world energy consumption, highly based on oil, coal and natural gas, is responsible for the anthropogenic release of greenhouse gases (GHG), which among others include carbon dioxide (CO₂), methane (CH₄), water vapour (H₂O) and nitrous oxide (N₂O). The

* OECD: The Organisation for Economic Co-operation and Development

International Energy Agency (IEA) estimated that in 2014 the 68% of GHG anthropogenic emissions came from the energy sector (including transportation sector), where CO₂ contributes with 90% of such emissions (see Figure 1-1).⁶ As example, in 2014, more than 33 billion tonnes of CO₂ were released into the atmosphere⁷ and although, from 2014 carbon emissions due to primary energy consumption were plateauing, in 2017 this figure increased 1.6%.³

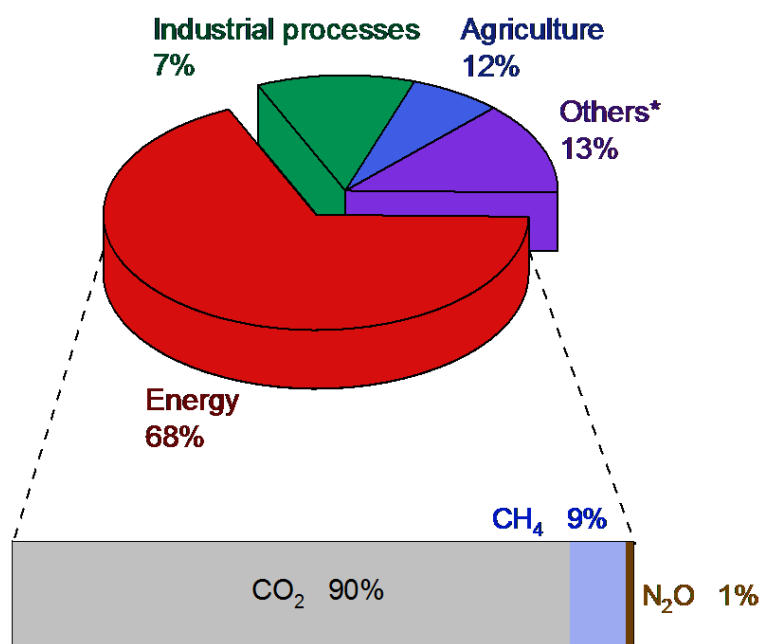


Figure 1-1. Anthropogenic greenhouse gas (GHG) estimated emissions in 2014. Data taken from the *CO₂ emissions from fuel combustion: Overview* report by the International Energy Agency.⁶

*Others include N₂O from non-agricultural emissions, waste, biomass burning and post-burn decay, among others.

Efforts to reduce GHG emissions have been made in the past few decades by signing different agreements in Kyoto, Cancun and more recently in Paris. In the Paris agreement, a global warming limit of 1.5 °C above pre-industrial levels started being pursued, compared to the 2 °C limit set before.^{8,9} It is clear that, to avoid exceeding this 1.5 °C global warming limit, collaborative efforts from different disciplines are required. In terms of climate change adaptation, GHG reduction targets appears to be decisive towards meeting this goal. These targets vary across the continents, with China, Russia and the European Union as the parties with more percentage of CO₂ reduced (~20% – 30%) based on their targets amongst the top 10 highest emitting parties.^{6,10} For adaptation purposes, more inclusive policies to avoid marginalisation and better education for people should also be considered. A synergy between a fair and inclusive political system and proper education would improve

communities decision making process towards a more rational energy consumption and even towards the development of net-zero energy communities.^{5,11} Regarding climate change mitigation efforts, essentially a decarbonisation process needs to take place *via* moving away from depleting fossil fuels^{12–14} through improving actual and generating new technologies, involving the use renewable sources of energy. These mitigation efforts, that would achieve more robust economies, particularly benefit communities historically socially and economically marginalised as they are more vulnerable to the climate change.⁵ Within this framework implementing the use of renewable energy sources is essential to achieve a more sustainable and equal society.

1.2. Example of Colombia

Colombia, the second most diverse country on planet Earth, has an economy that has grown an average of 4.3% in the past 15 years, which is above the average OECD growth of 1.7%.¹⁵ This sustained economic growth, the recently signed peace agreement with the FARC[†] guerrilla and the fulfilment of other requisites have recently granted Colombia a membership in the OECD. Colombia consumed an average of ~57 GW in 2017, with a share of carbon-based sources (oil, coal and natural gas) of ~70% of the primary energy consumption³ and with ~60-70% of the electricity being generated by hydropower.¹⁶ However, this share can change during the year according to the weather, which is highly dependent on climate phenomena such El Niño (dry season).¹⁷ This phenomenon leads to water scarcity for human consumption and in hydroelectric reservoirs, therefore it is vital not only to move away from fossil fuels, but also to reduce the dependence on hydropower for electricity generation in tropical countries.

As mentioned before, according to the IPCC, socially and economically marginalised communities are potentially more vulnerable to the effects of climate change. A clear example of this is the *National Interconnected System* that covers 97% of Colombians to the grid across 48% of the country.¹⁶ The 3% non-connected population live in rural areas where a significant portion of the economy comes from the agroindustry, which is very susceptible to climate change. A consequence of this is the perspective, for example, of famous Colombian coffee plantations to migrate towards higher lands in the following decades.⁵

[†] Fuerzas Armadas Revolucionarias de Colombia

Therefore, not only climate change adaptation efforts, but mitigation is key for a sustainable growth of emergent economies.

Adaptation to climate change in Colombia has particularly focused on improving the management of natural hazards as well as economical subsidies, driven by recent flooding events caused by La Niña phenomenon (opposite to El Niño, when extreme rainfalls take place). Concerning policies, although, there is a program to attend vulnerable communities, especially women in poverty, strong inclusive policies towards equity and education need to be designed.^{18,19} Climate change mitigation efforts in Colombia had involved the connection to the grid of the non-interconnected zones to move from burning fossil fuels and the increase of biofuel production. However, it was not until 2013 that policy makers started to look at other renewables with a target of 6.5% from renewable sources to generate electricity.^{20,21} These efforts led Colombia to reduce its CO₂ emissions in 7.1% in 2017.³ More importantly, this emissions reduction could continue at similar levels as long as the investment in renewables is maintained, with a significant potential for wind and solar power generation.¹⁶ In the following section, the potential of solar energy, among the renewable energy sources, is explored.

1.3. Solar energy

The efforts towards a sustainable economy in a more equal society must be done alongside implementing the use of renewable energy sources, which in turn need to be both abundant and available for everybody. As such, the sun, which is the ultimate fount of most of renewable and non-renewable energy sources, fulfils both requirements: it is abundant and available across the planet. Figure 1-2 compares the annual energy consumption with the proven reserves of fossil and nuclear energy sources and the yearly renewables potential.

It is apparent from Figure 1-2 that today's world primary energy requirement could be still fulfilled by fossil fuels. However, their total proven reserves (~62 ZJ) are comparable to the potential of only tidal, biomass and wind energy combined for the coming 2 decades (potentially ~66 ZJ), with some of these lacking wide availability across the Earth. The potential of solar energy on our planet is ~23000 TW, for the coming ~5 billion years, which exceeds by far the 18 TW of primary energy on Earth. This makes the sun as one of the most attractive alternatives to decarbonise our energy production.

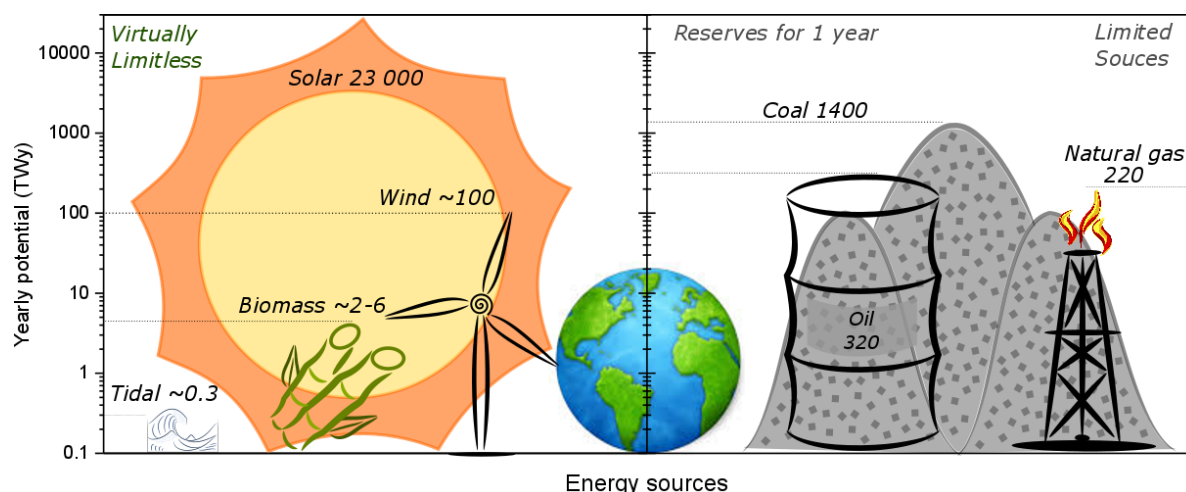


Figure 1-2. Yearly potential of the most common renewable energy sources, *i.e.* tidal, biomass, wind and solar expressed in terawatts of energy that could be utilised in average in a year in a logarithmic scale (left box), data from the *International Energy Agency*.²² The ~18 TW of primary energy consumed in 2017 are represented by the Earth globe in the figure and the proven fossil fuels reserves are displayed in the right box, data from *BP Statistical Review of World Energy*.³ Note that the fossil fuels potential is calculated with the base of one year.

One of the most important ways of utilising solar energy nowadays is the use of photovoltaic materials, to transform photons into an electrical current in a solar cell. A great variety of materials, from inorganic to organic, have been investigated for solar-to-electricity purposes giving rise to different families of solar cells. Currently, the most used material is silicon, used to manufacture single and polycrystalline Si solar cells with efficiencies between 20 and 30% depending on the device structure. Elements from the groups III and V, such Ga, In, P and As, have shown to form appropriate junctions, between them, for solar cells holding the largest efficiencies world records ranging from ~30% to 46%. Other inorganic elements such Cu, Sn, In, Zn and Se forming chalcopyrite (CIGS) and kesterite (CZTS) structures in thin films have been shown to exhibit photovoltaic efficiencies ranging from ~12 to 25%.²³ However, the production costs of some of these solar cells remain high and some of them use toxic and rare metals. A low-cost type of solar cell, a dye-sensitised solar cell (DSSC), was reported to be 7 – 8% efficient by O'Regan and Grätzel in 1991.²⁴ Although, efficiencies in DSSC technology remains ~12-14%, several systems have been inspired on this concept,²⁵ for example from studying different electrolyte solutions to different type of sensitizers.^{26–28} More recently, another inorganic material, perovskite type of solar cells, has attracted the attention of the community for their good performance and rapid improvement in their efficiencies increasing from ~14% to ~23% in less than a decade.^{29–31} However, there are still important challenges to overcome for this promising technology to be commercially exploited

such as their use of heavy metals and their limited stability.^{32,33} Furthermore, organic materials such conjugated polymers and fullerenes have extensively been investigated to produce organic solar cells,³⁴ with a recently published efficiency record of 17.3% for a tandem device³⁵ and the possibility to design flexible organic solar cells ahead.³⁶

Some of the common limiting factors, among the different materials used in solar cells, are exciton generation and diffusion and losses during charge carrier separation at interfaces.^{37–41} The understanding of these photophysical processes have led to a rapid progress in developing more efficient solar cells, which are being widely implemented. This brings therefore, the attention to the limitation of the intermittency (as represented in Figure 1-3) and seasonality for solar energy to be even more employed in the household sector. Such limitations are also important for the industrial and transport sectors, for which energy storage will be discussed in the following section.

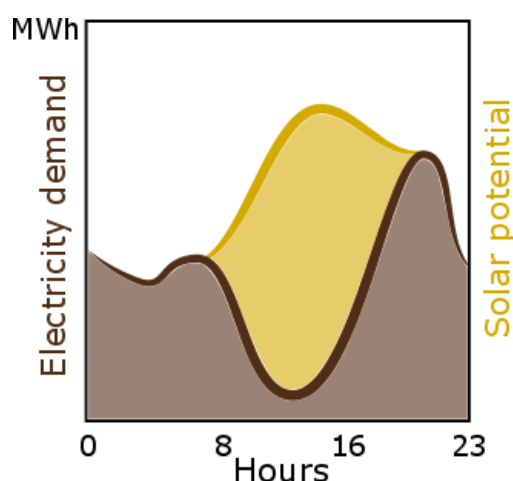


Figure 1-3. Schematic representation of electricity demand in the household sector (brown) compared to the solar potential (yellow) in a typical summer day in Texas, U.S.A. For reference.⁴²

1.4. From natural to artificial photosynthesis

With the efficiency of solar cells increasing rapidly and their production and subsequent installation costs decreasing, storing the electricity produced is paramount to overcome the challenges derived from the intermittency of sunlight, such as the day/night cycle or clouds, as well as seasonality. Solar energy can be stored either by electricity accumulation in a battery or by transformation into other type of energies such as potential, thermal or chemical.

Thermal energy storage for example, uses solar concentrators to heat fluids (water, thermal oils, organic fluids, liquid metals or molten salts), which would produce steam on-demand to generate electricity. Hydraulic potential energy is another example of storing electricity from renewables, known as pumped hydro energy storage, when water is transported (pumped) from a lower to an upper reservoir in dams.^{43–45} On the other hand, batteries (often referred as electrochemical energy technologies to account for the different types) have attracted a lot of attention as energy storing systems due to their cost and storing efficiency. The use of this technology has been focused on powering relatively small devices and some electric vehicles, mostly with lithium batteries. However, the low energy density and the weight of the batteries, as well as challenges in their long-term stabilities and life cycles, have hampered their extended implementation in the household and transport sectors.^{46–48} An alternative and globally utilised strategy to store solar energy is in the form of chemical bonds carried out by photosynthetic organisms with plants as one of the closest examples.

The natural photosynthesis process (Figure 1-4.a) has served as an inspiration to develop artificial photosynthetic systems (Figure 1-4.b) capable of storing the energy of sunlight in high energy content chemicals. Such chemicals are, amongst others, hydrogen (H_2) *via* water splitting or into carbon-based fuels such as methanol (CH_3OH), ethanol (CH_3CH_2OH), dimethyl ether (CH_3OCH_3), among others through CO_2 reduction strategies (also known as solar fuels).^{49–55} In green plants, natural photosynthesis is described by the Z-scheme, depicted in Figure 1-4, where sunlight is stored in NADPH molecules using water as electron donor. Solar energy is absorbed in the photosystem II (PS II) exciting a chlorophyll molecule (P680 referring to the ground state and P680* to the excited state). Charge carrier separation is achieved by transferring electrons from the excited state P680* to the photosystem I (PS I) through an electron transport chain, which produces also ATP units. In PS I electrons are excited by light absorption and are subsequently transported to the $NADP^+$ reductase protein, which reduces $NADP^+$ to NADPH. This process synthesises two high energy molecules (ATP and NADPH), which then take part in the CO_2 fixation process during the Calvin cycle. Upon illumination and charge carrier generation in PS II, the oxidised form of the P680 chlorophyll, receives electrons from the oxygen evolution centre that extract electrons from the oxidation of water.^{55–57} This concept of a light-induced redox reaction is applied in photoelectrochemical

water splitting systems and is the subject of the next section, ever since Fujishima and Honda reported PEC water splitting on TiO_2 .⁵⁸

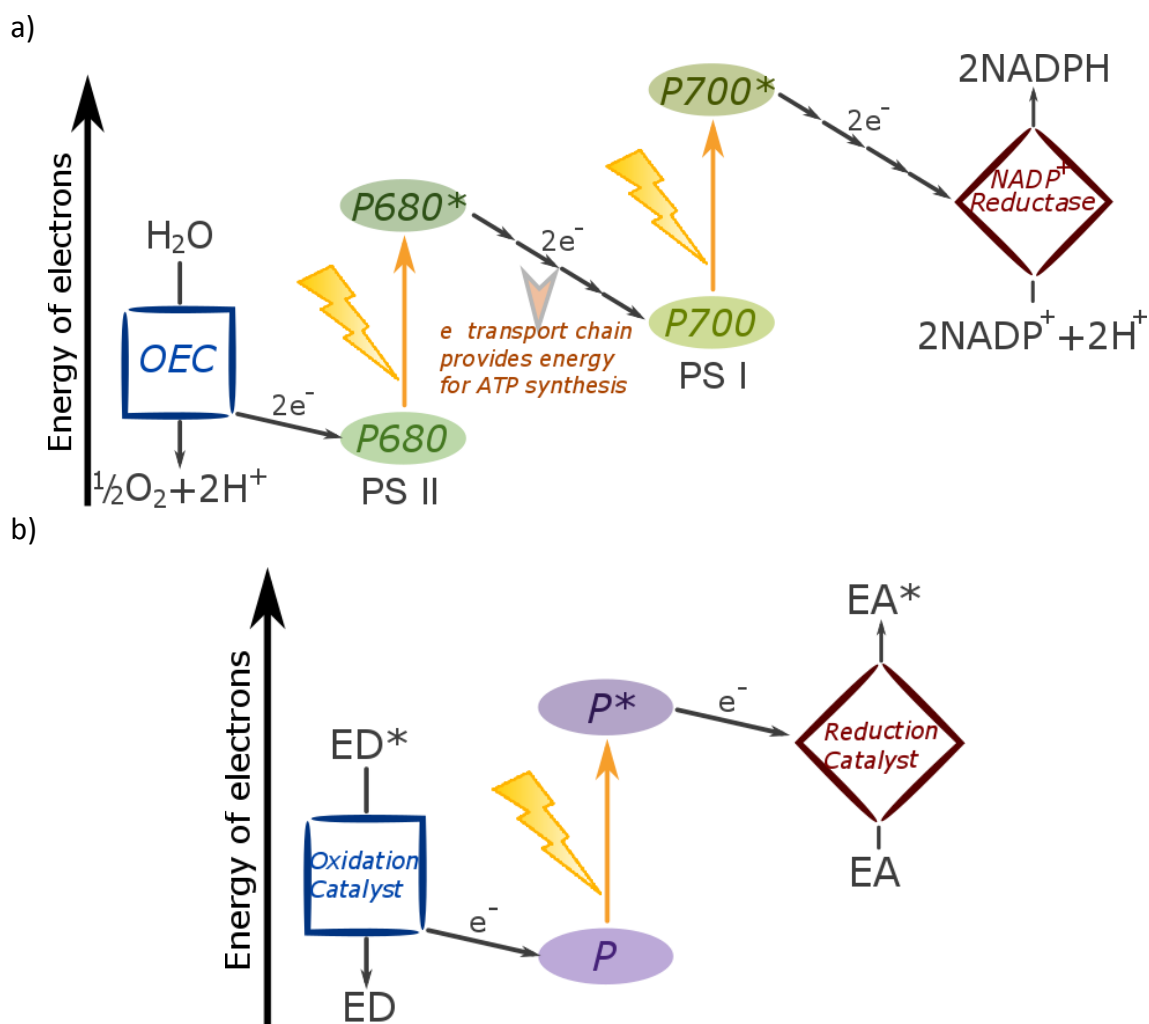


Figure 1-4. a) Schematic representation of the Z-scheme in natural photosynthesis, where light is absorbed in photosystems I and II, PS I and PS II respectively. Electrons are donated from water at the oxygen evolution centre (OEC) and are finally transferred to produce NADPH, which participates in the Calvin cycle (CO_2 fixation process). b) Artificial photosynthesis scheme, where light excites electrons in a photoabsorber (P for ground state and P^* for its excited state), which are transferred to an electron acceptor species (EA) through a reduction catalyst. An electron donor (ED) acts as source of electrons to complete the chain.

1.5. PEC water splitting

In a photoelectrochemical (PEC) cell, a light-induced redox reaction would store sunlight into the chemical bonds of a reduced electron acceptor (EA^*) with an electron donor (ED) being oxidised to complete the reaction (see Figure 1-4.b). As such, PEC water splitting to produce hydrogen has emerged as a promising clean and potentially inexpensive renewable solar fuel, most often using semiconductor metal-oxides as both, photoanode and photocathode (a schematic representation is shown in Figure 1-5).⁵⁴ In solar driven H_2

evolution process, the proton reduction reaction takes place at the photocathode, where to produce one H_2 molecule 2 reducing equivalents are required (Equation 1-1). These electrons are provided by the water oxidation process (Equation 1-2) on the photoanode. This water oxidation reaction has been found to be slow and kinetically demanding and as such it is often considered the bottleneck of the overall water splitting process.⁵⁹ This reaction will be the focus of study in *Chapters 3 and 5* of this thesis. The water splitting reaction, when conducted at standard conditions, occurs with an electrochemical cell potential of -1.23 V , which corresponds to a Gibbs free energy (ΔG) of $+237\text{ KJ mol}^{-1} H_2$, indicating that water splitting is not a spontaneous reaction and thermodynamically uphill.

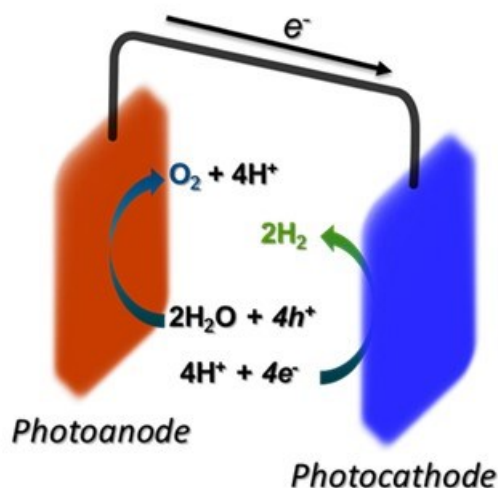
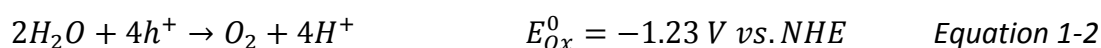


Figure 1-5. Schematic representation of a PEC water splitting system. Water, as electrons source, is oxidised in the photoanode, releasing 4 H^+ , which are subsequently reduced in the photocathode, producing H_2 .

PEC water splitting based on metal oxide photoelectrodes is not the only strategy for solar fuels synthesis. Different approaches and materials are being investigated to achieve more efficient solar to hydrogen (STH) conversion efficiencies. For example, some $Ru^{60,61}$ and Ir -based⁶² homogeneous molecular catalysts (WOC) have shown fast water oxidation kinetics (turn-over frequencies, TOFs) comparable to that for PS II. For the H_2 evolution reaction, Ni and Fe -based homogeneous molecular catalysts inspired in the hydrogenase enzyme have also been shown to evolve hydrogen efficiently.^{63,64} One of the major drawbacks of homogeneous reactions is product and catalyst separation from the medium and therefore, to overcome this problem, hydrogenases have been immobilized on solid electrodes in

semiautificial photosynthetic systems.^{64,65} This heterogeneous molecular catalysis approach have also been used for both water oxidation and proton reduction catalysts, either by anchoring catalysts on conducting electrodes, on dye-sensitised semiconductors or visible light absorbing semiconductors.^{66–68} Further information on these strategies and materials for solar water splitting can be found in a recently published review paper in this topic by Tang and co-workers.⁶⁹

Up to this point, the mentioned technologies consist of integrated light absorbers and catalysts. However, a technology that could be considered for a short-term implementation is to have the best of both technologies, light absorption and conversion to electricity, *i.e.* photovoltaics (PV), and electrocatalytic water splitting, also known as PV + electrolysis.⁷⁰ Currently, the electrodes for electrocatalytic water splitting are mainly made of precious metals, Pt, Ru, Ir and their oxides⁷¹ and although these materials are stable and achieve high current densities, other electrode approaches and materials are being investigated to lower electrode costs. Ir-based catalysts and NiOOH and FeOOH are promising electrocatalysts that have also shown to increase the efficiency of water splitting when deposited on metal-oxide photoanodes such α -Fe₂O₃ and BiVO₄,^{72–74} which brings the attention to metal-oxide semiconductors as promising materials for PEC water splitting.⁷⁵

1.5.1. Semiconductor electrochemistry

Any semiconductor material is normally characterised primarily by its valence and conduction band positions, giving rise to its band gap, as well as by its Fermi level (see Figure 1-6.a). A key aspect of a PEC cell is the semiconductor/electrolyte interface where charge transfer to the electrolyte occurs, bringing the attention to n-type semiconductor photoanodes where water oxidation takes place.

When a n-type semiconductor is brought in contact with an electrolyte solution, the Fermi level of the semiconductor equilibrates with the redox potential of the electrolyte by transferring electrons (majority carriers) from the electrode to the electrolyte. As such, the Fermi level is moved to more positive potentials and the redox potential in the Helmholtz layer of the electrolyte increases until equilibrium is reached (Figure 1-6.b). In equilibrium, the reduction in the density of majority carriers (electrons) near the surface, causes the formation of a space charge layer (SCL), which becomes a depletion layer when electrons are depleted from the SCL. An electric field (built-in voltage) is therefore formed across the SCL

giving rise to a band bending effect. This plays a key role in the separation of charge carriers generated upon illumination of photoelectrodes with photons more energetic than the bandgap (E_g). Under illumination, electron/hole pairs are generated within the space charge layer in metal-oxide photoanodes, the band bending drives electrons away from the surface and holes towards it. This causes a perturbation in the equilibrium, increasing the population of positive charges (holes) in the SCL,^{76–78} generating a photovoltage understood as the difference between the fermi level of holes and the semiconductor fermi level.

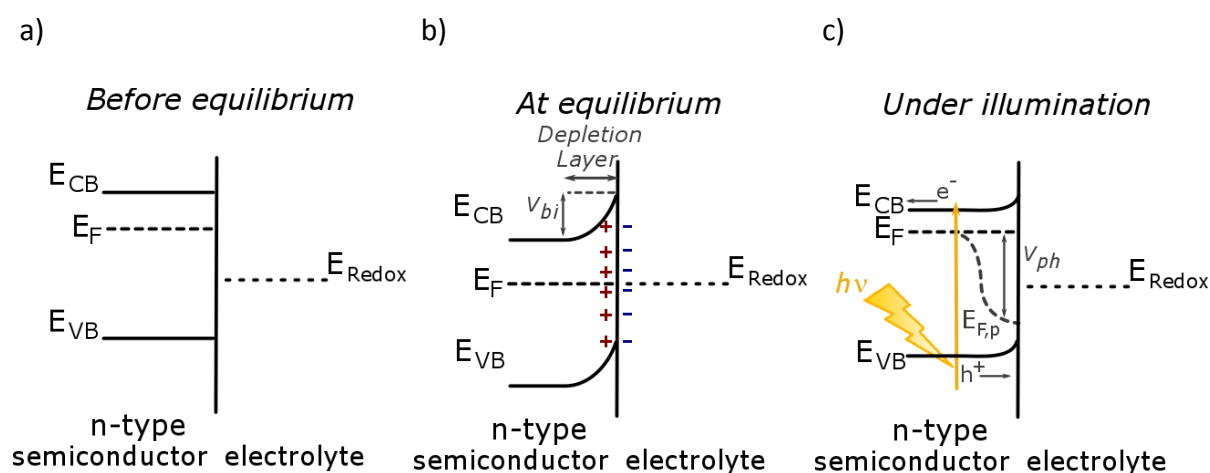


Figure 1-6. Energy band diagrams for an electrode (n-type semiconductor) / electrolyte interface, a) before equilibrium in dark (flat band conditions), b) once equilibrium is reached in dark and c) under illumination. E_{CB} and E_{VB} correspond to the conduction and valence band edges, respectively and E_F and E_{Redox} to the fermi level and the electrolyte redox potential, respectively. $E_{F,p}$ refers to the fermi level of holes under illumination. V_{bi} and V_{ph} correspond to the built-in potential and photovoltage respectively.

The most common method to evaluate a photoanode performance is measuring its (photo)current / potential response (also known as J - V curves), where the current is monitored while the applied potential is changed (see Figure 1-7 for a schematic illustration). Ideally, a photoanode material in dark should initiate the catalysis (*i.e.*, should have its current onset potential) at 1.23 V corresponding to an overpotential (η_{OER}) of 0 V (light blue curve in Figure 1-7). Upon illumination, the photocurrent onset is limited by the flat band potential of the photoanode (~ 0.3 V for hematite, for example, as shown in Figure 1-8). As such, ideally hematite should exhibit a photocurrent onset near 0.3 V_{RHE} and plateau rapidly to its maximum photocurrent to produce a fill factor (ff) close to the unity (see dark blue curve in Figure 1-7). Lower ff values are often associated with bulk electron-hole and back electron-hole recombination as well as uncompensated solution resistances. This along with other loss

pathways, that will be discussed in the following sections, causing the J - V to deviate from the ideal behaviour, lower plateau photocurrents and large η_{OER} , as exemplified in Figure 1-7, red curve. Such overpotential in Figure 1-7 is defined as the extra potential required to reach the onset of catalysis. Note that it is currently being discussed in literature the report of overpotentials at a defined photocurrent density. It is also important to note that, net power storage only takes place when the applied potential is $<1.23 \text{ V}_{\text{RHE}}$.^{49,79–81}

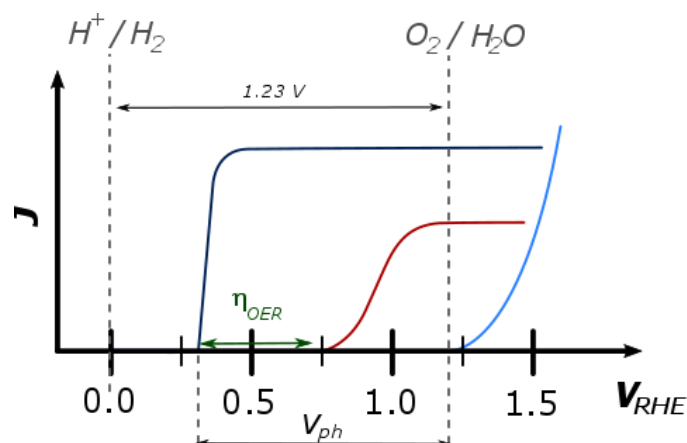


Figure 1-7. Schematic illustration of a current / potential (J - V) curve. The redox potentials for proton reduction and water oxidation are indicated by the dashed lines, separated by the 1.23 V required to split water. The ideal J - V curves in dark (light blue) and under illumination (dark blue) conditions for a photoanode with a flat band $\sim 0.3 \text{ V}$, resembling a hematite photoanode. The red curve exhibits a schematic illustration of the actual J - V behaviour of a hematite photoanode. η_{OER} corresponds to the overpotential required by the photoanode to start driving water oxidation and V_{ph} corresponds to the photovoltage.

Before turning to review the loss pathways (recombination) for holes and the kinetics of hole transfer to the electrolyte, I will turn to discuss the key requirements for a good semiconductor photoanode.

1.5.2. Metal-oxide photoanodes

Efficient photoelectrode materials for solar hydrogen synthesis, should fulfil some requirements. Firstly, *efficient absorption of visible light*, given by the semiconductor band gap (E_g), is fundamental. This is due to the solar spectrum has its maximum photon flux in the visible-near infrared region, from $\sim 400 \text{ nm}$, which correspond to a band gap of $\sim 3.1 \text{ eV}$. Figure 1-8 shows the band gap and band edges for some of the most studied metal-oxide semiconductor materials, where it is apparent that TiO_2 is in the limit of absorption, whereas $\alpha\text{-Fe}_2\text{O}_3$ and BiVO_4 are considered promising materials, whose band gap (2.1 eV and 2.4 eV, respectively) corresponds to an absorption edge of 590 and 520 nm, respectively.⁵⁵

Figure 1-8 highlights a thermodynamics requirement, *i.e.*, the suitability of *band edges position*, where the conduction band must be negative enough to drive proton reduction and/or the valence band must be positive enough to be able to oxidise water. In this case, the four metal oxides shown in Figure 1-8 are able to oxidise water, but only TiO_2 would be able to reduce protons to hydrogen whereas the other 3 materials require the application of external applied potentials or the use of a complementary photocathode.^{50,82,83}

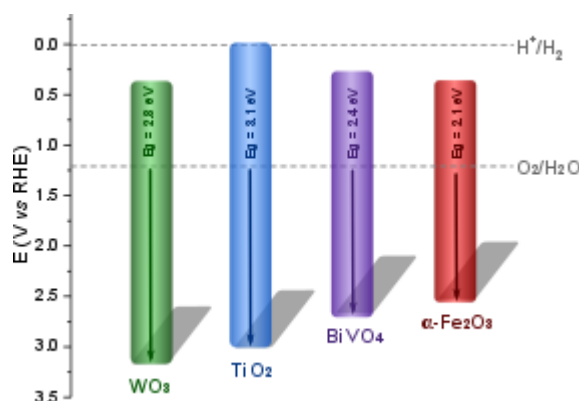


Figure 1-8. Band positions for some of the most common metal-oxide semiconductors used in water oxidation, compared to the redox potential for hydrogen and oxygen evolution at their best performing pH conditions. pH 13 for $\alpha\text{-Fe}_2\text{O}_3$ and TiO_2 , pH 7 for BiVO_4 and pH 1 for WO_3 . E_g : $\alpha\text{-Fe}_2\text{O}_3$ (2.1 eV), BiVO_4 (2.4 eV), TiO_2 (3.1 eV) and WO_3 (2.8 eV).

Two important photoelectrode requirements to be able to scale-up a PEC water splitting technology are *low cost* and *stability* under both, dark and illumination, conditions. This is a particular problem for most non-metal oxide semiconductors (with low band gaps) that can be more expensive (use more scarce metals) and can easily undergo in photocorrosion, such as GaAs or GaP.

Efficient charge transport is also an important requirement for an efficient photoelectrode, as charge collection depends upon how easily charges can move through the material. This, for example, gives rise to differences when illuminating from the electrode/electrolyte interface or through the back contact of the semiconductor.

It is also ideal that the charge transfer to the electrolyte takes place with *low overpotentials*. These are normally associated to the kinetics of hole transfer to the electrolyte that are frequently in competition with surface recombination. Such losses are overcome by increasing the applied potential (not desired) or by depositing other metal-oxide overlayers to passivate the surface or to catalyse the water oxidation reaction.⁸²

As such, one of the metal oxides that fulfils some of these requirements as a photoanode (low cost, chemical stability, visible light absorption and suitable valence band to oxidise water) is Fe_2O_3 in its hematite structure, which is the main material studied in this thesis.

1.5.3. $\alpha\text{-Fe}_2\text{O}_3$

Iron oxides appear in very different polymorphic forms in nature, with hematite ($\alpha\text{-Fe}_2\text{O}_3$) being the most abundant, stable and oldest known iron-based mineral. Due to its abundance, stability in alkaline solutions and visible light absorption, hematite has attracted the attention of a wide community as photoanode for solar water oxidation. A simple search of the concepts “ $\alpha\text{-Fe}_2\text{O}_3$ ” and “water oxidation” shows more than 2000 references in *SciFinder*, and more than 5000 entries in *Google Scholar*.

1.5.3.1. Crystalline and electronic properties

Crystalline hematite is an n-type semiconductor, which has a corundum structure with a hexagonal unit cell with oxygen anions (O^{2-}) arranged along the [001] direction. In this hexagonal closed-packing array, the iron cations (Fe^{3+}) occupy two thirds the interstices of the formed octahedral structures (two occupied sites per vacant site). This crystalline structure produces pairs of $\text{Fe}(\text{O})_6$ octahedra, with tetragonal vacant sites formed when the octahedral share 3 of their edges (face sharing), being the [110] crystal plane the most common orientation found in hematite photoanodes (see Figure 1-9).⁸⁴ Structural disorder in this structure can be caused by temperature treatment and ion substitution. For example, Fe^{3+} vacancies can be accompanied by OH^- substituting O^{2-} or by OH^- incorporation in low synthesis temperature.⁸⁵

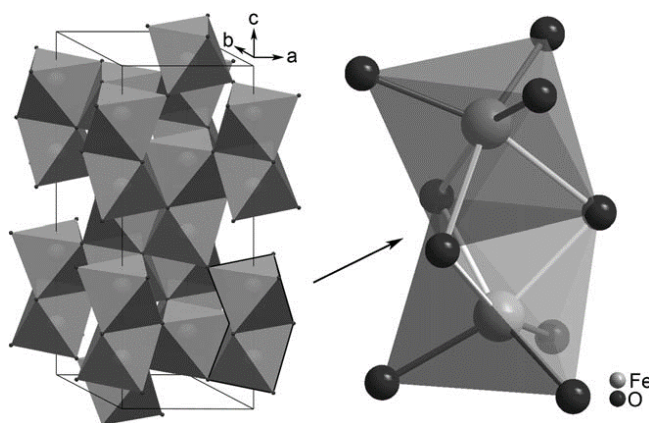
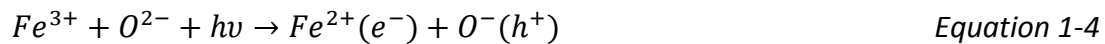
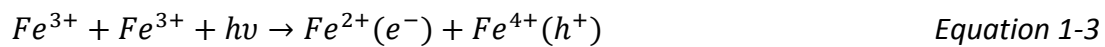


Figure 1-9. Crystalline structure of $\alpha\text{-Fe}_2\text{O}_3$. The octahedral structure forming pairs of $\text{Fe}(\text{O})_6$ units along the [001] direction is shown. This figure is from the reference ⁸⁶.

Hematite is mainly composed, in terms of its cation, by Fe^{3+} , which has a d^5 electronic configuration where, in an octahedral coordination such as in hematite, the t_{2g} orbitals have lower energies than the e_g . Computational chemistry, including DFT+U and wave-function based calculations as well as the GW approximation (Green's function method with screened Coulomb potential)^{87,88} have suggested these d^5 orbitals hybridize with O_{2p} orbitals forming the valence band of hematite. These calculations, in conjunction with X-ray emission and absorption spectroscopies (XES and XAS), have shown such hybridization, with the conduction band dominated by Fe $3d$ states.^{88–90} For example, Ansari *et. al.*, noted that the mixed Fe-O character of valence band holes, show a higher density of Fe states (PDOS). This implies that those holes would have more Fe character than O, whereas the conduction band is dominated by Fe $3d$ states.^{90,91} However, the results of these calculations change with the level of doping or vacancies as well as the crystal phase, complicating direct connection to real materials.⁹²

Hematite has a reported indirect bandgap, depending on the synthesis method, between 2.0 – 2.2 eV, corresponding to an absorption edge between 650 and 560 nm. The absorption of photons in the visible region by α - Fe_2O_3 , has been assigned to $d-d$ transitions from coupled Fe^{3+} ions with absorption coefficients (α) of the order of 10^3 cm^{-1} . Ligand to metal charge transfer (LMCT) transitions have been reported to occur in the UV region for hematite with α of 10^5 cm^{-1} .^{86,93,94} This also results in one of the strongest limitations for hematite photoanodes, the large absorption depth (α^{-1} of 118 nm at $\lambda = 550\text{ nm}$)⁹⁵ compared to the hole diffusion length (2 – 4 nm).⁹⁶ As such, upon photoexcitation two charge transfers (see Equation 1-3 and Equation 1-4) might take place in hematite:



where in both cases a conduction band electron would correspond to Fe^{2+} species and a photogenerated hole would correspond to an O^- when LMCT occurs and an Fe^{4+} species when a $d-d$ transition takes place. However, describing a photogenerated hole as either pure Fe^{4+} or O^- species might not be accurate due to the hybridized (O_{2p} with $Fe\ 3d$ orbitals) nature of the valence band in hematite.

1.5.3.2. Doping and vacancies

Electrical conductivities in polycrystalline hematite have been reported to be very low (in the order of $10^{-14} \Omega^{-1} \text{ cm}^{-1}$, with charge transport being suggested to take place *via* small localised polaron hopping, characterised for their low mobility, from $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ for electrons and $\text{Fe}^{4+} \rightarrow \text{Fe}^{3+}$ for holes.^{97,98} Doping strategies, introducing foreign atoms, have shown to improve hematite photoanodes performance towards water oxidation. The most common strategy is to increase the density of majority carriers (electrons in an n-type semiconductor) of hematite by substituting Fe^{3+} for M^{4+} ions such as, Zr^{4+} , Sn^{4+} , Ti^{4+} or Si^{4+} , inducing the formation of Fe^{2+} and oxygen vacancies, resulting in donor density levels of $\sim 10^{19} \text{ cm}^{-3}$ and conductivities of $\sim 0.1 \Omega^{-1} \text{ cm}^{-1}$.^{86,99–101}

The effect of vacancies in hematite, such as Fe vacancies, have been studied by DFT calculations, although yet to be experimentally observed. Interestingly, these vacancies have been suggested to be present at the $\alpha\text{-Fe}_2\text{O}_3$ surface, localized on uncoordinated O atoms with energies $\sim 0.6 \text{ eV}$ above the valence band edge of hematite,^{102,103} opposite to the energetic position where O vacancies are normally reported, mid-bandgap or closer to the conduction band as explained below. The effect of oxygen vacancies, intrinsic or induced by M^{4+} ion substitution, in the band structure of hematite is of a high interest as this is a strategy to improve conductivities in hematite. Electrochemical impedance spectroscopy (EIS) have been used by several groups to study the effect of such O vacancies on the performance of $\alpha\text{-Fe}_2\text{O}_3$ photoanodes towards water oxidation. These vacancies are frequently associated with ‘surface states’ and are normally assigned to be located between ~ 0.4 and 0.9 eV below the conduction band of hematite.^{104,105} The effect of such oxygen vacancies in electron trapping has also been optically observed by means of transient absorption spectroscopy by our group and will be further discussed in *Chapter 5* in this thesis.

The presence of two distributions of states associated to the surface of hematite have been reported by Hamann and co-workers¹⁰⁶ by means of cyclic voltammetry (CV) measurements, affecting the onset of water oxidation catalysis. These distributions of states are located $\sim 0.1 \text{ eV}$ below the conduction band, which are removed upon high temperature (800°C) annealing and $\sim 0.4 \text{ eV}$ below the conduction band (previously mentioned), which have been proposed as surface states driving water oxidation (although they might not have enough ΔG to drive the reaction).^{106,107} Similar CV measurements, by Peter and co-workers, have also reported

mid-gap states associated to the surface of hematite between ~ 0.4 and 1.0 eV above the valence band, also associated with surface states driving water oxidation.^{108,109} Opposite to Shavorskiy *et. al.*,¹¹⁰ who propose that such electronic states are not always present, by means of *operando* XPS measurements, and still hematite photoanodes drive water oxidation. Yatom *et. al.*,^{87,111} have suggested, by means of DFT calculations, that the mid band gap states originated from oxygen vacancies are localised ~ 2 eV above the valence band edge. As such, it appears that the use of the term '*surface states*' in literature has been used to describe any energetic state (with a specific chemical structure) present within the space charge layer of hematite photoanodes.^{112,113} Some of them have been associated with recombination centres^{114–116} and some with water oxidation intermediates,^{107,117,118} where some of them seem to be located at potentials that are not oxidative enough to drive water oxidation. This discussion will be further addressed in *Chapter 5*.

1.5.3.3. Increasing hematite photoanodes performance

Theoretically, the maximum photocurrent an $\alpha\text{-Fe}_2\text{O}_3$ photoanode, with a bandgap of 2.1 eV, can deliver under one sun conditions (AM 1.5G) is 12.5 mA cm^{-2} , equivalent to an efficiency of 15.4% STH (solar to hydrogen).¹¹⁹ Note that such maximum photocurrent is calculated for a thick hematite photoanode with an absorptance of unity and no light reflection. A more realistic model to predict maximum photocurrents accounting for different absorptances is given by Cendula *et. al.*¹²⁰ Although rapid progress has been made in the last decade towards increasing the performance of hematite photoanodes, as shown in Figure 1-10, the current state-of-the-art film reaches $\sim 48\%$ of the theoretical maximum limit. This hydrogen treated $\alpha\text{-Fe}_2\text{O}_3$ photoanodes include a $\sim 3.5\text{ nm}$ TiO_2 and a 'Co-Pi' overlayers, prepared by a controlled chemical bath deposition, exhibit photocurrent densities of $\sim 6\text{ mA cm}^{-2}$ at 1 sun illumination conditions and $1.23\text{ V}_{\text{RHE}}$.¹²¹

Different strategies have been used historically to increase the performance of hematite photoanodes towards water oxidation. Doping with M^{4+} ions, as stated in the previous section, can aid with the conductivity problems of $\alpha\text{-Fe}_2\text{O}_3$ and has been used successfully according to Figure 1-10. Other common strategy is to modify the photoanode surface where different treatments have been explored, from film dipping in for example Co^{2+} ions solution to deposition of metal-oxide overlayers. Some of those overlayers, for example the inexpensive 'Co-Pi' water oxidation electrocatalyst which is an amorphous CoO_x ,¹²⁷ have been

claimed to be responsible for the catalysis water oxidation when deposited on hematite photoanodes, based on electrochemical and impedance measurements.^{107,128} However, evidence from intensity modulated photocurrent (IMPS), transient absorption spectroscopy (TAS) and light-induced spectroelectrochemistry (LI-SEC) spectroscopies (the two latter developed in Durrant group), have shown that although a Co-Pi overlayer might be able to accumulate a minimal density of holes. These findings suggest that water oxidation takes place from hematite holes rather than at the Co-Pi surface,^{117,129,130} and the performance improvement is due to reduction in surface recombination.

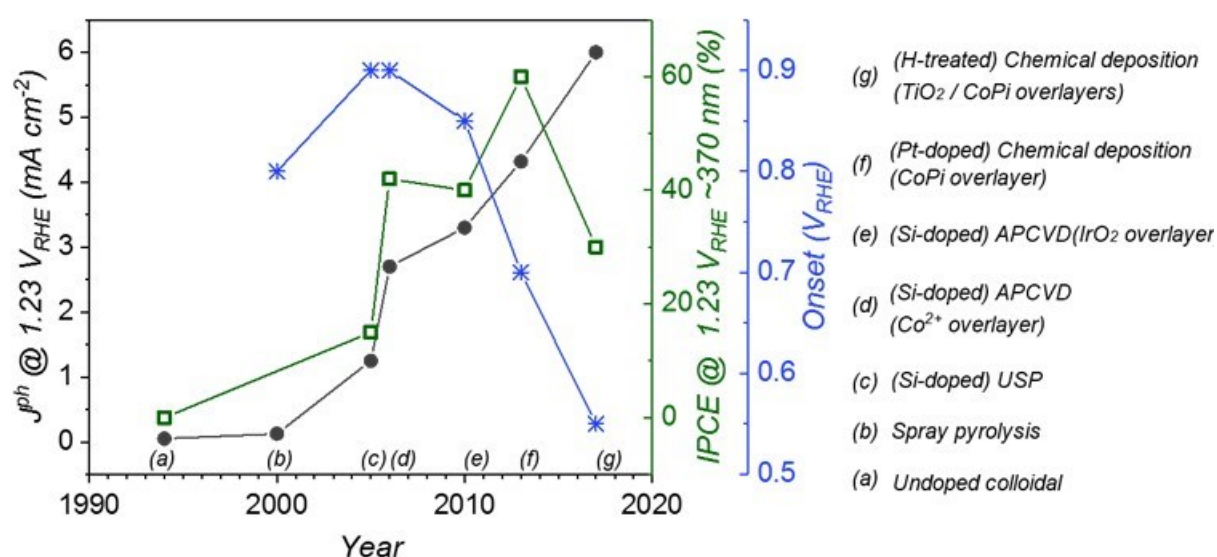


Figure 1-10. Progress on hematite photoanodes performance to date, based on photocurrent density (J^{ph}) measurements at 1.23 V vs RHE at one sun illumination conditions. The incident photon to current efficiency (IPCE) is shown in green and the catalytic onset potentials for such photoanodes are shown in blue. This includes nanostructuring and doping as well as surface modification, all indicated next to the corresponding J^{ph} value. USP: Ultrasonic spray pyrolysis, APCVD: Atmospheric pressure chemical vapour deposition, H-treated: annealing under a hydrogen flow and Co-Pi: Cobalt-phosphate overlayer.^{84,121–126}

It is apparent from Figure 1-10 that, at least in part, improving the synthesis of hematite has aid the quantum efficiency that correlates with the photoanodes better performance (*i.e.*, better photocurrents). Additionally, the addition of metal-oxide overlayers are shown to improve the catalytic onset potential, in some cases, as discussed above, due to reduction in surface recombination and in other cases due to an improvement in the catalysis. Such catalytic effect towards water oxidation has been observed, by electrochemical and IMPS techniques, when IrO_x is deposited on hematite photoanodes, by increasing the reaction rate

constant.^{126,131} Nanostructuring $\alpha\text{-Fe}_2\text{O}_3$ photoanodes have also been used widely to increase their photocurrent densities by increasing the material surface area, light absorption and reducing, in some cases, the distance that holes have to diffuse to reach the surface. As such, different nanostructures have been investigated, including dendrites, rods, tubes, sheets and cones, etc, with cauliflower mesostructured produced by APCVD being one of the most studied structures due to its high performance compared to others.^{84,86,119,132}

1.5.3.4. Charge carriers kinetics in hematite

The strategies to increase the photocurrent density of a $\alpha\text{-Fe}_2\text{O}_3$ photoanode mentioned before have a paramount effect on the kinetics of photogenerated electrons and holes in such photoanodes, from reducing recombination to increase water oxidation rate constants. These light-induced processes in $\alpha\text{-Fe}_2\text{O}_3$ photoanodes, *i.e.*, charge generation, separation, recombination and transfer (reaction), have been extensively studied previously by different optical and electrochemical techniques.^{50,82} Figure 1-11 depicts a general scheme for such light-induced processes. Slow recombination processes and hole transfer to the electrolyte, as introduced previously, have been debated to take place through ‘surface states’ (see Figure 1-11.a) or directly from the valence band (see Figure 1-11.b).

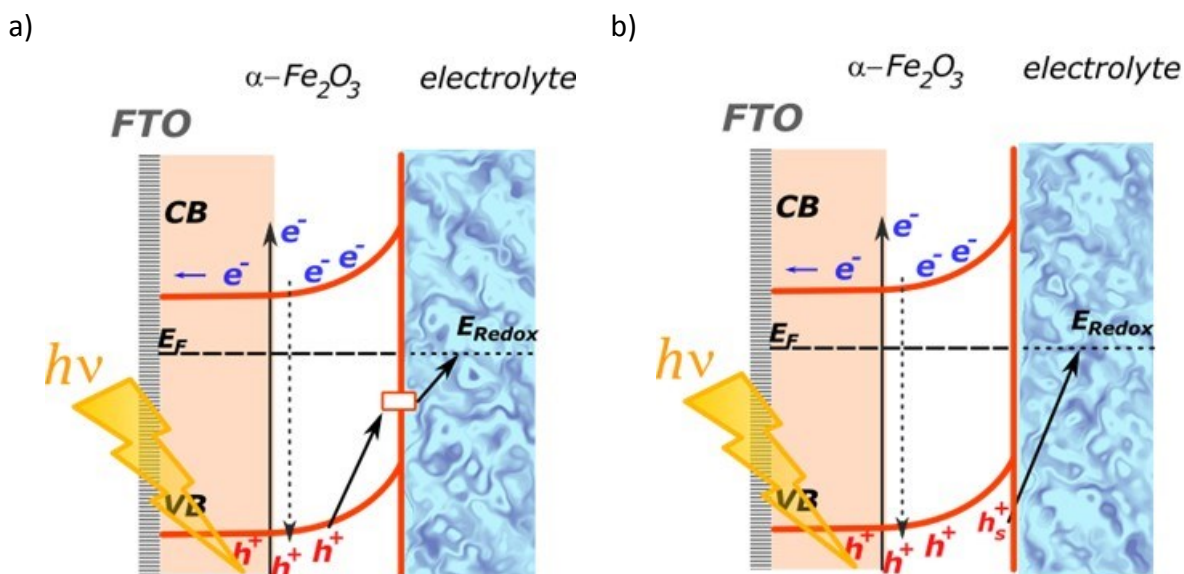


Figure 1-11. A general scheme of light-induced and catalytic events taking place in an $\alpha\text{-Fe}_2\text{O}_3$ photoanode, including the two discussed kinetic models a) charge transfer to the electrolyte (and also recombination) through ‘surface states’ and b) charge transfer to the electrolyte from valence band holes.

More specifically, some ultra-fast transient spectroscopies such as extreme-ultraviolet (XUV) and absorption (TAS), have proposed that upon excitation, charge separation takes

place within ~ 100 fs. This is followed by a fast trapping process in ps - ns timescale by photogenerated holes.¹³³ This fast trapping process has been observed optically following the optical absorption of holes and trap states at 750 and 580 nm, respectively.¹³⁴ Although, the kinetics of the photogenerated holes (probed at 750 nm) are bias sensitive, at high applied potentials more than 50% of the charges recombine within 1 ns. On the contrary, at those potentials within ~ 100 ps, electron traps (580 nm optical signal) are filled leading to a negative optical signal that corresponds to a ground state absorption bleach.

The surviving photogenerated holes and electrons undergo in non-geminate recombination, shown by TA spectroscopy, within the μs - ms timescale,¹³⁵ requiring the application of a positive potential for holes to be transferred to the electrolyte. Slower recombination processes also take place once the photogenerated holes arrive to the photoanode surface, known as back electron-hole, occurs within the ms timescale under small band-bending conditions making the need of applying a positive potential to suppress it (see Figure 1-12).^{136,137}

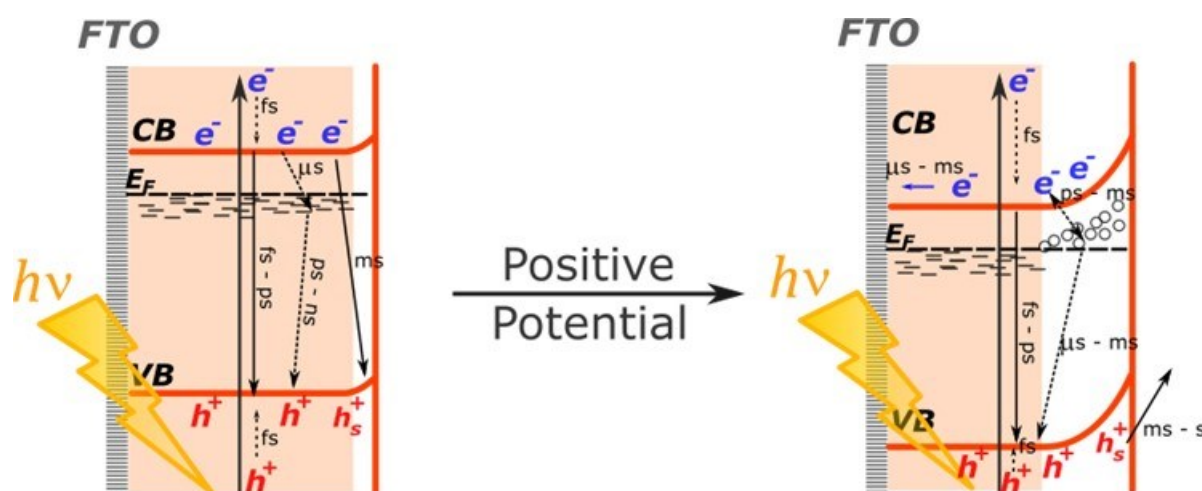


Figure 1-12. A more detailed scheme of light-induced and catalytic events taking place in an α - Fe_2O_3 photoanode, proposed in Durrant group. The timescales are a general picture as geminate and non-geminate recombination as well as charge carrier separation, transport and reaction are different hematite.

These light-induced processes are connected with the catalytic process at the surface, where good charge transport and fast water oxidation kinetics are key for efficient photoanodes. Long-lived photogenerated holes have been shown to be a crucial factor in photoanode efficiency as, for many different metal-oxide photoanodes, the oxygen evolution reaction has been reported to take place within the early $ms - s$ timescale.^{138–140} In the

particular case of hematite photoanodes, slow *ms* – *s* water oxidation has been observed by means of TAS,^{139,141,142} electrochemical impedance spectroscopy (EIS)¹⁴³ and intensity-modulated photocurrent spectroscopy (IMPS).^{108,117} The fact that the water oxidation reaction is well-established to take place within seconds timescale, allow us to design strategies to further study its kinetics and reaction mechanism, by rate law analyses. This is the monitoring of the rate of reaction as a function of the concentration of the reacting species, to be addressed in the following section.

1.6. Rate law analysis

Light-initiated processes in α -Fe₂O₃ photoanodes *i.e.*, charge generation, separation and recombination are relatively well understood, as seen in the previous section. However, the ultimate goal of such processes is charge transfer, *i.e.* chemical reaction. Therefore, it is of paramount importance to understand such catalytic chemical processes.

Traditionally, for most of the chemical reactions the kinetic and mechanistic information, especially in homogeneous systems, is obtained by means of rate law analyses.¹⁴⁴ A rate law correlates the rate of a chemical reaction (see a general example in Equation 1-5) with the concentration of reactants. A rate law (see Equation 1-6) is always established experimentally and can provide mechanistic insights when combined with other experimental methods.



where A and B are the reactants and C and D are the products of the reaction. The rate law of this reaction as a function of the reactants is:

$$r = k_{Rxn} \cdot [A]^{\alpha} \cdot [B]^{\beta} \quad \text{Equation 1-6}$$

where k_{Rxn} is the reaction rate constant, [A] and [B] and α and β correspond to the concentrations and reaction order respectively, with respect to the reactants A and B.

This approach to investigate chemical reactions have been used historically in the solar fuels field, to study solar-driven water splitting with molecular catalysts.^{60,145,146} However, its use in heterogeneous PEC water splitting have been hampered by the multi-redox chemistry of metal-oxide photoanodes. A wide-used strategy to approach a rate law is to vary the concentration of one of the reactants whilst the rest are in excess. This will provide insights about the rate constant (kinetic information) and the order of reaction (mechanistic

information) of the studied reaction as a function of the selected reactant. In heterogeneous catalysts, this approach has been used for H₂ evolution and CO₂ reduction as a function of H⁺ or CO₂ concentrations,^{147–149} but not as a function of the concentration of photogenerated charges (catalytic sites), which would enlighten the understanding of the photocatalytic water splitting.

Opposite to electrocatalytic systems, where information about the rate determining step (rds) of the reaction is obtained from Tafel plots (therefore, from *JV* curves),¹⁵⁰ for photoelectrocatalytic systems, the analysis of Tafel plots is diffculted by the multi-redox chemistry in metal oxides,¹⁵¹ the presence of surface and/or intraband states¹⁵² as well as back electron-hole (surface) recombination processes.¹³⁷ Recently, we have developed a new method to study the rate law of heterogeneous photocatalytic reactions, focusing on analysing water oxidation. This method (details described in *Chapter 2*) combines the concomitant analysis of the rate of reaction (*i.e.* charge transfer to the electrolyte) with the quantification of the population (*i.e.* concentration) of accumulated charges. The rate of reaction in a PEC cell is obtained electrochemically by means of transient photocurrent (TPC) measurements and the charge (electrons for *p*-type or holes for *n*-type semiconductors) population is monitored optically by means of a photo-induced absorption (PIA) analysis and are correlated by the kinetic model described in the next *Chapter*.

1.7. In the next chapters

Renewable hydrogen generation through solar water splitting to achieve more sustainable and equal societies is hampered by the sluggish kinetics of water oxidation on metal-oxide photoanodes, such as α -Fe₂O₃. Although, the major loss source for low solar-to-hydrogen efficiencies is fast recombination processes, very little is known on how oxidation reactions proceed at the surface of α -Fe₂O₃ photoanodes. Therefore, after explaining the materials and techniques used for this thesis in *Chapter 2*, the main purpose of *Chapter 3* is to study *in-operando*, the kinetics and the mechanism of water oxidation on a state-of-the-art hematite photoanode. In this chapter, other metal oxides are studied to propose a general water oxidation mechanism of reaction. This chapter is followed by the study of the kinetics and mechanism of methanol oxidation, on a nanostructured hematite photoanode, as a model organic substrate intended to substitute water as electron donor for more efficient hydrogen evolution in *Chapter 4*. As discussed above, different synthetic methods and temperature

treatments have been used to improve the efficiency of water oxidation on hematite, as such in *Chapter 5*, the kinetics of recombination, charge trapping, accumulation and reaction on two undoped flat hematite photoanodes are studied.

1.8. References

1. United Nations, D. of E. and S. A. *World Population Prospects: The 2017 Revision*. (2017).
2. Gerland, P. *et al.* World population stabilization unlikely this century. *Sci.* **346**, 234–7 (2014).
3. BP. *BP Statistical Review of World Energy 2018*. (2018).
4. U.S. Energy Information Administration. *International Energy Outlook 2017*. (2017).
5. IPCC. *Climate Change 2014: Impacts, Adaptation and Vulnerability. Part A:* (Cambridge University Press, 2014).
6. International Energy Agency. *CO2 emissions from fuel combustion: Overview*. (2017).
7. Commission, E. *EU energy in figures. Statistical pocketbook 2017*. (2017). doi:10.2833/80717
8. Meinshausen, M. *et al.* Greenhouse-gas emission targets for limiting global warming to 2 °C. *Nature* **458**, (2009).
9. UNFCCC. *ADOPTION OF THE PARIS AGREEMENT - Paris Agreement text English*. (2015).
10. European Commission. *Third report on the State of the Energy Union*. (2017).
11. Karunathilake, H., Hewage, K., Mérida, W. & Sadiq, R. Renewable energy selection for net-zero energy communities: Life cycle based decision making under uncertainty. *Renew. Energy* **130**, 558–573 (2019).
12. Höök, M. & Tang, X. Depletion of fossil fuels and anthropogenic climate change-A review. *Energy Policy* **52**, (2013).
13. Chiari, L. & Zecca, A. Constraints of fossil fuels depletion on global warming projections. *Energy Policy* **39**, 5026–5034 (2011).
14. Murray, J. & King, D. Climate policy: Oil’s tipping point has passed. *Nature* **481**, 433–435 (2012).
15. Olaberría, E. *Reigniting growth through productivity-enhancing reforms in Colombia*. (2017). doi:10.1787/dac4e274-en
16. Procolombia. *Electric Power in Colombia Power Generation*. (2015).
17. World Energy Council. *World Energy Issues Monitor 2018: PERSPECTIVES ON THE GRAND ENERGY TRANSITION*. (2018).
18. Campillo, G., Mullan, M. & Vallejo, L. *Climate Change Adaptation and Financial Protection - SYNTHESIS OF KEY FINDINGS FROM COLOMBIA AND SENEGAL*. (2017). doi:10.1787/0b3dc22a-en
19. Ramirez-Villegas, J., Salazar, M., Jarvis, A. & Navarro-Racines, C. E. A way forward on adaptation to climate change in Colombian agriculture: perspectives towards 2050. *Clim. Change* **115**, 611–628 (2012).
20. Ruiz, B. J. & Rodríguez-Padilla, V. Renewable energy sources in the Colombian energy policy, analysis and perspectives. *Energy Policy* **34**, 3684–3690 (2006).
21. GlobalData. *Colombia Renewable Energy Policy Handbook 2017*. (2017).
22. Perez, M. & Perez, R. *Update 2015 - A fundamental look at supply side energy reserves for the planet*. (2015).
23. NREL. *Best research cell efficiencies*. (2017).

24. O'Regan, B. & Grätzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* **353**, 737–740 (1991).
25. Hagfeldt, A., Boschloo, G., Sun, L., Kloo, L. & Pettersson, H. Dye-Sensitized Solar Cells. *Chem. Rev.* **110**, 6595–6663 (2010).
26. Lee, H. *et al.* PbS and CdS Quantum Dot-Sensitized Solid-State Solar Cells: “Old Concepts, New Results”. *Adv. Funct. Mater.* **19**, 2735–2742 (2009).
27. Ueno, K., Oshikiri, T., Sun, Q., Shi, X. & Misawa, H. Solid-State Plasmonic Solar Cells. *Chem. Rev.* **118**, 2955–2993 (2018).
28. Ravirajan, P. *et al.* Hybrid nanocrystalline solar cells with a fluorene-thiophene copolymer as a sensitizer and hole conductor. *J. Appl. Phys.* **95**, 1473 (2004).
29. Grätzel, M. The light and shade of perovskite solar cells. *Nat. Mater.* **13**, 838–842 (2014).
30. Green, M. A., Ho-Baillie, A. & Snaith, H. J. The emergence of perovskite solar cells. *Nat. Photonics* **8**, 506–514 (2014).
31. Niu, G., Guo, X. & Wang, L. Review of recent progress in chemical stability of perovskite solar cells. *J. Mater. Chem. A* **3**, 8970–8980 (2015).
32. Saliba, M. *et al.* Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. *Energy Environ. Sci.* **9**, 1989–1997 (2016).
33. Pont, S. *et al.* Tuning CH₃NH₃Pb(I_{1-x}Br_x)₃ perovskite oxygen stability in thin films and solar cells. *J. Mater. Chem. A* **5**, 9553–9560 (2017).
34. Günes, S., Neugebauer, H. & Sariciftci, N. S. Conjugated Polymer-Based Organic Solar Cells. *Chem. Rev.* **107**, 1324–1338 (2007).
35. Meng, L. *et al.* Organic and solution-processed tandem solar cells with 17.3% efficiency. *Science*. **ASAP**, (2018).
36. Qian, D. *et al.* Design rules for minimizing voltage losses in high-efficiency organic solar cells. *Nat. Mater.* **17**, 703–709 (2017).
37. Clarke, T. M. & Durrant, J. R. Charge Photogeneration in Organic Solar Cells. *Chem. Rev.* **110**, 6736–6767 (2010).
38. Bruno, A., Reynolds, L. X., Dyer-Smith, C., Nelson, J. & Haque, S. A. Determining the Exciton Diffusion Length in a Polyfluorene from Ultrafast Fluorescence Measurements of Polymer/Fullerene Blend Films. *J. Phys. Chem. C* **117**, 19832–19838 (2013).
39. Nelson, J., Haque, S. A., Klug, D. R. & Durrant, J. R. Trap-limited recombination in dye-sensitized nanocrystalline metal oxide electrodes. *Phys. Rev. B* **63**, 205321 (2001).
40. Haque, S. A. *et al.* Charge Separation versus Recombination in Dye-Sensitized Nanocrystalline Solar Cells: the Minimization of Kinetic Redundancy. *J. Am. Chem. Soc.* **127**, 3456–3462 (2005).
41. Haque, S. A. *et al.* Parameters Influencing Charge Recombination Kinetics in Dye-Sensitized Nanocrystalline Titanium Dioxide Films. *J. Phys. Chem. B* **104**, 538–547 (2000).
42. Schmalensee, R. *The Future of Solar Energy*. (2015).
43. Armaroli, N. & Balzani, V. *Energy for a sustainable world*. (WILEY-VCH Verlag, 2011).
44. Deane, J. P., Gallachor, B. P. & Mckeogh, E. J. Techno-economic review of existing and new pumped hydro energy storage plant. *Renew. Sustain. Energy Rev.* **14**, 1293–1302 (2010).

45. Vignarooban, K., Xu, X., Arvay, A., Hsu, K. & Kannan, A. M. Heat transfer fluids for concentrating solar power systems - A review. *Appl. Energy* **146**, 383–396 (2015).
46. Yuan, C., Wu, H. Bin, Xie, Y. & Lou, X. W. D. Mixed Transition-Metal Oxides: Design, Synthesis, and Energy-Related Applications. *Angew. Chemie Int. Ed.* **53**, 1488–1504 (2014).
47. Weber, A. Z. *et al.* Redox flow batteries: a review. *J. Appl. Electrochem.* **41**, 1137–1164 (2011).
48. Etacheri, V., Marom, R., Elazari, R., Salitra, G. & Aurbach, D. Challenges in the development of advanced Li-ion batteries: a review. *Energy Environ. Sci.* **4**, 3243–3262 (2011).
49. Walter, M. G. *et al.* Solar Water Splitting Cells. *Chem. Rev.* **110**, 6446–6473 (2010).
50. van de Krol, R. & Grätzel, M. *Photoelectrochemical Hydrogen Production*. (Springer, 2012). doi:10.1007/978-1-4614-1380-6
51. Lewis, N. S. & Nocera, D. G. Powering the planet: chemical challenges in solar energy utilization. *Proc. Natl. Acad. Sci. U. S. A.* **103**, 15729–35 (2006).
52. Dunn, S. Hydrogen futures: toward a sustainable energy system. *Int. J. Hydrogen Energy* **27**, 235–264 (2002).
53. Zhu, S. & Wang, D. Photocatalysis: Basic Principles, Diverse Forms of Implementations and Emerging Scientific Opportunities. *Adv. Energy Mater.* 1700841 (2017).
54. Grätzel, M. Photoelectrochemical cells. *Nature* **414**, 338–344 (2001).
55. Berardi, S. *et al.* Molecular artificial photosynthesis. *Chem. Soc. Rev.* **43**, 7501–7519 (2014).
56. Barber, J. Photosynthetic energy conversion: natural and artificial. *Chem. Soc. Rev.* **38**, 185–196 (2009).
57. Tachibana, Y., Vayssieres, L. & Durrant, J. R. Artificial photosynthesis for solar water-splitting. *Nat. Photonics* **6**, 511–518 (2012).
58. Fujishima, A. & Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **238**, 37–38 (1972).
59. Peter, L. M. Semiconductor electrochemistry. in *Photoelectrochemical Solar Fuel Production: From Basic Principles to Advanced Devices* (2016). doi:10.1007/978-3-319-29641-8_1
60. Duan, L. *et al.* A molecular ruthenium catalyst with water-oxidation activity comparable to that of photosystem II. *Nat. Chem.* **4**, 418–423 (2012).
61. Francàs, L. *et al.* Kinetic Analysis of an Efficient Molecular Light-Driven Water Oxidation System. *ACS Catal.* **7**, 5142–5150 (2017).
62. Thomsen, J. M., Huang, D. L., Crabtree, R. H. & Brudvig, G. W. Iridium-based complexes for water oxidation. *Dalt. Trans.* **44**, 12452–12472 (2015).
63. Caserta, G. *et al.* Engineering an [FeFe]-Hydrogenase: Do Accessory Clusters Influence O₂ Resistance and Catalytic Bias? *J. Am. Chem. Soc.* **140**, 22 (2018).
64. Wombwell, C., Caputo, C. A. & Reisner, E. [NiFeSe]-Hydrogenase Chemistry. *Acc. Chem. Res.* **40**, 2858–2865 (2015).
65. Sokol, K. P. *et al.* Bias-free photoelectrochemical water splitting with photosystem II on a dye-sensitized photoanode wired to hydrogenase. *Nat. Energy* **1** (2018). doi:10.1038/s41560-018-0232-y

66. Schreier, M. *et al.* Covalent Immobilization of a Molecular Catalyst on Cu₂O Photocathodes for CO₂ Reduction. *J. Am. Chem. Soc.* **138**, 1938–1946 (2016).
67. Liu, X., Inagaki, S. & Gong, J. Heterogeneous Molecular Systems for Photocatalytic CO₂ Reduction with Water Oxidation. *Angew. Chemie Int. Ed.* **55**, 14924–14950 (2016).
68. Willkomm, J. *et al.* Dye-sensitised semiconductors modified with molecular catalysts for light-driven H₂ production. *Chem. Soc. Rev.* **45**, 9 (2016).
69. Wang, Y. *et al.* Mimicking Natural Photosynthesis: Solar to Renewable H₂ Fuel Synthesis by Z-Scheme Water Splitting Systems. *Chem. Rev.* **118**, 5201–5241 (2018).
70. Ardo, S. *et al.* Pathways to electrochemical solar-hydrogen technologies. *Energy Environ. Sci.* (2018).
71. Li, X., Hao, X., Abudula, A. & Guan, G. Nanostructured catalysts for electrochemical water splitting: current state and prospects. *J. Mater. Chem. A* **4**, 11973–12000 (2016).
72. Mulder, F. M., H Weninger, B. M., Middelkoop, J., B Ooms, F. G. & Schreuders, H. Efficient electricity storage with a battolyser, an integrated Ni-Fe battery and electrolyser. *Energy Environ. Sci.* **10**, 756 (2017).
73. Kim, T. W. & Choi, K.-S. Nanoporous BiVO₄ photoanodes with dual-layer oxygen evolution catalysts for solar water splitting. *Science*. **343**, 990–4 (2014).
74. Jang, J.-W. *et al.* Enabling unassisted solar water splitting by iron oxide and silicon. *Nat. Commun.* **6**, (2015).
75. Roger, I., Shipman, M. A. & Symes, Ma. D. Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting. *Nat. Rev. Chem.* **1**, (2017).
76. Zhang, Z. & Yates, J. T. Band Bending in Semiconductors: Chemical and Physical Consequences at Surfaces and Interfaces. *Chem. Rev.* **112**, 5520–5551 (2012).
77. Memming, R. *Semiconductor Electrochemistry*. (WILEY-VCH Verlag, 2001).
78. Bisquert, J., Cendula, P., Bertoluzzi, L. & Gimenez, S. Energy Diagram of Semiconductor/Electrolyte Junctions. *J. Phys. Chem. Lett.* **5**, 205–207 (2014).
79. Mayer, M. T. Photovoltage at semiconductor–electrolyte junctions. *Curr. Opin. Electrochem.* **2**, 104–110 (2017).
80. Nozik, A. J. & Memming, R. Physical Chemistry of Semiconductor–Liquid Interfaces. *J. Phys. Chem.* **100**, 13061–13078 (1996).
81. Peter, L. M. Dynamic aspects of semiconductor photoelectrochemistry. *Chem. Rev.* **90**, 753–769 (1990).
82. van de Krol, R., Liang, Y. & Schoonman, J. Solar hydrogen production with nanostructured metal oxides. *J. Mater. Chem.* **18**, 2311–2320 (2008).
83. Francàs, L. *et al.* Rational design of a neutral pH functional and stable organic photocathode. *Chem. Commun.* **5732**, 5732 (2018).
84. Kay, A., Cesar, I. & Grätzel, M. New Benchmark for Water Photooxidation by Nanostructured α -Fe₂O₃ Films. *J. Am. Chem. Soc.* **128**, 15714–15721 (2006).
85. Cornell, R. M. & Schwertmann, U. *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*. (WILEY-VCH Verlag, 2003). doi:10.1002/3527602097

86. Sivula, K., Le Formal, F. & Grätzel, M. Solar Water Splitting: Progress Using Hematite (α -Fe₂O₃) Photoelectrodes. *ChemSusChem* **4**, 432–449 (2011).
87. Yatom, N. & Caspary Toroker, M. Electronic Structure of Catalysis Intermediates by the G0W0 Approximation. *Catal. Lett.* **146**, 2009–2014 (2016).
88. Liao, P. & Carter, E. A. Testing variations of the GW approximation on strongly correlated transition metal oxides: hematite (α -Fe₂O₃) as a benchmark. *Phys. Chem. Chem. Phys.* **13**, 15189–15199 (2011).
89. Fujimori, A., Saeki, M. & Kimizuka, N. Photoemission satellites and electronic structure of Fe₂O₃. *Phys. Rev. B* **34**, 7318 (1986).
90. Grave, D. A., Yatom, N., Ellis, D. S., Toroker, M. C. & Rothschild, A. The “Rust” Challenge: On the Correlations between Electronic Structure, Excited State Dynamics, and Photoelectrochemical Performance of Hematite Photoanodes for Solar Water Splitting. *Adv. Mater.* 1706577 (2018).
91. Ansari, N. *et al.* Hole localization on Fe₂O₃ from density functional theory and wave-function-based methods. *Phys. Rev. Mater.* **1**, 035404 (2017).
92. Lany, S. Semiconducting transition metal oxides. *J. Phys. Condens. Matter* **27**, 1–18 (2015).
93. Sherman, D. M. & David Waite, T. Electronic spectra of Fe³⁺ oxides and oxide hydroxides in the near IR to near UV. *Am. Mineral.* **70**, 1262–1269 (1985).
94. Galuza, A. I., Beznosov, A. B. & Eremenko, V. V. Optical absorption edge in The exciton-magnon structure. *Low Temp. Phys.* **24**, 144305 (1998).
95. Balberg, I. & Pinch, H. L. The optical absorption of iron oxides. *J. Magn. Magn. Mater.* **7**, 12–15 (1978).
96. Kennedy, J. H. & Frese, K. W. Photooxidation of Water at α -Fe₂O₃ Electrodes. *J. Electrochem. Soc.* **125**, 709 (1978).
97. Rettie, A. J. E., Chemelewski, W. D., Emin, D. & Mullins, C. B. Unravelling Small-Polaron Transport in Metal Oxide Photoelectrodes. *J. Phys. Chem. Lett* **7**, (2016).
98. Iordanova, N., Dupuis, M. & Rosso, K. M. Charge transport in metal oxides: A theoretical study of hematite α -Fe₂O₃. *J. Chem. Phys.* **122**, 124706 (2005).
99. Zandi, O. & Hamann, T. W. The potential versus current state of water splitting with hematite. *Phys. Chem. Chem. Phys.* **17**, 22485–22503 (2015).
100. Mock, J. *et al.* Oxygen vacancy doping of hematite analyzed by electrical conductivity and thermoelectric power measurements. *Phys. Rev. Mater.* **1**, 065407 (2017).
101. Bedoya-Lora, F. E. *et al.* Effects of low temperature annealing on the photo-electrochemical performance of tin-doped hematite photo-anodes. *Electrochim. Acta* **251**, 1–11 (2017).
102. Negreiros, F. R., Pedroza, L. S., Souza, L. & Dalpian, G. M. Surface Fe vacancy defects on haematite and their role in light-induced water splitting in artificial photosynthesis. *Phys. Chem. Chem. Phys* **19**, 31410 (2017).
103. Nguyen, M.-T., Piccinin, S., Seriani, N. & Gebauer, R. Photo-Oxidation of Water on Defective Hematite(0001). *ACS Catal.* **5**, 715–721 (2015).
104. Franking, R. *et al.* Facile post-growth doping of nanostructured hematite photoanodes for enhanced photoelectrochemical water oxidation. *Energy Environ. Sci.* **6**, 500 (2013).

105. Klahr, B., Gimenez, S., Fabregat-Santiago, F., Bisquert, J. & Hamann, T. W. Electrochemical and photoelectrochemical investigation of water oxidation with hematite electrodes. *Energy Environ. Sci.* **5**, 7626–7636 (2012).
106. Zandi, O. & Hamann, T. W. Enhanced Water Splitting Efficiency Through Selective Surface State Removal. *J. Phys. Chem. Lett.* **5**, 1522–1526 (2014).
107. Young, K. M. H., Klahr, B. M., Zandi, O. & Hamann, T. W. Photocatalytic water oxidation with hematite electrodes. *Catal. Sci. Technol.* **3**, 1660–1671 (2013).
108. Cummings, C. Y., Marken, F., Peter, L. M., Wijayantha, K. G. U. & Tahir, A. A. New Insights into Water Splitting at Mesoporous α -Fe₂O₃ Films: A Study by Modulated Transmittance and Impedance Spectroscopies. *J. Am. Chem. Soc.* **134**, 1225–1234 (2012).
109. Peter, L. Energetics and kinetics of light-driven oxygen evolution at semiconductor electrodes: the example of hematite. *J. Solid State Electrochem.* **17**, 315–326 (2013).
110. Shavorskiy, A. *et al.* Direct Mapping of Band Positions in Doped and Undoped Hematite during Photoelectrochemical Water Splitting. *J. Phys. Chem. Lett.* **8**, 33 (2017).
111. Yatom, N., Neufeld, O. & Toroker, M. C. Toward Settling the Debate on the Role of Fe₂O₃ Surface States for Water Splitting. *J. Phys. Chem. C* **119**, 24789–24795 (2015).
112. Sivula, K. Metal Oxide Photoelectrodes for Solar Fuel Production, Surface Traps, and Catalysis. *J. Phys. Chem. Lett.* **4**, 1624–1633 (2013).
113. Hu, Y. *et al.* Molecular Origin and Electrochemical Influence of Capacitive Surface States on Iron Oxide Photoanodes. *J. Phys. Chem. C* **120**, 3250–3258 (2016).
114. Glasscock, J. A., Barnes, P. R. F., Plumb, I. C. & Savvides, N. Enhancement of Photoelectrochemical Hydrogen Production from Hematite Thin Films by the Introduction of Ti and Si. *J. Phys. Chem. C* **111**, 16477–16488 (2007).
115. Ahmed, A. Y., Kandiel, T. A., Oekermann, T. & Bahnemann, D. Photocatalytic Activities of Different Well-defined Single Crystal TiO₂ Surfaces: Anatase versus Rutile. *J. Phys. Chem. Lett.* **2**, 2461–2465 (2011).
116. Le Formal, F., Sivula, K. & Grätzel, M. The Transient Photocurrent and Photovoltage Behavior of a Hematite Photoanode under Working Conditions and the Influence of Surface Treatments. *J. Phys. Chem. C* **116**, 26707–26720 (2012).
117. Peter, L. M., Upul Wijayantha, K. G. & Tahir, A. A. Kinetics of light-driven oxygen evolution at a-Fe₂O₃ electrodes. *Faraday Discuss.* **155**, 309–322 (2012).
118. Klahr, B., Gimenez, S., Fabregat-Santiago, F., Hamann, T. & Bisquert, J. Water Oxidation at Hematite Photoelectrodes: The Role of Surface States. *J. Am. Chem. Soc.* **134**, 4294–4302 (2012).
119. Tamirat, A. G., Rick, J., Dubale, A. A., Su, W.-N. & Hwang, B.-J. Using hematite for photoelectrochemical water splitting: a review of current progress and challenges. *Nanoscale Horiz.* **1**, 243–267 (2016).
120. Cendula, P., Steier, L., Losio, P. A., Grätzel, M. & Schumacher, J. O. Analysis of Optical Losses in a Photoelectrochemical Cell: A Tool for Precise Absorptance Estimation. *Adv. Funct. Mater.* **28**, (2018).
121. Hwa Jeon, T., Moon, G., Park, H. & Choi, W. Ultra-efficient and durable photoelectrochemical water oxidation using elaborately designed hematite nanorod arrays. *Nano Energy* **39**, 211–

- 218 (2017).
122. Young Kim, J. *et al.* Single-crystalline, wormlike hematite photoanodes for efficient solar water splitting. *Sci. Rep.* (2013). doi:10.1038/srep02681
 123. Bjorksten, U., Moser, J. & Gratzel, M. *Photoelectrochemical Studies on Nanocrystalline Hematite Films*. *Chem. Mater* **6**, (1994).
 124. Qian, X. *et al.* Photoelectrochemical characteristics of α -Fe₂O₃ nanocrystalline semiconductor thin film. *Journal of Nanoparticle Research* **2**, (2000).
 125. Duret, A. & Gratzel, M. Visible Light-Induced Water Oxidation on Mesoscopic α -Fe₂O₃ Films Made by Ultrasonic Spray Pyrolysis. *J. Phys. Chem. B* **109**, 17184–17191 (2005).
 126. Tilley, S. D., Cornuz, M., Sivula, K. & Grätzel, M. Light-Induced Water Splitting with Hematite: Improved Nanostructure and Iridium Oxide Catalysis. *Angew. Chemie Int. Ed.* **49**, 6405–6408 (2010).
 127. Kanan, M. W. & Nocera, D. G. In Situ Formation of an Oxygen-Evolving Catalyst in Neutral Water Containing Phosphate and Co²⁺. *Science*. **321**, 1072–1075 (2008).
 128. Zhong, D. K., Cornuz, M., Sivula, K., Gratzel, M. & Gamelin, D. R. Photo-assisted electrodeposition of cobalt-phosphate (Co-Pi) catalyst on hematite photoanodes for solar water oxidation. *Energy Environ. Sci.* **4**, 1759 (2011).
 129. Barroso, M. *et al.* Dynamics of photogenerated holes in surface modified α -Fe₂O₃ photoanodes for solar water splitting. *Proc. Natl. Acad. Sci.* **109**, 15640–15645 (2012).
 130. Ma, Y., Le Formal, F., Kafizas, A., Pendlebury, S. R. & Durrant, J. R. Efficient suppression of back electron/hole recombination in cobalt phosphate surface-modified undoped bismuth vanadate photoanodes. *J. Mater. Chem. A* **3**, (2015).
 131. Li, W. *et al.* Comparison of heterogenized molecular and heterogeneous oxide catalysts for photoelectrochemical water oxidation. *Energy Environ. Sci.* **9**, 1794–1802 (2016).
 132. Warren, S. C. *et al.* Identifying champion nanostructures for solar water-splitting. *Nat. Mater.* **12**, (2013).
 133. Carneiro, L. M. *et al.* Excitation-wavelength-dependent small polaron trapping of photoexcited carriers in α -Fe₂O₃. *Nat. Mater.* **16**, 819 (2017). doi:10.1038/NMAT4936
 134. Pendlebury, S. R. *et al.* Ultrafast Charge Carrier Recombination and Trapping in Hematite Photoanodes under Applied Bias. *J. Am. Chem. Soc.* **136**, 9854–9857 (2014).
 135. Pendlebury, S. R. *et al.* Dynamics of photogenerated holes in nanocrystalline α -Fe₂O₃ electrodes for water oxidation probed by transient absorption spectroscopy. *Chem. Commun.* **47**, 716–718 (2011).
 136. Peter, L. *Kinetics and Mechanisms of Light-Driven Reactions at Semiconductor Electrodes: Principles and Techniques. Photoelectrochemical Water Splitting: Materials, Processes and Architectures* (RCS Publishing, 2013). doi:10.1039/9781849737739-00019
 137. Le Formal, F. *et al.* Back Electron–Hole Recombination in Hematite Photoanodes for Water Splitting. *J. Am. Chem. Soc.* **136**, 2564–2574 (2014).
 138. Cristino, V. *et al.* Some aspects of the charge transfer dynamics in nanostructured WO₃ films. *J. Mater. Chem. A* **4**, 2995–3006 (2016).
 139. Cowan, A. J. & Durrant, J. R. Long-lived charge separated states in nanostructured

- semiconductor photoelectrodes for the production of solar fuels. *Chem. Soc. Rev.* **42**, 2281–2293 (2013).
140. Peter, L. M. & Wijayantha, K. G. U. Photoelectrochemical Water Splitting at Semiconductor Electrodes: Fundamental Problems and New Perspectives. *ChemPhysChem* **15**, 1983–1995 (2014).
 141. Pendlebury, S. R. *et al.* Correlating long-lived photogenerated hole populations with photocurrent densities in hematite water oxidation photoanodes. *Energy Environ. Sci.* **5**, 6304–6312 (2012).
 142. Barroso, M., Pendlebury, S. R., Cowan, A. J. & Durrant, J. R. Charge carrier trapping, recombination and transfer in hematite ($\alpha\text{-Fe}_2\text{O}_3$) water splitting photoanodes. *Chem. Sci.* **4**, 2724–2734 (2013).
 143. Cummings, C. Y., Marken, F., Peter, L. M., Tahir, A. A. & Wijayantha, K. G. U. Kinetics and mechanism of light-driven oxygen evolution at thin film $\alpha\text{-Fe}_2\text{O}_3$ electrodes. *Chem. Commun.* **48**, 2027 (2012).
 144. Atkins, P. *Physical Chemistry*. (Oxford University Press, 2001).
 145. Smieja, J. M. *et al.* Kinetic and structural studies, origins of selectivity, and interfacial charge transfer in the artificial photosynthesis of CO. *Proc. Natl. Acad. Sci. U. S. A.* **109**, 15646–50 (2012).
 146. Kang, P., Meyer, T. J. & Brookhart, M. Selective electrocatalytic reduction of carbon dioxide to formate by a water-soluble iridium pincer catalyst. *Chem. Sci.* **4**, 3497–3502 (2013).
 147. Dunwell, M. *et al.* The Central Role of Bicarbonate in the Electrochemical Reduction of Carbon Dioxide on Gold. *J. Am. Chem. Soc.* **139**, 3774–3783 (2017).
 148. Fan, X. *et al.* Atomic H-Induced Mo₂C Hybrid as an Active and Stable Bifunctional Electrocatalyst. *ACS Nano* **11**, 384–394 (2017).
 149. Mao, R. *et al.* Dechlorination of Trichloroacetic Acid Using a Noble Metal-Free Graphene–Cu Foam Electrode via Direct Cathodic Reduction and Atomic H*. *Environ. Sci. Technol.* **50**, 3829–3837 (2016).
 150. Holewinski, A. & Linic, S. Elementary Mechanisms in Electrocatalysis: Revisiting the ORR Tafel Slope. *J. Electrochem. Soc.* **159**, H864–H870 (2012).
 151. Hammarström, L. Accumulative Charge Separation for Solar Fuels Production: Coupling Light-Induced Single Electron Transfer to Multielectron Catalysis. *Acc. Chem. Res.* **48**, 840–850 (2015).
 152. Tan, M. X. *et al.* Principles and Applications of Semiconductor Photoelectrochemistry. in *Progress in Inorganic Chemistry* (ed. D. Karlin) 21–144 (John Wiley & Sons, Inc., 2007). doi:10.1002/9780470166420.ch2

Chapter 2. Experimental methods



Word cloud of this *Chapter*

In this chapter I present: (1) details of the different metal oxide photoanodes studied in this thesis and (2) the main experimental techniques such as, linear sweep voltammetry (LSV), chronoamperometry (CA), UV-Vis spectroscopy, transient absorption spectroscopy (TAS), light-induced spectroelectrochemistry (LI-SEC) and transient photocurrent (TPC) are also described.

2.1. Sample preparation

Some of the most promising metal oxide photoanodes for solar fuels applications, introduced in *Chapter 1*, that are studied herein, have been reported and tested for stability and reproducibility previously elsewhere. However, I present briefly their synthetic methods as well as relevant characterisation in the following sections, please for a detailed description of synthesis methods refer to the references indicated in each subsection. I note here that, the nanostructured and planar $\alpha\text{-Fe}_2\text{O}_3$ films used in the studies presented in *Chapters 3, 4 and 5* were prepared and kindly provided by Prof. Michael Grätzel's group at EPFL. Dense BiVO_4 was synthesised and kinetic water oxidation data, presented in *Chapter 3*, was collected and kindly provided at Imperial College by Dr. Yimeng Ma. Similarly, mesoporous TiO_2 was prepared and studied at Imperial College by Dr. Andreas Kafizas who also provided kindly water and methanol oxidation data for the study in *Chapters 3 and 4*. Additionally, mesoporous WO_3 photoanodes were prepared and kindly provided by prof. Erwin Reisner's group at University of Cambridge, whilst WO_3 data used in *Chapter 4* was kindly provided by Dr. Laia Francàs at Imperial College.

2.1.1. $\alpha\text{-Fe}_2\text{O}_3$

Nanostructured, silicon doped hematite (Si-doped $\alpha\text{-Fe}_2\text{O}_3$) films were grown by atmospheric pressure chemical vapour deposition, with $\text{Fe}(\text{CO})_5$ and tetraethoxysilane (TEOS) as precursors at an optimised gas flow rate of 6 L min^{-1} , on fluorine tin doped (FTO) glass following a procedure detailed elsewhere.^{1,2} These films contain 1.5% silicon as dopant and include a SiO_x buffer layer between the FTO surface and the hematite that improve the crystallinity of the $\alpha\text{-Fe}_2\text{O}_3$ next to the interface with the FTO.³

The APCVD hematite $\sim 400 \text{ nm}$ thick films studied herein present a cauliflower like dendritic structure with a surface feature size $\sim 5\text{-}10 \text{ nm}$ and a roughness factor of ~ 21 , as shown in Figure 2-1.a, presenting a predominant (110) crystal face at the surface (see Figure 2-1.b).

These films normally exhibit a donor density of $\sim 10^{20} \text{ cm}^{-3}$ and a flat band potential of $\sim 0.55 V_{RHE}$, estimated by impedance spectroscopy.⁴

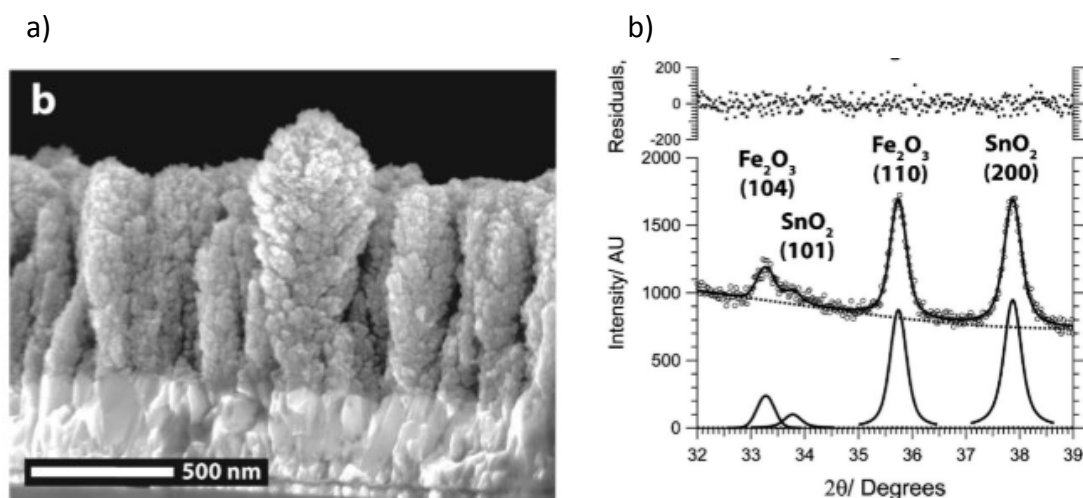


Figure 2-1. Si-doped $\alpha\text{-Fe}_2\text{O}_3$ photoanode characterisation, a) SEM image (cross-section) showing the cauliflower-like nanostructure typical of these films, and b) XRD spectrum showing the preferential crystal face (110). These images were taken from Cornuz, M., et. al.²

Planar un-doped $\alpha\text{-Fe}_2\text{O}_3$ photoanodes were deposited by atomic layer deposition (ALD) at 230 °C on TiO_2 coated FTO glass (see Figure 2-2 for characterisation). The TiO_2 blocking layer, of $\sim 2 \text{ nm}$ thickness, was ALD deposited at 170 °C on FTO glass followed by hematite deposition using *N,N*-(dymethylaminomethyl)ferrocene as precursor and O_3 as oxidant.⁵

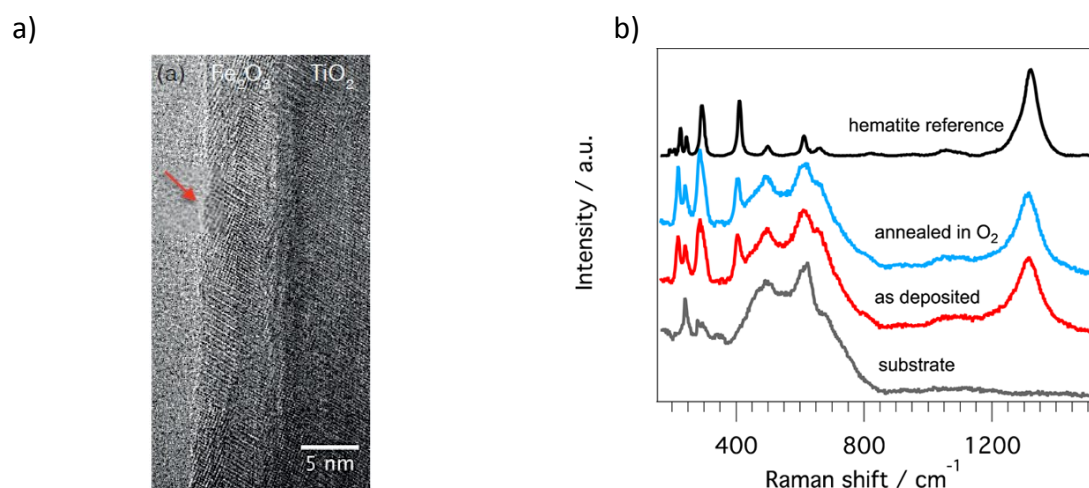


Figure 2-2. a) HR-TEM images of the $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ interface. I note here that these images were taken on TiO_2 nanowires with a thin ALD deposited $\alpha\text{-Fe}_2\text{O}_3$ layer, and b) Raman spectra of the $\alpha\text{-Fe}_2\text{O}_3$ photoanodes compared to a reference hematite spectrum and the FTO/ TiO_2 substrate. These images were taken from Steier, L., et. al.⁵

These planar films, as shown in Figure 2-2.a, have been found to exhibit $\sim 0.5 - 0.6 \text{ mA cm}^{-2}$, which is remarkable for un-doped hematite films. These phase pure and crystalline films (as confirmed by the Raman spectra shown in Figure 2-2.b) are 20 nm thick with a charge carrier

concentration, N_D , of $\sim 3 \times 10^{19} \text{ cm}^{-3}$ and a space charge layer width, W_{SC} , of $\sim 11 \text{ nm}$ at 1.23 V, covering for $\sim 60\%$ of the total film thickness.⁵

2.1.2. TiO_2

Mesoporous anatase films (TiO_2) were prepared following a procedure developed by Xiao-e et al.⁶ The film preparation consists of doctor-blading a colloidal anatase paste, prepared from the aqueous hydrolysis of titanium isopropoxide, on clean FTO glass followed by heat treatment at 450°C in air for 30 minutes. These well-characterised $\sim 1 \mu\text{m}$ mesoporous films showed anatase crystallites $\sim 40 \text{ nm}$ wide and a roughness factor of 120 (as seen in Figure 2-3).^{7,8}

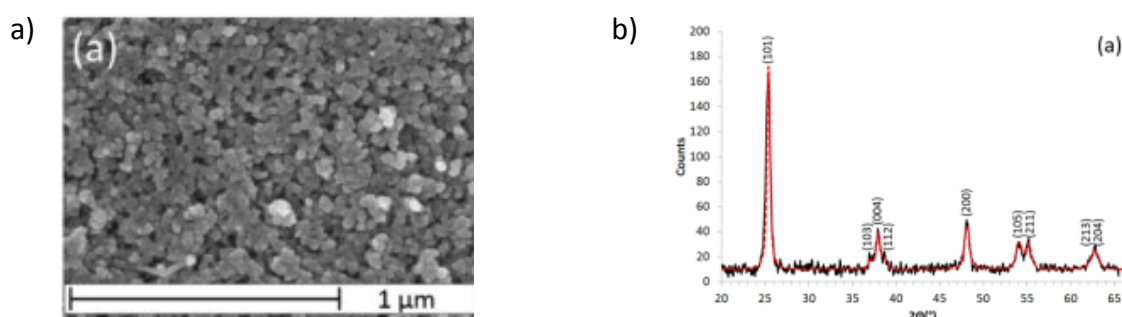


Figure 2-3. TiO_2 anatase films characterisation by a) SEM images and b) XRD spectroscopy (black line, experimental data and red line, fitted data). These images were taken from Wang, X., et. al.⁸

2.1.3. BiVO_4

Un-doped bismuth vanadate (BiVO_4) films were deposited by a modified metal-organic deposition method reported elsewhere.⁹

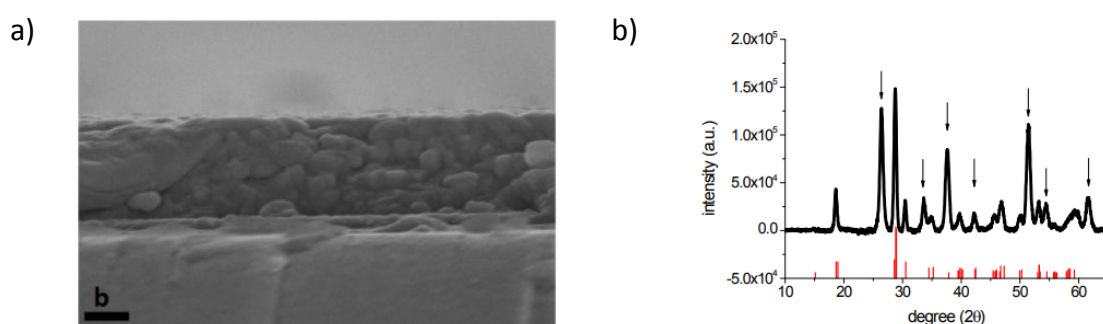


Figure 2-4. BiVO_4 films characterisation by a) cross section SEM images, the bar corresponds to 200 nm in length and b) XRD spectroscopy (black line, experimental data and red lines, BiVO_4 reference), the arrows indicate peaks of SnO_2 and FTO substrate. These images were taken from Ma, Y., et. al.⁹

A bismuth nitrate pentahydrate and vanadyl acetylacetonate containing solution was spin-coated onto clean FTO glass followed by calcination at 450°C for 30 min after every deposited layer and a final calcination at 450°C for 10 hours. Figure 2-4 shows that this method

produced ~ 500 nm thick, relatively flat and dense films with a roughness factor of ~ 1 , with a flat band potential measured by impedance spectroscopy of ~ 0.1 V_{RHE} and a donor density of 10^{18} cm^{-3} , leading to a space charge layer width, W_{SC} , of ~ 90 nm at 1.2 V.

2.1.4. WO_3

Mesoporous tungsten oxide (WO_3) photoanodes were produced by a hydrothermal method, with tungstic acid as main precursor.¹⁰ Vertically aligned monoclinic WO_3 nanostructures are obtained after a hydrothermal treatment, of a previously spin-coated WO_3 film (seed layer), at 180 °C for 2.5 hours followed by annealing at 500 °C for 1 hour.

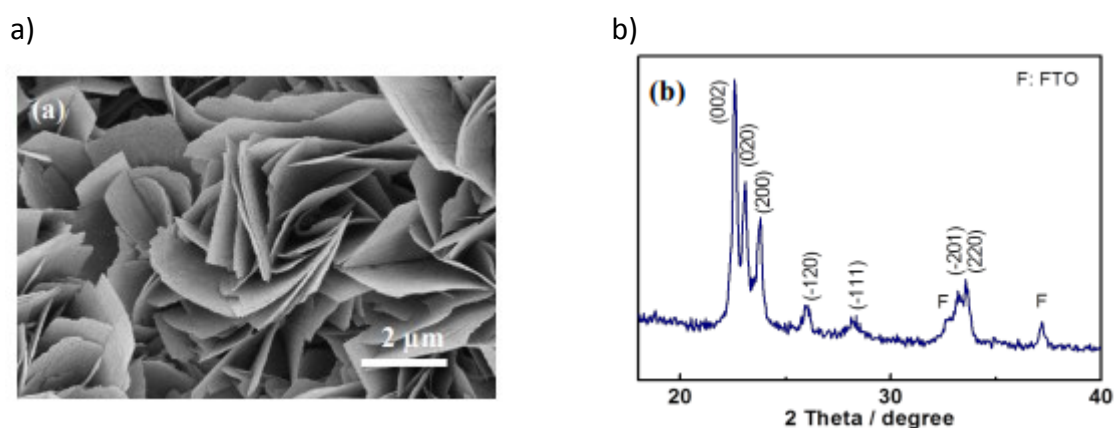


Figure 2-5. WO_3 films characterisation by a) SEM images, the bar corresponds to 2 μm in length and b) XRD spectroscopy, where F indicates peaks of the FTO substrate. These images were taken from Lai, Y., et. al.¹⁰

2.2. Photoelectrochemical (PEC) set-up

Photoelectrochemical (PEC) measurements, such as current/potential (JV) curves as well as chronoamperometries, were performed in a spectroelectrochemical system depicted in Figure 2-6, consisting of a light source, a series of filters and focusing lenses, a home-made three-electrode cell and a potentiostat.

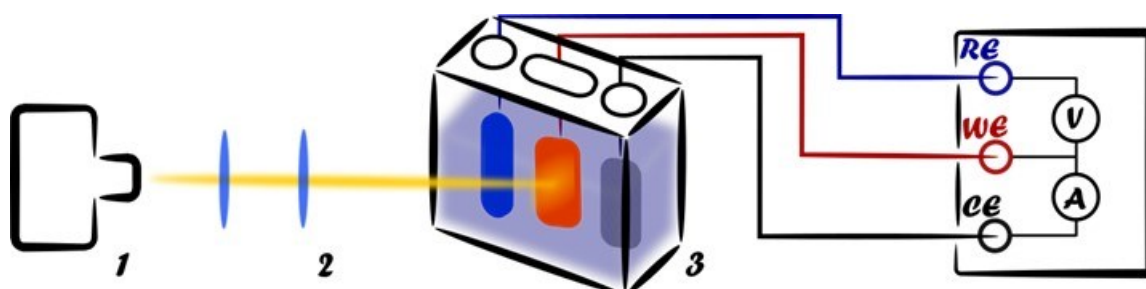


Figure 2-6. Schematic representation of the photoelectrochemical (PEC) set-up. 1) Xe lamp, 2) filters and focusing lenses, 3) PEEK 3-electrode cell and 4) potentiostat.

The light source used for the current-potential (*JV*) curves was a 75 W ozone-free xenon lamp (Hamamatsu). A KG3 filter was used as IR absorber to resemble the solar spectrum before the PEC cell. A Si photodiode was used to adjust the position of the sample to correspond to 1 sun irradiation conditions. Under solar AM 1.5.G irradiation, by integrating the solar spectrum up to 650 nm, the Si photoanode should produce 0.914 mA of photocurrent according to its area. All measurements were done in a typical ‘cappuccino’, a home-made PEEK (polyetheretherketone), cell with quartz windows (0.5 cm²) at the front and back sides. The same configuration of three-electrode cell was used for all measurements, comprising a platinum (Pt) mesh as counter electrode, a Ag/AgCl electrode as reference (detailed in the following paragraph) and the semiconductor (α -Fe₂O₃, TiO₂, BiVO₄ or WO₃) as working electrodes. I note here that in some *JV* measurements, as noted through the Chapters, the illumination used for the experiments in this chapter was from a 365 nm LED, with the power controlled by the current passing through it. This allowed the photon flux to be tuned until appropriate plateau photocurrents equivalent to AM 1.5.G illumination conditions were reached.

The applied potential, controlled by the potentiostat, was measured using a potassium chloride saturated silver/silver chloride (Ag/AgCl/saturated KCl, Metrohm) as reference electrode. The reaction of the AgCl|Ag reference electrode is:



When Equation 2-1 takes place in a KCl saturated solution the standard electrode potential (E°) at 298 K is +0.197 V relative to the normal hydrogen electrode (NHE) ($E^{\circ}_{Ag/AgCl} = +0.197$ V vs NHE). The electrode potentials were converted to be relative to the reversible hydrogen electrode (RHE) using Equation 2-2.

$$E_{RHE}(V) = E^{\circ}_{Ag/AgCl} + E'_{Ag/AgCl} + 0.059 \cdot pH \quad \text{Equation 2-2}$$

where $E'_{Ag/AgCl}$ corresponds to the potential applied with the potentiostat. The *pH* value varies with the electrolyte used according to the experiment performed or the material used, which is stated accordingly in each chapter.

An Autolab 101 potentiostat was used for the PEC measurements. Note that *iR* drops are caused by changing the size of the working electrode or the position of the electrodes, when

high current densities as well as a low conductivity of the electrolyte solution. As such, iR drops are expected to be negligible in the experiments conducted for this thesis as the electrodes were in a constant position due to the cell design, the electrolyte always contained an electrolyte support for conductivity and the photocurrents were always no more than a few mA cm^{-2} .

2.3. Transient Absorption Spectroscopy (TAS)

2.3.1. TAS Set-up

A home-built pump-probe transient absorption spectroscopy (TAS) system (see Figure 2-7) was used to monitor the time evolution population of the photo-induced charge carriers. This technique, also known as flash photolysis, was developed originally by Lord George Porter to study free radical reactions.¹¹

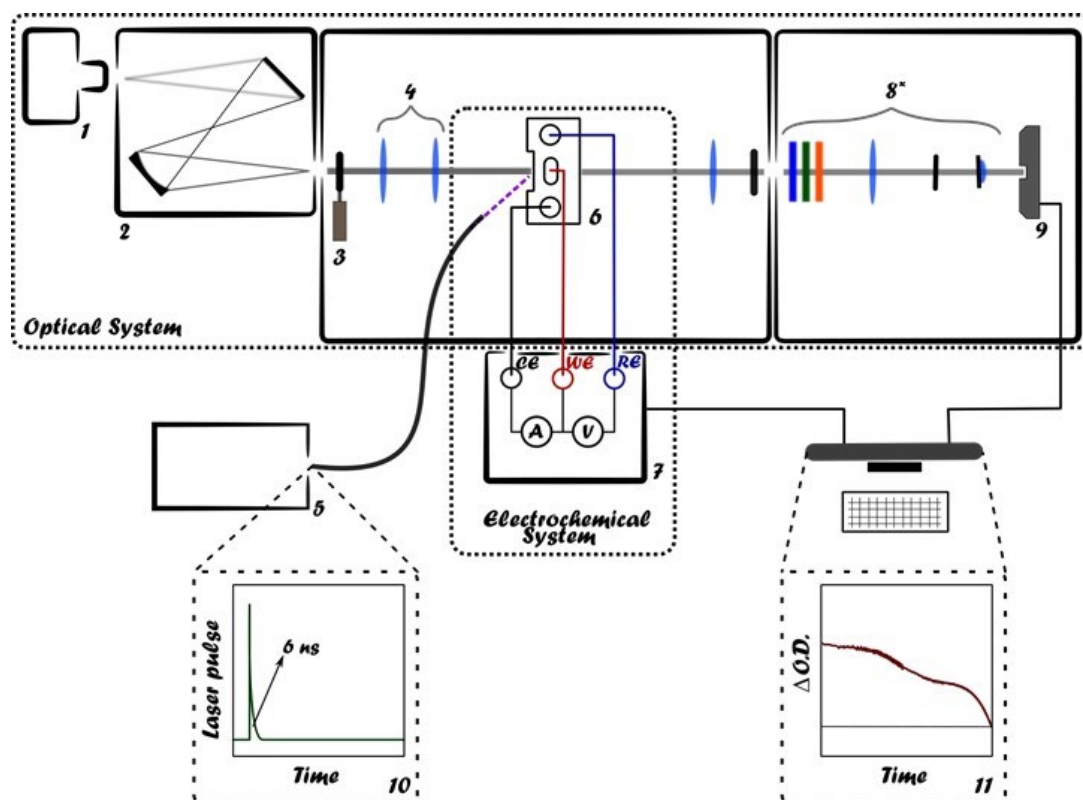


Figure 2-7. Schematic representation of the home-built TAS system.

- | | |
|---|--|
| 1. W lamp | 2. Monochromator |
| 3. Chopper | 4. Lenses |
| 5. Nd:YAG Laser | 6. PEC Cell |
| 7. Potentiostat | 8. Long and band pass filters.* These can be replaced by a second monochromator. |
| 9. Si photodiode detector | 11. Sample spectroscopical response (TA decay) |
| 10. Excitation source (6 ns laser pump) | |

In a semiconductor, the photogenerated charges induce alterations in its optical absorption. This transient change in the optical absorption takes place upon illumination with a short (6 ns) laser pulse (pump) from the third harmonic (355 nm) of a Nd:YAG laser (Big Sky laser technologies). This excitation wavelength corresponds to photons more energetic than the band gap of the semiconductors studied in this thesis ($E > E_g$), therefore electrons from the valence band are excited to the conduction band in the sample. A Si-photodiode, upon illumination, triggers the time-resolved absorption measurement, for which a second and continuous light beam is utilised (probe). This continuous and monochromatic probe beam is generated by a tungsten (W) lamp (100W Bentham IL) and filtered by a monochromator (OBB-2001, Photon Technology International). The transient change in absorbance of the sample at the selected probe wavelength, triggered by the photogenerated species, is recorded by a Si photodiode (Hamatsu S3071) and the output is split into two signals. One of the signals is electronically amplified (Constronics amplifier) and recorded in an oscilloscope (Tektronics TDS 2012c) for timescales from μs to ms and the second signal is recorded by a data acquisition (DAQ) card (National Instruments USB-6211) for $ms - s$ timescales. The data were acquired from an average of 100 to 500 laser pulses by a *LabView* based software converting the measured signal into change in absorbance ($\Delta O.D.$) as a function of wavelength (λ) and time (t).

2.3.2. Signal conversion to $\Delta O.D.$

The change in optical density ($\Delta O.D.$) is calculated from the light intensity change detected by the photodiode. Based on the Beer-Lambert law, the optical density (O.D.) is defined as:

$$O.D.(\lambda, t) = -\text{Log}(T(\lambda, t)) = -\text{Log}\left(\frac{I(\lambda, t)}{I(\lambda, T)}\right) = \varepsilon(\lambda) \cdot c(t) \cdot l \quad \text{Equation 2-3}$$

where $\varepsilon(\lambda)$ is the species molar extinction coefficient at the wavelength (λ), $c(t)$ is the concentration of the transient species at the time (t) and l is the length of the optical pathway, T is the sample transmittance, $I(\lambda, i)$ and $I(\lambda, T)$ are the intensities of the incident and transmitted light, respectively. Such $I(\lambda, t)$ would change upon the laser excitation and therefore (when probing with a monochromatic beam), from Equation 2-3, the change in optical density is:

$$\Delta O.D.(t) = -\text{Log}\left(\frac{I(i)}{I(T, t)}\right) + \text{Log}\left(\frac{I(i)}{I(T, t_0)}\right) = \text{Log}\left(\frac{I(T, t)}{I(T, t_0)}\right) \quad \text{Equation 2-4}$$

where $I_{(T,t0)}$ is the transmitted light intensity at the time, which effectively is the transmitted light before the excitation pulse and $I_{(T,t)}$ is the intensity at the time (t). Due to the transmitted light intensity as a function of time ($I_{(T,t)}$) equals the intensity before the excitation pulse ($I_{(T,t0)}$) plus the change in the intensity of the transmitted light ($\Delta I_{(T,t)}$), Equation 2-4 can be rewritten as:

$$\Delta O.D._{(t)} = \text{Log} \left(\frac{I_{(T,t0)} + \Delta I_{(T,t)}}{I_{(T,t0)}} \right) = \text{Log} \left(1 + \frac{\Delta I_{(T,t)}}{I_{(T,t0)}} \right) \quad \text{Equation 2-5}$$

The change in the transmitted light intensity ($\Delta I_{(T,t)}$) is proportional to the change in voltage (ΔV_t) measured by the photodiode. Note that due to the change in voltage (ΔV_t) in the experiments performed in this thesis is in the order of 10^{-2} , the Equation 2-5 can be approximated and subsequently rewritten as:

$$\Delta O.D._{(t)} = \text{Log} \left(1 + \frac{\Delta V_t}{V_0} \right) \approx \frac{1}{\text{Ln}(10)} \cdot \frac{\Delta V_t}{V_0} = \frac{1}{2.303} \cdot \frac{\Delta V_t}{V_0} \quad \text{Equation 2-6}$$

where V_0 is the voltage, previous excitation, measured by the photodiode (9 in Figure 2-7).

2.3.3. Contributions to the observed $\Delta O.D.$

Upon excitation from the ground to an excited state of the sample, the observed change in the optical density ($\Delta O.D._{(t)}$) could appear as:¹²

- A *positive* signal corresponding to the appearance of a new absorption band originated by the excited state.
- A *negative* signal corresponding to the loss (bleaching) of ground state absorption caused by the depopulation of it. Additionally, stimulated emission (*i.e.* fluorescence) can cause an increase of photons arriving to the detector appearing as a negative $\Delta O.D.$

2.4. Light-Induced Spectroelectrochemistry (LI-SEC)

With the aim to study the catalytic performance of the materials presented in section 2.1 under steady-state conditions, a modification of the TAS system was implemented to monitor spectroscopically, the steady-state population of charges under continuous illumination conditions at conditions of a constant applied potential. This spectroelectrochemical measurement, also known as ‘Photo-Induced Absorption’ (PIA), is used herein concomitant to Transient Photocurrent (TPC) measurements (see details in section 2.5). Therefore, this

technique can be considered as two simultaneous but independent type of measurements (PIA + TPC) and will be referred throughout this thesis as light-induced spectroelectrochemistry (LI-SEC).

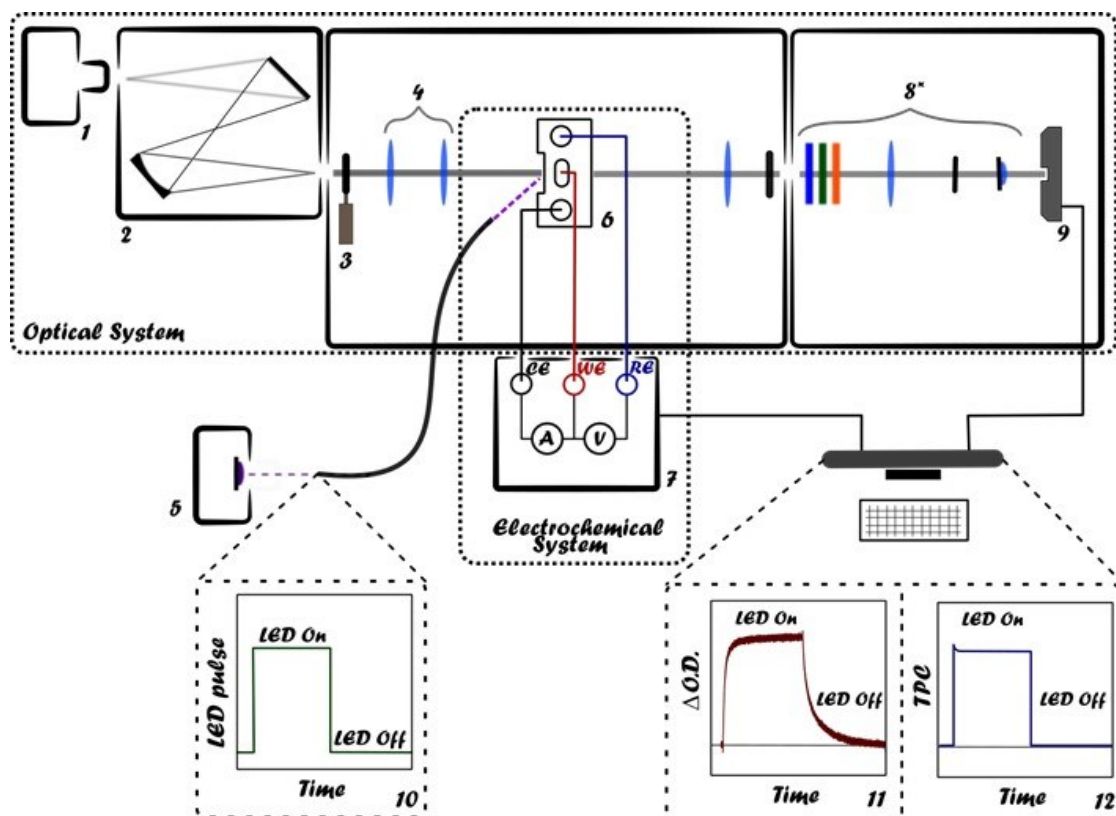


Figure 2-8. Schematic representation of the simultaneous PIA (optical system) and TPC (electrochemical system) spectrometer.

- | | |
|----------------------------------|--|
| 1. W lamp | 2. Monochromator |
| 3. Chopper | 4. Lenses |
| 5. 365nm LED | 6. PEC Cell |
| 7. Potentiostat | 8. Long and band pass filters.* These can be replaced by a second monochromator. |
| 9. Si photodiode detector | 11. Sample spectroscopical response (PIA decay) |
| 10. Excitation source (LED pump) | 12. Sample electrochemical response (transient photocurrent) |

The aforementioned photo-induced absorption (PIA) is a pump-probe spectroscopy, which has been widely used in the study of charge carriers generation, trapping, recombination and transfer in different materials for decades, normally within timescales ranging from milliseconds to seconds. The previously mentioned modification to the TAS system consists of substituting the length and excitation source from the 6 ns laser pulse (5 in Figure 2-7) to a sufficiently long (seconds timescale), tuneable irradiation pulse from a Light Emitting Diode (LED) (5 in Figure 2-8), to observe a quasi-steady state absorption of the studied system. For example, PIA spectroscopy has been used to study recombination kinetics in dye-sensitized

solar cells (DSSC) and perovskite solar cells by Boschloo and co-workers, by using LED pulses (millisecond timescale).^{13–16} Additionally, the charge transfer kinetics in DSSC between the interfaces $\text{TiO}_2/\text{dye}/\text{electrolyte}$ have been studied by means of PIA measurements simultaneously with spectroelectrochemistry.^{17–19} However, to the best of my knowledge, the use of LI-SEC (*i.e.* PIA concomitant with TPC measurements (see Figure 2-8)) was first reported by our group,²⁰ with the kinetic study of the transfer of photogenerated holes from a hematite surface to the electrolyte (1 M NaOH),²¹ followed by the study of various multielectron redox reactions in different photoelectrochemical systems.^{22–26}

The optical system depicted in Figure 2-8 is a pump-probe technique. The *pump* consists of one or two UV (365 nm) LEDs delivering a photon flux between 1 and 40 mW cm^{-2} measured by a Si photodiode (FDS100-CAL, Thorlabs). This photon flux is controlled by the current passing (from 0.02 to 0.6 A) through the LEDs (LZ1–10U600, LedEngin Inc.) applied and modulated from a power supply (TTi QL564P). The length and symmetry of the irradiation pulse, that is light ON and light OFF time, was adjusted by a function generator (TTi TG230) by controlling the frequency and symmetry of a square wave set in series between the LEDs and the power supply. A mosfet was used as switch ON/OFF interface between the function generator and the circuit power supply/LEDs for a fast electrical response.

The *probe* system is identical to the TAS Set-up (see section 2.3.1), except for the optical signal recording for which only the DAQ is used. The data acquisition was triggered by a parallel square wave from the function generator and the data corresponds to the average of 10 to 100 LED pulses.

2.5. Transient Photocurrent (TPC)

The transient photocurrent measurements (TPC) were carried out in the electrochemical system depicted in Figure 2-8 simultaneously with the PIA signal monitoring. The TPC is recorded by a potentiostat while the photoanode is illuminated by the LEDs as well as in the darkness using a standard PEC cell (3 in Figure 2-6). Alternatively, for the experiments in *Chapters 3, 4 and 5*, the TPC can be measured by monitoring the potential drop across a 98 Ω resistor set in series between the counter electrode and the potentiostat (Ministat). In both cases, the TPC signal was recorded by an oscilloscope (TDS 2012c, Tektronics) triggered by the square wave from the function generator.

2.6. Rate law kinetic model

The concomitant assay of the hole optical signal and the corresponding rate of reaction is analysed by the following kinetic model. This model is considered for an *n*-type photoanode, although it can be applied for a *p*-type one, where photogenerated holes have to migrate to the photoanode surface for charge transfer (reaction). It is important to note that, this model is considered for quantitative hole transfer to the electrolyte (*i.e.* 100% Faradaic efficiency and no self-oxidation of the photoanode). Additionally, this model considers that the measured surface hole density in a metal-oxide photoanode is in direct correlation with the quasi-Fermi level of surface holes and therefore with the free energy to drive water oxidation. In this model, the change in the density of holes at the surface (p_s) depends upon one incoming flux (J_{holes}) and two consuming processes, reaction with the electrolyte ($-k_{WO} \cdot p_s^\beta$, for water oxidation) and surface recombination ($-k_{SR} \cdot p_s^\gamma$) if present, as shown in Equation 2-7, where k_{WO} and k_{SR} correspond to the water oxidation and surface recombination rate constants, and β and γ to their respective order of reactions.

$$\frac{dp_s}{dt} = J_{holes} - k_{WO} \cdot p_s^\beta - k_{SR} \cdot p_s^\gamma \quad \text{Equation 2-7}$$

Assuming a positive applied potential enough to suppress surface recombination, the model can be simplified to Equation 2-8 and depicted schematically in Figure 2-9.

$$\frac{dp_s}{dt} = J_{holes} - k_{WO} \cdot p_s^\beta \quad \text{Equation 2-8}$$

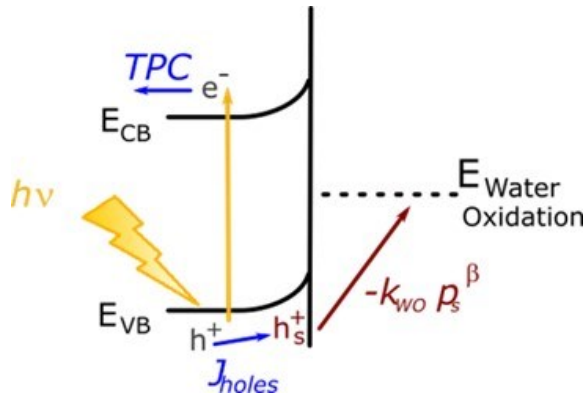


Figure 2-9. Schematic representation of the kinetic model shown in Equation 2-8. The photogenerated holes flux to the surface (J_{holes}) is equivalent to the photocurrent whereas the hole consuming process (*i.e.* water oxidation reaction) is equal to $(-k_{WO} \cdot p_s^\beta)$, with β as the reaction order and k_{WO} as the water oxidation rate constant.

The kinetic model shown in Equation 2-8, can be studied in two particular conditions, under steady-state illumination and immediately after illumination is turned off. For the first scenario, upon steady-state the change in surface hole density is zero ($\frac{dp_s}{dt} = 0$), therefore the photocurrent (J_{holes}) is equal to the rate of reaction ($k_{WO} \cdot p_s^\beta$), as expressed logarithmically in Equation 2-9.

$$J_{holes} = k_{WO} \cdot p_s^\beta \rightarrow \log(J_{holes}) = \beta \cdot \log(p_s) + \log(k_{WO}) \quad \text{Equation 2-9}$$

where, the slope of such logarithmic plot corresponds to the order of reaction, which is associated with the number of holes that need to be accumulated to overcome the rate determining step of reaction, and the intercept to the rate constant. For further reading, please refer to recent papers²¹⁻²⁶ and a full description of the technique in a chapter in the book entitled *Advances in Photoelectrochemical Water Splitting: Theory, Experiment and Systems analysis*.²⁷

The order of reaction extracted from a rate law analysis under certain conditions can provide mechanistic information of the rate determining step (rds) of a chemical reaction. Further analysis of a rds can include studying the kinetic effect of changing isotopes in the reaction. This kinetic isotope effect will be introduced in the next section.

2.7. Kinetic isotope effect

One of the most common techniques to study the rate determining step of reaction in physical-chemistry is the isotope labelling method. The most used is to follow the reaction kinetics upon H/D labelling as the atomic mass increments 100% when substituting a hydrogen for a deuterium atom. As such, the kinetic isotope effect (KIE) experiments are designed to provide essential information about the reaction coordinate.²⁸⁻³⁰

The kinetic isotope effect can be defined as the relation of rate constants upon isotope substitution (see Equation 2-10).

$$KIE = \frac{k_H}{k_D} \quad \text{Equation 2-10}$$

where k_H and k_D correspond to the hydrogenated and deuterated rate of reactions respectively. The origin of the KIE lies in the zero-point energies difference of the atoms sharing a bond, which is related to the bond vibration according to Equation 2-11, for which its energy levels (E_n) are quantized,

$$E_n = \left(n + \frac{1}{2}\right) h\nu = \left(n + \frac{1}{2}\right) hc\bar{\nu} \quad \text{Equation 2-11}$$

where h is the Plank's constant, ν corresponds to the bond vibration, c is the speed of light and $\bar{\nu}$ corresponds to the wavenumber of such vibration. The zero-point energy is then defined for $n = 0$. When the bond breaks the stretch vibration of such bond in the reaction coordinate depends on the bond force constant (f) and the reduced mass (m_r) as shown in Equation 2-12.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{m_r}}, \text{ where } m_r = \frac{m_1 \cdot m_2}{m_1 + m_2} \quad \text{Equation 2-12}$$

For the case of H/D substitution in a typical C-H bond, the reduced mass increases ~86% having an important effect in the zero-point energies for both, C-H and C-D bonds. This different zero-point energy affects the electron transfer rate constants (k_H and k_D) that can be calculated as:

$$k_H = A \cdot e^{-E/k_b \cdot T} \quad \text{Equation 2-13}$$

where, A is the Arrhenius constant and k_b the Boltzmann constant. As such, the KIE can be calculated as:

$$KIE = \frac{k_H}{k_D} = \frac{A \cdot e^{-E_H/k_b \cdot T}}{A \cdot e^{-E_D/k_b \cdot T}} = e^{\Delta E/k_b \cdot T} \quad \text{Equation 2-14}$$

where ΔE is the difference in the zero-point energy between the C-H and C-D bonds that correlate with their vibration wavenumbers ($\bar{\nu}$) according to Equation 2-11, therefore the kinetic isotope effect in Equation 2-14 can be rewritten as:

$$KIE = e^{hc \cdot \Delta \bar{\nu} / 2k_b \cdot T} \quad \text{Equation 2-15}$$

As example, the predicted primary KIE for C-H and O-H bonds breaking are calculated from their symmetric stretching wavenumbers. Additionally, the secondary KIE for the same C-H and O-H bonds breaking in a methane and water molecules respectively are also considered from their bending modes. The wavenumbers and predicted KIE values are shown in Table 2-1.

Table 2-1. Wavenumbers and KIE values predicted from Equation 2-15 for the O-H bond breaking in H₂O and the C-H bond breaking in CH₄.

Molecule	Wavenumbers (cm ⁻¹)*		Primary	Secondary
	Symmetric Stretching	Bending mode	KIE	KIE
H ₂ O	3657	1595	10.73	2.72
D ₂ O	2671	1178		
CH ₄	2917	1534	6.99	2.90
CD ₄	2109	1092		

*Data recovered from reference.³¹

2.8. Heating device

In *Chapter 3*, temperature dependence experiments were conducted to study the activation energy of the water oxidation reaction on hematite photoanodes. The used custom-made heating device is composed by an aluminum cell insulated with calcium silicate (Duratec 750) of 6 mm width. Two resistive heaters (50 W) and a K-type thermocouple linked to a PID controller was adapted to regulate the temperature of the PEC cell. For these experiments, instead of the ‘cappuccino cell’, a closed quartz contained the working and counter electrodes. The Ag/AgCl reference electrode was placed in a separate container connected by a salt bridge therefore, no temperature correction for the applied potential was required.

2.9. UV-Vis

An UV-Vis spectrometer (Perkin-Elmer, Lambda 25) was used to measure the UV-Vis spectral features of the α -Fe₂O₃, TiO₂ and BiVO₄ films used herein. The UV-Vis spectrum of the WO₃ film was measured with an integrating sphere accessory due to its low transmission. (see Figure 2-10 for the used metal-oxide photoanodes characterisation)

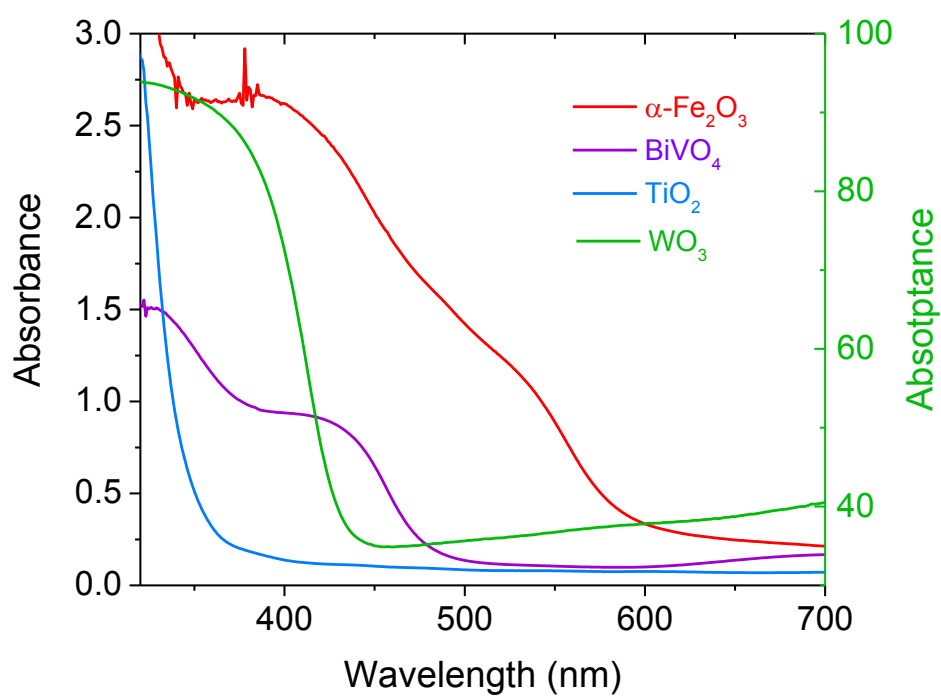


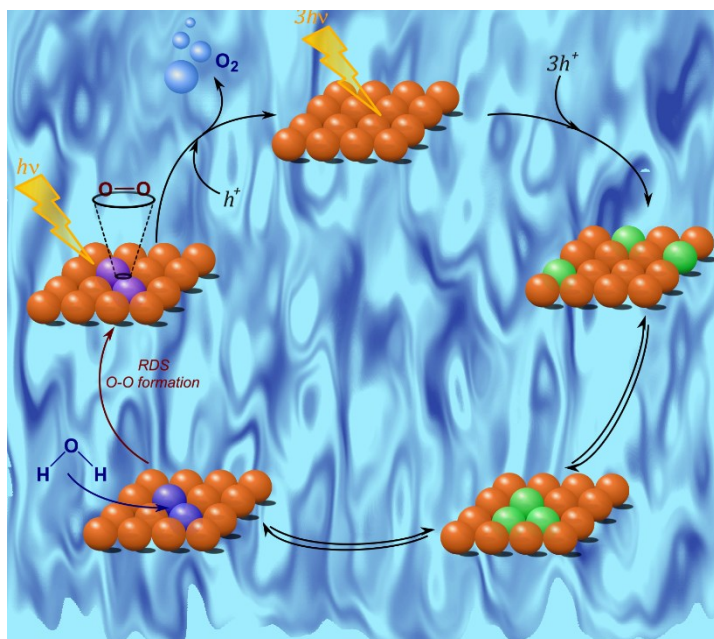
Figure 2-10. UV-Vis spectra of $\alpha\text{-Fe}_2\text{O}_3$ (red), BiVO_4 (purple), TiO_2 (blue) acquired in transmittance mode and WO_3 (green) acquired in diffuse reflectance mode.

2.10. References

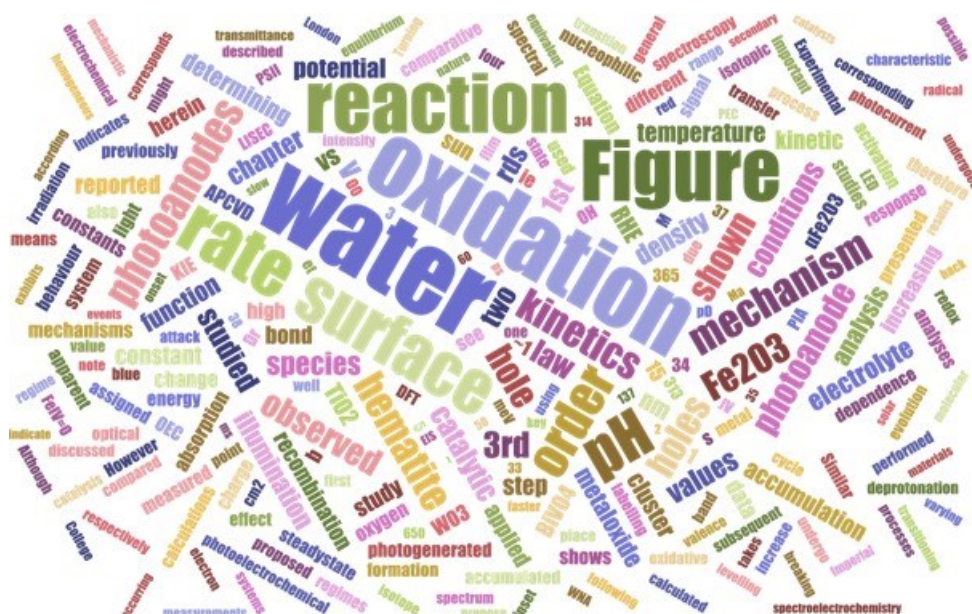
1. Kay, A., Cesar, I. & Grätzel, M. New Benchmark for Water Photooxidation by Nanostructured α -Fe₂O₃ Films. *J. Am. Chem. Soc.* **128**, 15714–15721 (2006).
2. Cornuz, M., Grätzel, M. & Sivula, K. Preferential Orientation in Hematite Films for Solar Hydrogen Production via Water Splitting. *Chem. Vap. Depos.* **16**, 291–295 (2010).
3. Le Formal, F., Grätzel, M. & Sivula, K. Controlling Photoactivity in Ultrathin Hematite Films for Solar Water-Splitting. *Adv. Funct. Mater.* **20**, 1099–1107 (2010).
4. Le Formal, F. *et al.* Back Electron–Hole Recombination in Hematite Photoanodes for Water Splitting. *J. Am. Chem. Soc.* **136**, 2564–2574 (2014).
5. Steier, L. *et al.* Low-Temperature Atomic Layer Deposition of Crystalline and Photoactive Ultrathin Hematite Films for Solar Water Splitting. *ACS Nano* **9**, 11775–11783 (2015).
6. Xiao-e, L., Green, A. N. M., Haque, S. A., Mills, A. & Durrant, J. R. Light-driven oxygen scavenging by titania/polymer nanocomposite films. *J. Photochem. Photobiol. A Chem.* **162**, 253–259 (2004).
7. Kafizas, A. *et al.* Where Do Photogenerated Holes Go in Anatase:Rutile TiO₂ ? A Transient Absorption Spectroscopy Study of Charge Transfer and Lifetime. *J. Phys. Chem. A* **120**, 715–723 (2016).
8. Wang, X. *et al.* Transient Absorption Spectroscopy of Anatase and Rutile: The Impact of Morphology and Phase on Photocatalytic Activity. *J. Phys. Chem. C* **119**, 10439–10447 (2015).
9. Ma, Y., Pendlebury, S. R., Reynal, A., Le Formal, F. & Durrant, J. R. Dynamics of photogenerated holes in undoped BiVO₄ photoanodes for solar water oxidation. *Chem. Sci.* **5**, 2964–2973 (2014).
10. Lai, Y.-H., King, T. C., Wright, D. S. & Reisner, E. Scalable One-Step Assembly of an Inexpensive Photoelectrode for Water Oxidation by Deposition of a Ti- and Ni-Containing Molecular Precursor on Nanostructured WO₃. *Chem. – A Eur. J.* **19**, 12943–12947 (2013).
11. Porter, G. Flash photolysis and spectroscopy A new method for the study of free radical reactions. *Proc. R. Soc. London. Ser. A, Math. Phys. Sci. Proc. R. Soc. London. Ser. A Math. Phys. Sci. This* **200**, 284–300 (1950).
12. Durrant, J. R. Transient absorption spectroscopy of the photosystem II. (Imperial College London, 1991).
13. Boschloo, G. & Hagfeldt, A. Photoinduced absorption spectroscopy of dye-sensitized nanostructured TiO₂. *Chem. Phys. Lett.* **370**, 381–386 (2003).
14. Boschloo, G. & Hagfeldt, A. Photoinduced absorption spectroscopy as a tool in the study of dye-sensitized solar cells. *Inorganica Chim. Acta* **361**, 729–734 (2008).
15. Bi, D., Yang, L., Boschloo, G., Hagfeldt, A. & Johansson, E. Effect of Different Hole Transport Materials on Recombination in CH₃NH₃PbI₃ Perovskite-Sensitized Mesoscopic Solar Cells. *J. Phys. Chem. Lett.* **4**, 1532–1536 (2013).
16. Pazoki, M., Cappel, U. B., Johansson, E. M. J., Hagfeldt, A. & Boschloo, G. Characterization techniques for dye-sensitized solar cells. *Energy Environ. Sci.* **672**, 672–709 (2017).
17. Cappel, U. B., Gibson, E. A., Hagfeldt, A. & Boschloo, G. Dye Regeneration by Spiro-MeOTAD in Solid State Dye-Sensitized Solar Cells Studied by Photoinduced Absorption Spectroscopy and

- Spectroelectrochemistry. *J. Phys. Chem. C* **113**, 6275–6281 (2009).
18. Cappel, U. B., Feldt, S. M., Schö, J., Hagfeldt, A. & Boschloo, G. The Influence of Local Electric Fields on Photoinduced Absorption in Dye-Sensitized Solar Cells. *J. Am. Chem. Soc.* **132**, 9096–9101 (2010).
 19. Yang, W., Pazoki, M., Eriksson, A. I. K., Hao, Y. & Boschloo, G. A key discovery at the TiO₂/dye/electrolyte interface: slow local charge compensation and a reversible electric field. *Phys. Chem. Chem. Phys.* **17**, 16744–16751 (2015).
 20. Francàs, L., Mesa, C. A., Pastor, E., Le Formal, F. & Durrant, J. R. Rate Law Analysis of Water Splitting Photoelectrodes. in *Advances in Photoelectrochemical Water Splitting: Theory, Experiment and Systems Analysis* (eds. Tilley, S. D., Lany, S. & van de Krol, R.) in press (Royal Society of Chemistry, 2018).
 21. Le Formal, F. *et al.* Rate Law Analysis of Water Oxidation on a Hematite Surface. *J. Am. Chem. Soc.* **137**, 6629–6637 (2015).
 22. Ma, Y. *et al.* Rate Law Analysis of Water Oxidation and Hole Scavenging on a BiVO₄ Photoanode. *ACS Energy Lett.* 618–623 (2016). doi:10.1021/acsenergylett.6b00263
 23. Ma, Y., Kafizas, A., Pendlebury, S. R., Le Formal, F. & Durrant, J. R. Photoinduced Absorption Spectroscopy of CoPi on BiVO₄: The Function of CoPi during Water Oxidation. *Adv. Funct. Mater.* **26**, (2016).
 24. Pastor, E. *et al.* Spectroelectrochemical analysis of the mechanism of (photo)electrochemical hydrogen evolution at a catalytic interface. *Nat. Commun.* **8**, 14280 (2017).
 25. Kafizas, A. *et al.* Water Oxidation Kinetics of Accumulated Holes on the Surface of a TiO₂ Photoanode: A Rate Law Analysis. *ACS Catal.* **7**, 4896–4903 (2017).
 26. Mesa, C. A. *et al.* Kinetics of Photoelectrochemical Oxidation of Methanol on Hematite Photoanodes. *J. Am. Chem. Soc.* **139**, 11537–11543 (2017).
 27. Francàs, L., Mesa, C. A., Pastor, E., Le Formal, F. & Durrant, J. R. *Chapter 5: Rate Law Analysis of Water Splitting Photoelectrodes. RSC Energy and Environment Series* (2018). doi:10.1039/9781782629863-00128
 28. Anslyn, E. V. & Dougherty, D. A. *Modern Physical Organic Chemistry*. (University Science Books, 2006).
 29. Atkins, P. *Physical Chemistry*. (Oxford University Press, 2001).
 30. Omez-Gallego, M. G. & Sierra, M. A. Kinetic Isotope Effects in the Study of Organometallic Reaction Mechanisms. *Chem. Rev.* **111**, 4857–4963 (2011).
 31. *CRC Handbook of chemistry and physics*. (CRC Press, 2010).

Chapter 3. Kinetic and mechanistic study of water oxidation on metal-oxide photoanodes



TOC Figure



Word cloud for this *Chapter*

In this chapter, experimental data for the photoelectrochemical oxidation of water on hematite photoanodes is presented, enabling the proposal of a detailed, molecular level, reaction mechanism. The kinetics of water oxidation are observed to change upon increasing density of surface holes at the photoanode from a first to a third order. This 3rd order mechanism operates at ~1 sun conditions, with no O-H bond breaking at the rate determining step demonstrated by a secondary H/D kinetic isotope effect. The kinetics of this operating mechanism exhibits faster rate constants upon surpassing the point of zero charge of hematite. Temperature dependence studies shows a catalytic effect from hematite in the transition from first to third order by reducing the activation energy of the rate determining step from 300 to 60 *meV*. Further comparisons with other metal oxides such as TiO₂, BiVO₄ and WO₃ indicate substantial similitudes in the mechanism for evolving oxygen with an increasing rate constant with valence band energy. Furthermore, all of these materials share striking similitudes with other heterogeneous and homogeneous water oxidation catalysts, including the oxygen evolving complex from the photosystem II. These results provide insights into the nature of the electron transfer of water oxidation and try to establish a bridge between biological oxygen evolution and artificial photosynthesis.

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

- *“Multihole catalysis of water oxidation on hematite photoanodes: Insights from in operando spectroelectrochemistry and density functional theory”*, *Nat. Chem.*, under revision
- *“Rate law analysis of water oxidation on a hematite surface”*, *J. Am. Chem. Soc.*, **2015**, 137, 6629 – 6637
- *“Rate law analysis of water oxidation and hole scavenging on a BiVO₄ photoanode”*, *ACS Energy Lett.*, **2016**, 1, 618-623
- *“Water oxidation kinetics of accumulated holes on the surface of a TiO₂ photoanode: A rate law analysis”*, *ACS Catal.*, **2017**, 7, 4896-4903.

3.1. Introduction

Natural photosynthesis originated about 3 billion years ago when the enzyme photosystem II (PSII) emerged to provide electrons for plant CO₂ conversion.^{1,2} The source of electrons in this system is the oxidation of water, which takes place in the oxygen evolution centre (OEC) at the PSII, that undergoes in a catalytic cycle known as S-cycle. This S-cycle ($S_0 - S_4$), shown in see Figure 3-1.a, is particularly complex and with the rate determining step (rds), oxyl-oxo radical coupling or a water nucleophilic attack, yet to be fully understood. However, it is well accepted that a key part of this process is the subsequent oxidations the Mn-cluster undergoes at the OEC (see Figure 3-1.b) from S_0 to S_4 states, accumulating oxidative equivalents in a redox levelling process.³ This process has not only served as inspiration for the design of an artificial photosynthetic system to produce solar fuels,⁴⁻⁸ but also for the study of the water oxidation mechanism of reaction from a molecular point of view.

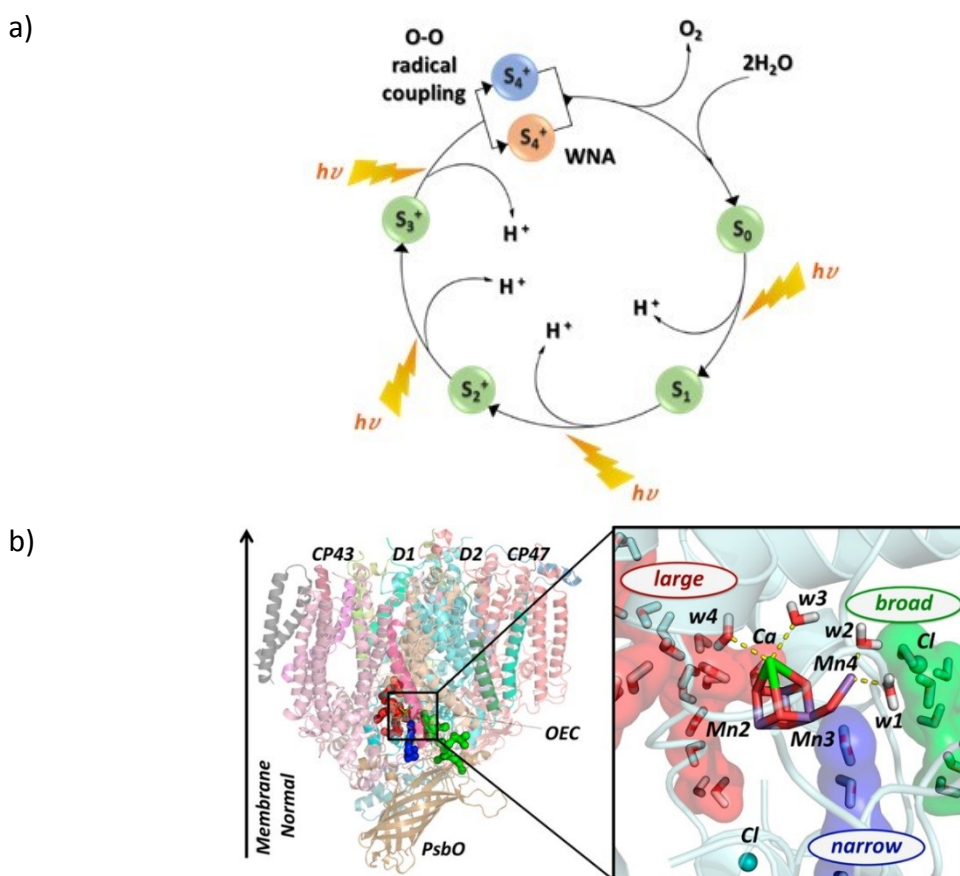


Figure 3-1. Schematic representation of water oxidation during natural photosynthesis. a) S-state cycle for the oxygen evolution reaction in the photosystem II, blue S_4^+ refers to an oxyl-oxo radical coupling as rds and orange S_4^+ to a water nucleophilic attack as rds and b) structure of the PSII (left) and the OEC cluster (right), image taken from Askerka *et. al.*⁹

Photoelectrochemical (PEC) water splitting to produce hydrogen, as explained in *Chapter 1*, is the strategy studied in this chapter to produce solar fuels, using a semiconductor metal-oxide as photoanode. It is well accepted in literature that, the oxidation of water on a metal-oxide surface (which involves 4 photogenerated holes) is considered the kinetic bottleneck of the water splitting process,^{10,11} in spite of the increasing efforts in producing more efficient catalysts.^{12,13}

Light-induced catalytic processes for solar fuels production are very challenging, especially for the oxygen evolution reaction occurring on a metal-oxide photoanode. In the literature, some well accepted characteristics an ideal photoanode have been identified: strong visible light absorption, stability under catalytic conditions, non-toxicity and inexpensiveness, appropriate valence band edge (VBE), *i.e.* VBE must be below the O₂/H₂O redox potential, as well as efficient charge separation and transport.^{14,15} However, it is not often mentioned that materials such as α -Fe₂O₃, BiVO₄, WO₃ and TiO₂, the light absorption and charge separation events, occurring in the bulk and space charge layer (occurring within *ps* to *ms* timescale),^{16–23} are coupled with the catalytic events (taking place in the *ms* to *s* timescale),^{24–27} occurring at the surface of the photoanodes. These coupled events make the system more complicated to control and this kinetic mismatch is, to some extent, the reason for the poor efficiencies some of the most studied metal-oxide photoanodes suffer, such as α -Fe₂O₃, BiVO₄, WO₃ and TiO₂.^{27–29} In the particular case of hematite photoanodes, the slow *ms* – *s* water oxidation kinetics has been observed by means of TAS by our group,^{19,27,30} electrochemical impedance spectroscopy (EIS)³¹ and intensity-modulated photocurrent spectroscopy (IMPS).^{32–34} However, the key factors involved in such slow kinetics are not yet well understood and the rate-limiting process still remains elusive.

Mechanistic studies are key for the understanding of the processes limiting the water oxidation catalysis. In general, such studies have focused particularly on the identification of reaction intermediates and whether the rds corresponds to a water nucleophilic attack (WNA) or to the interaction between two M-O species (I2M).³⁵ For a schematic representation of these two water oxidation rds, see Figure 1-1.

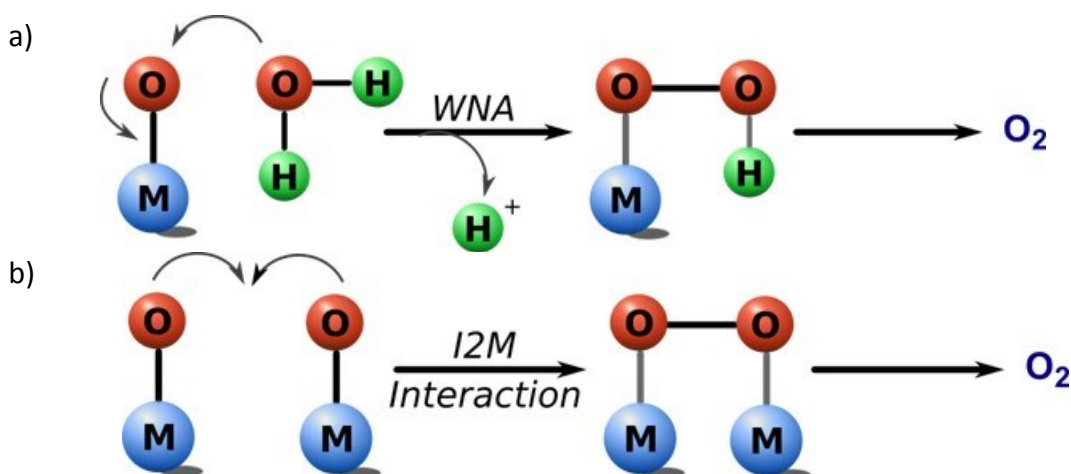
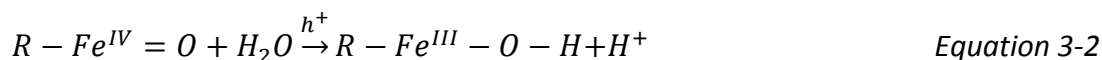


Figure 3-2. Two of the most discussed pathways for the O-O bond formation as rate determining step in the water oxidation catalytic cycle in metal oxide catalysts, a) water nucleophilic attack (WNA) and b) interaction between two M-O species (I2M).

The WNA and I2M mechanisms depicted in Figure 3-2.a and b respectively, have been extensively investigated in homogeneous water oxidation using molecular catalysts. A WNA mechanism, in homogeneous water oxidation, occurs when a molecule of water (with the oxygen atom as nucleophile) attacks a M-O species of the catalyst when the latter is electrophilic enough (*i.e.*, when the metal is in a high oxidation state). In contrast, the I2M mechanism operates when two neighbouring metal-oxo (or metal oxyl) undergo in a radical coupling. The study of these two mechanisms are of high interest due to the fast reaction kinetics (*i.e.*, high turnover frequencies) observed frequently during an I2M mechanism compared to a WNA.^{5,36,37}

Studying these two mechanisms during heterogeneous water oxidation, using metal oxides as catalysts or photocatalysts, has been much more challenging mainly due to analytical techniques limitations. However, optical spectroscopies in conjunction with electrochemical techniques, in both time and frequency domains, supported frequently with theoretical calculations, have been implemented to investigate the water oxidation catalytic cycle on metal oxides.³⁵ In the particular case of hematite photoanodes, the literature has been mainly focused on the nature of the surface holes and/or the reaction intermediate species and whether they localise in surface traps or not.^{38–40} Peter and co-workers, have suggested, by means of EIS and IMPS, that holes in hematite trap in surface states, that might exhibit a chemical nature of Fe^{4+} or Fe^{5+} , and exhibit slow first order rate constants for recombination and charge transfer.^{34,41,42} This has been supported by Hamann and co-workers, who, using EIS and attenuated total reflectance infrared spectroscopy (ATR-IR), have proposed that

water oxidation has a surface trapped intermediate (energetically localised mid-bandgap), which has a $\text{Fe}^{\text{IV}}=\text{O}$ chemical nature,^{43–45} where a mechanism for O-O bond formation is proposed as follows:



where R represents the bulk hematite and h^+ a photogenerated hole and the O-O bond formation is reached after a WNA over the $\text{Fe}^{\text{IV}}=\text{O}$ species after single consecutive charge transfers. Zhao and co-workers have recently, after the first publication suggesting surface hole accumulation by our group⁴⁶ and part of this thesis, suggested the possibility of a water nucleophilic attack mechanism with concerted proton electron transfer (CPET) with changes in the kinetics of electron transfer, by doing isotopic labelling and where the protonation state seems to play an important role in the catalytic cycle.^{47,48} However, further understanding of the catalytic function of water oxidation on hematite (and other metal-oxide photoanodes) and how it correlates with the slow kinetics is paramount to design better materials for solar fuels production. Although, Zhao and co-workers^{47,48} have studied the water oxidation reaction on hematite in parallel to the work presented herein, the conclusions of this Chapter (some of them already published)^{46,49,50} can be applied more widely.

As mentioned in *Chapter 1*, catalytic processes are characterised by the kinetics and mechanism of reaction, which can be studied by means of rate law analyses. In the case of metal-oxide semiconductor materials, their multi-redox nature complicates the study of the kinetics of catalysis. In our group, we have recently proposed a spectro(photo)electrochemical method^{28,46} (described in *Chapter 2*) to study the rate law for water oxidation on metal-oxide photoanodes focusing on the observed kinetics and order of reaction. The experimental determination of this order of reaction on different metal-oxide photoanodes can provide information about the water oxidation rate determining step in such systems.

3.2. Experimental

This Chapter focuses on studying the mechanism and kinetics of the water oxidation reaction on nanocrystalline Si-doped $\alpha\text{-Fe}_2\text{O}_3$ photoanodes, which then is compared to other promising metal-oxide photoanodes such as, BiVO_4 , TiO_2 and WO_3 .

I note here that, the following experiments were not performed by myself. APCVD α -Fe₂O₃ deposition by Dr. Matthew Mayer (École Polytechnique Fédérale de Lausanne). Film synthesis, *J-V* and Rate Laws of BiVO₄ by Dr. Yimeng Ma (Imperial College London), TiO₂ by Dr. Andreas Kafizas (Imperial College London). WO₃ film synthesis by Dr. Timothy Rosser (University of Cambridge) and *J-V* and Rate Law data by Dr. Laia Francàs (Imperial College London), respectively.

3.2.1. (Photo)electrochemical response

The electrochemical and photoelectrochemical (PEC) performance of the nanostructured hematite photoanode, was evaluated as current-potential (*J-V*) responses under dark and ~ 1 sun illumination conditions. I note here that, the illumination used for the experiments in this chapter was from a 365 nm LED, except for the comparative PEC performance of the four photoanodes used in this Chapter. For this comparative PEC responses, a 75 W ozone-free Xe-lamp was used as illumination source, with a KG3 filter to resemble the solar spectrum. The comparative *J-V* responses of the studied photoanodes were evaluated at their best performing electrolyte conditions. A solution of a pH 13.6, 1.0 M NaOH was used for α -Fe₂O₃ and TiO₂, a pH 7 0.1M phosphates buffer was used for BiVO₄ and pH 3 sulphuric acid solution in 0.1 M Na₂SO₃ for WO₃.

3.2.2. Rate law analysis

Rate law analyses were performed as a function of a 365 nm LED illumination, varying the LED intensity from 1 to 40 mW cm⁻², corresponding to intensities from ~ 0.05 to ~ 2.5 suns, therefore as a function of surface hole density, by LI-SEC (light-induced spectroelectrochemistry). The photoinduced absorption (PIA) and transient photocurrent (TPC) responses of the hematite photoanode were measured as a function of pH, temperature and isotope exchange as described below. Photogenerated holes were probed according to the visible spectral behaviour that was obtained for the steady-state photogenerated holes accumulated at the surface of hematite under absence of surface recombination conditions in 0.1 M NaOH.

The comparative study with other metal oxide photoanodes (TiO₂, BiVO₄ and WO₃) was performed using the best performing conditions described in the (Photo)electrochemical response section of this Chapter. The photoanodes were held at a high applied potential

versus the reversible hydrogen electrode (RHE) thereby avoiding back or 'surface' electron-hole recombination as follows, α -Fe₂O₃ and TiO₂ at 1.5 V, BiVO₄ at 1.7 V and WO₃ at 1.4 V.

3.2.3. pH dependency and kinetic isotope effect analysis

The pH dependency study performed on hematite was performed preparing 0.1 M phosphates buffer solutions of pH 6.5, 7.2 and 8.4 by varying the ratio [H₂PO₄⁻]/[HPO₄²⁻]. The solution electrolytes with pH values of 9.3, 11.0 and 12.3 were prepared varying the ratio [HPO₄²⁻]/[PO₄³⁻]. Electrolyte solutions of 0.1 M NaOH and 1.0 M NaOH were used for the pH values of 13.0 and 13.6 respectively. The isotopic exchange for the kinetic isotope effect study used the same reactants concentrations as for the pH study but using >99% deuterated reagents.

3.2.4. Temperature dependence studies

A home-made heating device was used for the temperature dependence study. This heating device is made of an aluminium cell holder, which is thermally insulated with calcium silicate walls (Duratec 750) of 6 mm width. The device contains two holes (front and back) to allow the optical measurements. Two resistive heaters (50 W) and a K-type thermocouple were used to regulate the temperature with the aid of a PID controller (a three term controller). The working and counter electrodes were enclosed in a quartz cuvette that fits in the aluminium cell holder. The reference (Ag/AgCl) electrode was held in another container that was salt-bridged to the reaction electrolyte in the quartz cuvette. Therefore, the applied potential was not corrected for temperature.

3.2.5. Density functional theory (DFT) calculations

Further mechanistic studies were undertaken by means of DFT calculations. The Vienna ab initio simulation package (VASP) was used. To account for d-electron correlation effects, DFT+*U* was used as well. A slab model of 110 hematite was constructed with a hydroxyl terminated surface, accounting for the interaction with water molecules. For simplicity, the slab was calculated as neutral in charge due to (as will be shown in the experimental results) the mechanism of water oxidation does not change with the protonation state of the surface. I note here that the DFT calculations were performed and the results were kindly provided by Mr. Pablo Garrido (ICIQ) and Dr. Ke Yang from Professor victor Batista's group at Yale University

3.3. Results

3.3.1. (Photo)electrochemical response

The electrochemical response (J^{ph} - V) of the APCVD hematite film under continuous light and in dark conditions is shown in Figure 3-3. Under one sun irradiation conditions, the α - Fe_2O_3 film has an onset potential of catalysis of ~ 1.0 V vs RHE and reaches a photocurrent density of $\sim 3.0 \text{ mA cm}^{-2}$ at 1.5 V vs RHE. The PEC response of this film is in agreement with the previously reported light and dark water oxidation on hematite by Kay et. al.⁵¹

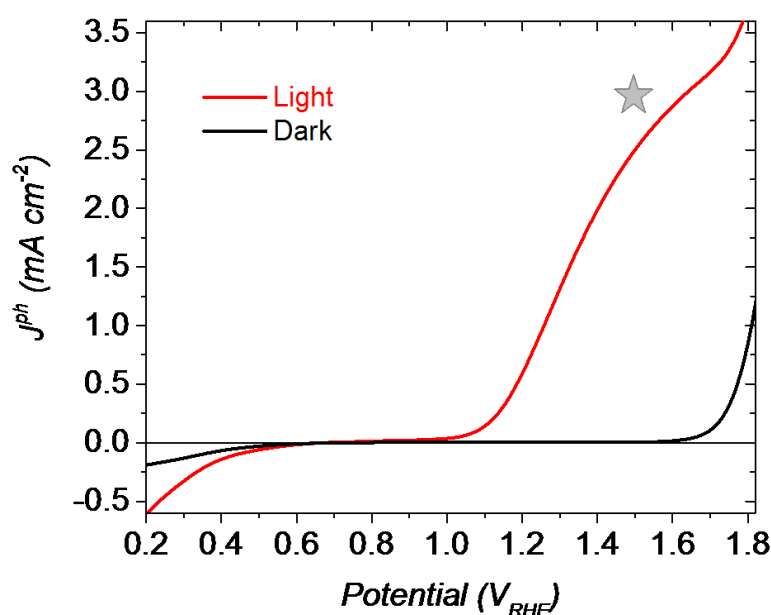


Figure 3-3. Current/potential (J - V) response of the APCVD α - Fe_2O_3 photoanode, under dark (black) and ~ 1 sun, front illumination (electrode/electrolyte) conditions (red) measured in 1 M NaOH. The star indicates the applied potential at which the photo-induced absorption spectroscopy studies were carried out.

As detailed in the *Chapter 1*, one of the main effects upon increasing in the applied potential is the suppression of the back electron-hole or ‘surface’ recombination, due to the increase in band bending.^{31,52} As such, in the experiments presented herein, a high potential was applied, in order to suppress back electron-hole recombination and study only the water oxidation kinetics by surface accumulated holes on hematite.

3.3.2. Spectral features of long-lived holes in α - Fe_2O_3

Upon illumination, photogenerated charge carriers undergo recombination, trapping and separation processes before reaching the surface to react with the electrolyte, as described in *Chapter 1*. As such, the spectral fingerprint of the α - Fe_2O_3 photoanode changes upon hole accumulation at the surface. This time evolution of the characteristic spectral

fingerprint of the α -Fe₂O₃ photoanode under hole accumulation conditions and in absence of surface recombination is presented in Figure 3-4.

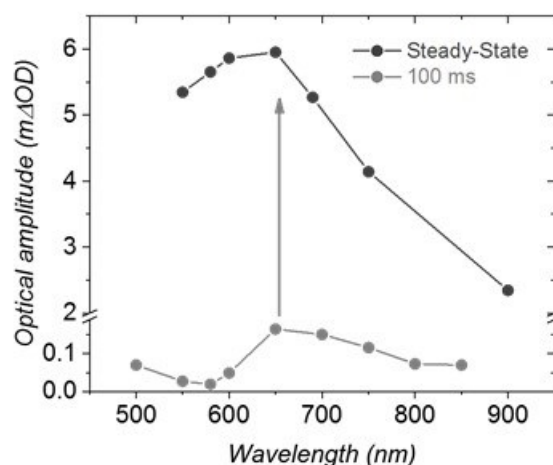


Figure 3-4. Spectra fingerprints upon illumination of the APCVD α -Fe₂O₃ photoanode. Light grey: spectrum measured at 100 ms after 355 nm laser pulse in the TAS system. Dark grey: spectrum measured after 5 s 365 nm continuous LED illumination. The arrow indicates the accumulation of photogenerated holes at the surface of the photoanode at high applied potential (1.5 V vs RHE) *i.e.* in absence of surface recombination, evidence provided by the absence of cathodic spikes in the TPC measurements shown in Figure 3-5.b.

Figure 3-4 shows a spectrum was recorded 100 ms after a 6 ns, 355 nm laser illumination by transient absorption spectroscopy means. This spectrum (light grey in Figure 3-4) shows the characteristic hematite spectral fingerprint previously reported in literature, presenting a weak positive absorption peak between 650 and 700 nm. This positive absorption has been shown to disappear upon addition of hole scavengers, consequently, it has previously been assigned to photogenerated holes at the hematite surface, which increase upon the applied potential, *i.e.* upon reducing surface recombination losses.^{19,28,30} Upon 5 s continuous 365 nm LED illumination a second spectrum was recorded (dark grey in Figure 3-4) by means of light-induced spectroelectrochemistry (LI-SEC). This spectrum shows a broad positive absorption peaking at 650 – 700 nm, in agreement with the long-lived absorption of photogenerated holes accumulated at the surface of hematite shown by Le Formal *et. al.*⁴⁶ Therefore 650 nm was the selected wavelength for the kinetic studies in the following sections.

3.3.3. Calculation of surface hole extinction coefficient

The surface holes optical absorption signal (measured at 650 nm) was converted into surface hole density using the following a procedure described by Le Formal *et. al.*⁴⁶ The α -Fe₂O₃ photoanode was held at 0.9 V vs RHE, where no water oxidation occurs (see Figure 3-3)

and only back electron-hole recombination takes place.⁴⁶ Figure 3-5.a shows the photo-induced absorption signal as a function of 5 s ON/5 s OFF 365 nm LED illumination intensities. The corresponding transient photocurrents, that were measured concomitantly with the optical signals) are shown in Figure 3-5.b, where no catalytic currents are observed and only back electron-hole recombination (*i.e.* anodic and cathodic spikes) is apparent. The accumulated hole density is calculated as the area under the curve of such spikes and correlated with the steady state optical absorption in Figure 3-5.c, leading to a hole extinction coefficient of $640 \text{ M}^{-1} \text{ cm}^{-1}$.⁴⁶

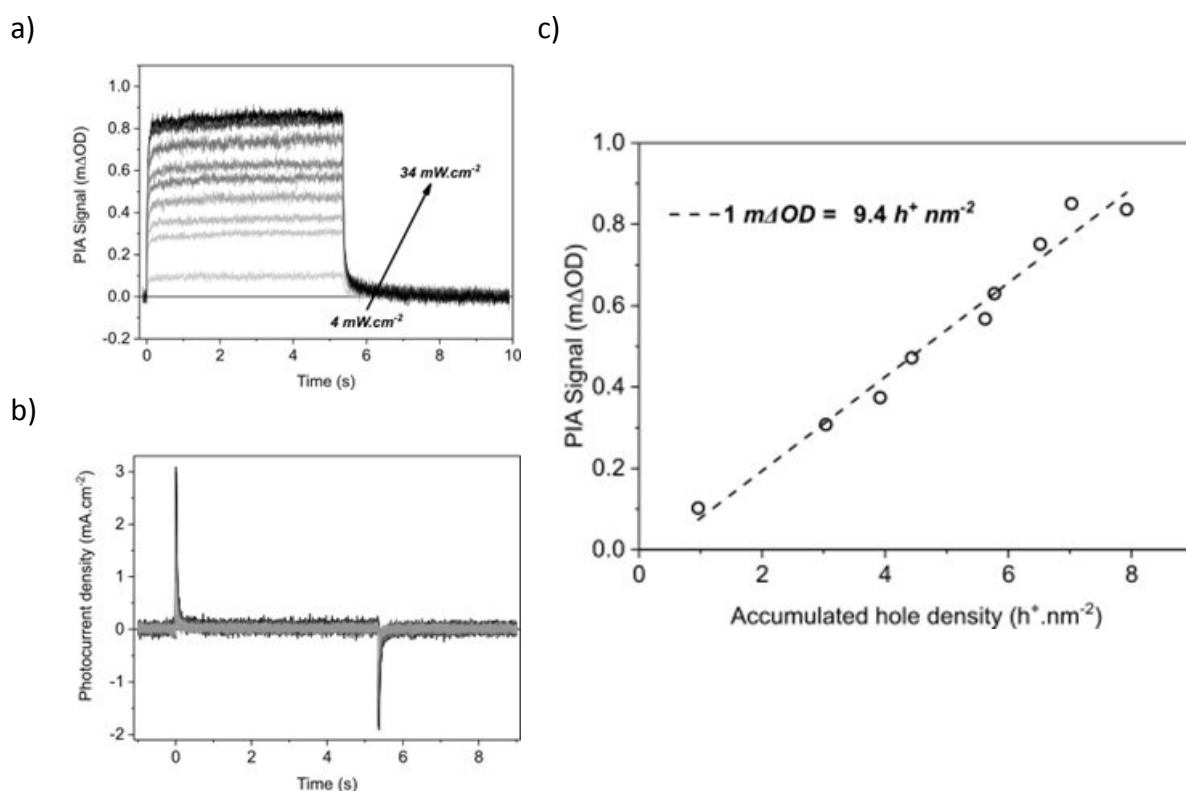


Figure 3-5. Photogenerated hole optical absorption calibration. a) PIA signal of the accumulated holes at the $\alpha\text{-Fe}_2\text{O}_3$ surface monitored at 650 nm during the 5 s ON/5 s OFF pulsed LED illumination at 0.9 V vs RHE, b) transient photocurrent density and c) correlation between the recombined charges and the steady-state optical absorption measured at 650 nm and 0.9 V vs RHE as a function of light intensity, leading to a hole extinction coefficient of $640 \text{ M}^{-1} \text{ cm}^{-1}$. These data were modified from Le Formal *et. al.*⁴⁶

3.3.4. Rate law analysis of water oxidation on $\alpha\text{-Fe}_2\text{O}_3$

Turning now to study the kinetics and mechanism of rate determining step (rds) of the PEC water oxidation on $\alpha\text{-Fe}_2\text{O}_3$ photoanodes by means of LI-SEC (*i.e.* the simultaneous measurement of the photo-induced absorption (PIA) and the transient photocurrent (TPC) of

the photoanode) as a function of light intensity. An example of the data collected is shown in Figure 3-6, for the oxidation of water on a $\alpha\text{-Fe}_2\text{O}_3$ photoanode at 1.5 V vs RHE. As stated previously in *Chapter 2*, the PIA, *i.e.* optical signal, is proportional to the density of holes accumulated at the surface of the photoanode, whereas the TPC, *i.e.* electrochemical signal monitors the rate of reaction, in other words the transfer flux of accumulated holes to the electrolyte.

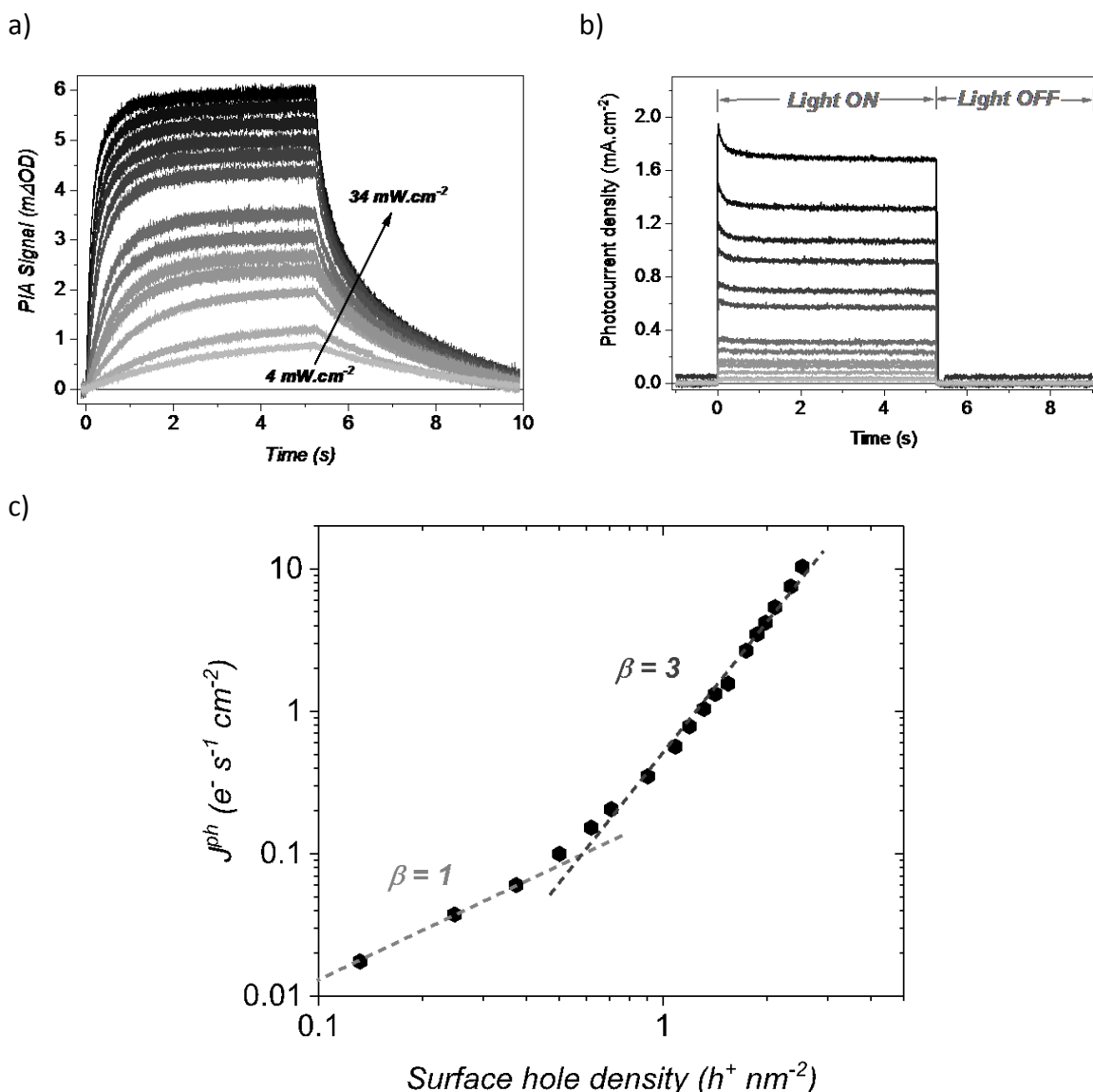


Figure 3-6. Light-induced spectroelectrochemistry (LI-SEC) data of water oxidation on $\alpha\text{-Fe}_2\text{O}_3$ as a function of 5 s on/5 s off pulsed 365 nm illumination (~ 4 to ~ 34 mW cm⁻²) under 1.5 V vs RHE applied potential, a) PIA signal of surface valence band hole density (p_s) probed at 650 nm, b) simultaneously assay of TPC and c) steady-state rate law analysis, rate of reaction (j^{ph}) vs surface hole density (p_s), the dashed lines represent the fitted functions for first and third order regimes. These data were modified from Francas *et. al.*²⁸

The optical signals shown in Figure 3-6.a, exhibit a characteristic rise and plateau when the flux of holes towards the surface is equal to the kinetics of holes transferred to the electrolyte. This rise and plateau are assigned therefore to the accumulation and steady-state of photogenerated hole flux. Once the LED is turned off, the decay of this PIA signal is assigned to the reaction of holes with the electrolyte, when no surface recombination processes are present, corroborated by the absence of negative spikes, characteristic of back electron-hole ('surface') recombination, when the light was turned off in the TPC signal (see Figure 3-6.b) as previously shown in literature.^{41,52-54} These TPC signals, shown in Figure 3-6.b, exhibit a sharp rise and decays when light is turned on and off, respectively, compared to the PIA signal. This is assigned to the faster electron extraction compared to the hole transfer characteristic of hematite photoanodes. As described in *Chapter 2*, these two sets of data allow the analysis of the water oxidation steady-state rate law (see Equation 3-1 for reference, previously derived in *Chapter 2*), shown in Figure 3-6.c.

$$\log(J^{ph}) = \beta \cdot \log(p_s) + \log(k_{wo}) \quad \text{Equation 3-3}$$

where β corresponds to the order of water oxidation reaction. It is apparent from Figure 3-6.c that water oxidation transitions from a 1st to a 3rd order of reaction upon increasing the surface hole density (p_s). This indicates that water oxidation undergoes in two different rate determining steps, that are tentatively assigned to different reaction pathways, according to the surface hole accumulation. Strikingly, the steady-state response of $\alpha\text{-Fe}_2\text{O}_3$ under 1 sun irradiation ($\sim 3 \text{ mA cm}^{-2}$) falls within the 3rd order reaction region. To further study these two water oxidation mechanisms, their change in kinetics was studied upon variation in the electrolyte pH, temperature and isotopic labelling of the electrolyte. All these results are presented in the following 3 subsections.

3.3.5. Temperature dependence study (LI-SEC measurements)

The kinetics of the two water oxidation mechanisms were studied as a function of the reaction temperature. Figure 3-7 shows the dependence of the reaction kinetics upon increasing the temperature from 21 to 50 °C, under conditions of no surface recombination.

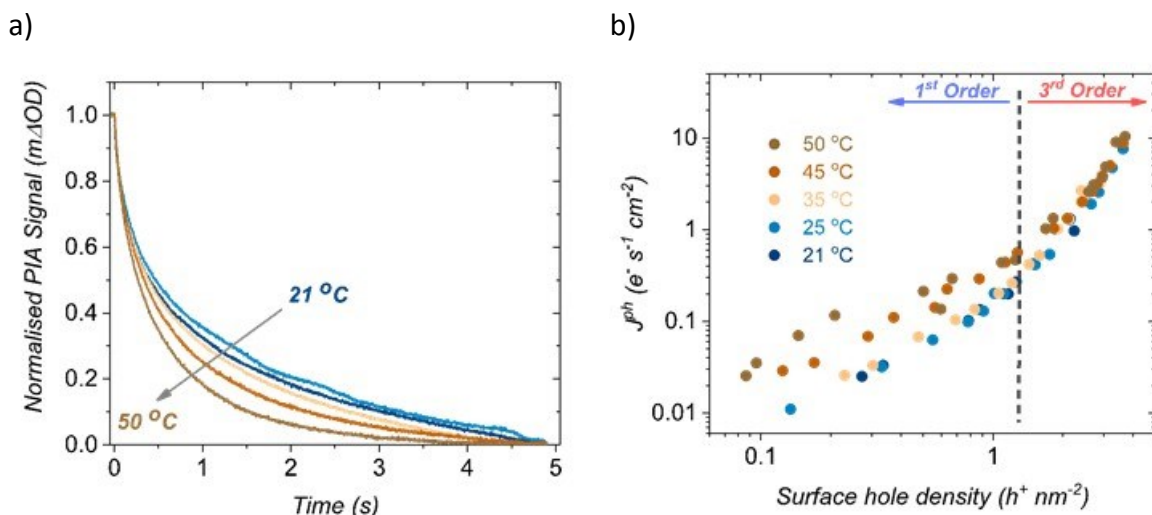


Figure 3-7. Temperature dependence of the water oxidation kinetics. a) PIA signal decay dynamics, normalised at $\sim 7 m\Delta OD$. and b) steady-state rate law analysis, rate of reaction (J^{ph}) vs surface hole density (p_s) of water oxidation on $\alpha\text{-Fe}_2\text{O}_3$ as a function of 5 s on/5 s off pulsed 365 nm illumination (~ 1 to $\sim 35 mW cm^{-2}$) under 1.5 V vs RHE applied potential and as a function of temperature from 21 to 50 °C. The dashed line represents approximately the transition point from 1st to 3rd order.

Figure 3-7.a shows the PIA decays upon turning off the irradiation as a function of the temperature. The full data set of LI-SEC measurements can be found in Figure A-1 in the appendix. For the presented figure, the optical signal corresponding to one light intensity (PIA signal that plateaus at $\sim 7 m\Delta OD$) of each temperature was normalised for comparison. The dynamics of the PIA signal decays corresponds to the water oxidation kinetics in absence of surface recombination. As such, Figure 3-7.a indicates, qualitatively, that upon increasing temperature the reaction rate increases at the same initial surface hole density (*i.e.* same plateau optical amplitude).⁵² An analysis of the steady-state, shown in Figure 3-7.b, confirms the dependency of the reaction rate constant with respect to the temperature change. A qualitative analysis of the water oxidation rate constants in Figure 3-7.b yields to the observation of the 1st order rate constant (left side of the dashed line in the Figure) undergoing in a larger temperature dependence compared to the 3rd order reaction mechanism. This observation would support the hypothesis of the catalytic effect by $\alpha\text{-Fe}_2\text{O}_3$ photoanodes doing water oxidation.

3.3.6. pH dependence and isotopic labelling studies

Turning now to the physicochemical study of the semiconductor-liquid junction by varying the pH of the electrolyte, first the photoelectrochemical response of the $\alpha\text{-Fe}_2\text{O}_3$ photoanode is shown followed by its spectral characteristics and finally the LI-SEC data is presented.

The photoelectrochemical response (J^{ph} - V) under chopped ~ 1 sun illumination of the α - Fe_2O_3 photoanode at different electrolyte pH conditions is shown in Figure 3-8. The APCVD hematite film exhibits a catalytic onset potential which, qualitatively, decreases as the pH increases from ~ 1.2 to ~ 1.0 V vs RHE. This behaviour is in agreement with similar trends previously reported by Klahr *et. al.*⁵⁵ and Zhang *et. al.*,⁴⁷ for flat undoped and nanowire arranged hematite photoanodes. On the other hand, the α - Fe_2O_3 film achieves a photocurrent density of $\sim 3.0 \text{ mA cm}^{-2}$ at alkaline pH and drops to $\sim 2.0 \text{ mA cm}^{-2}$ at mildly acidic pH measured at 1.5 V vs RHE.

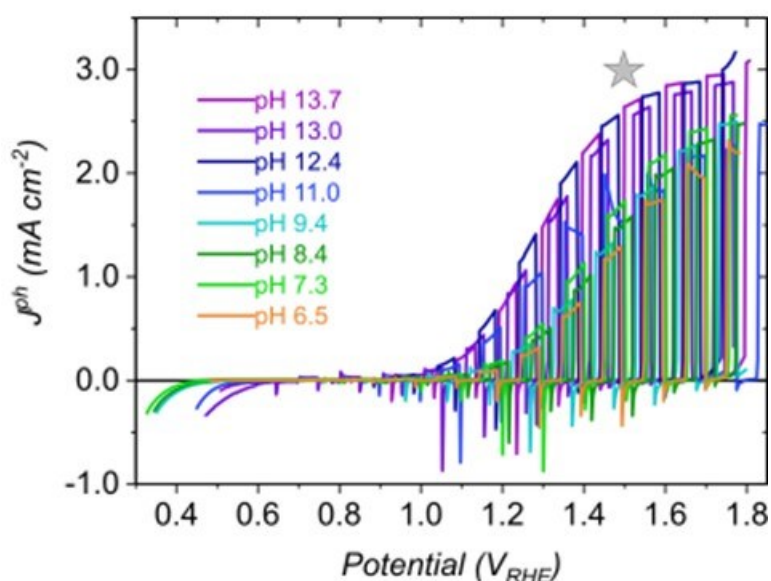


Figure 3-8. Photocurrent/potential (J^{ph} - V) response of the APCVD α - Fe_2O_3 photoanode, under ~ 1 sun chopped illumination (electrode/electrolyte) conditions measured in a range of electrolyte pH values from 6.5 to 13.7. The star indicates the applied potential at which the photo-induced absorption spectroscopy studies were carried out.

It should be noted that, although the high applied potential, for electrolytes with pH values below 12.4, negative current spikes can be observed in Figure 3-8, previously assigned to back electron-hole recombination.^{31,52} These recombination losses are not expected to influence directly the steady-state kinetic analysis, only the optical decays upon turning the light off. This is due to the steady-state rate law analysis depends upon the overall population of holes at the photoanode surface.⁵⁶ This will be further discussed in *Chapters 4 and 5*.

Before undertaking the LI-SEC analysis to extract kinetic information of the water oxidation reaction upon different pH values, it is important to verify that the catalytic species in steady-state conditions are comparable through the studied pH values range. Spectral fingerprints (see Figure 3-9) were measured, at two different pH values, upon 5 s continuous 365 nm LED

illumination (equivalent to ~ 1 sun). The spectral response of the APCVD hematite film at pH 6.9 shown in Figure 3-9 resembles the corresponding for pH 13.0 (also shown in Figure 3-4) with a broad positive absorption peaking at 650 – 700 nm. From Figure 3-9, two main differences (spectra maxima and optical features) in the spectra are apparent. The observed difference in the optical amplitude is assigned here to a lower accumulation of holes at the $\alpha\text{-Fe}_2\text{O}_3$ surface due to the surface recombination losses observed in Figure 3-8. The observed difference in optical features, a sharper absorption peak, might correspond to a spectral change in the 580 nm absorbing species. Their spectral change can be due to the protonation state at pH 6.9 and therefore, be in a different chemical environment, since the point of zero charge (PZC) in hematite is reported at pH values $\sim 8.8\text{--}10$.^{57–60}

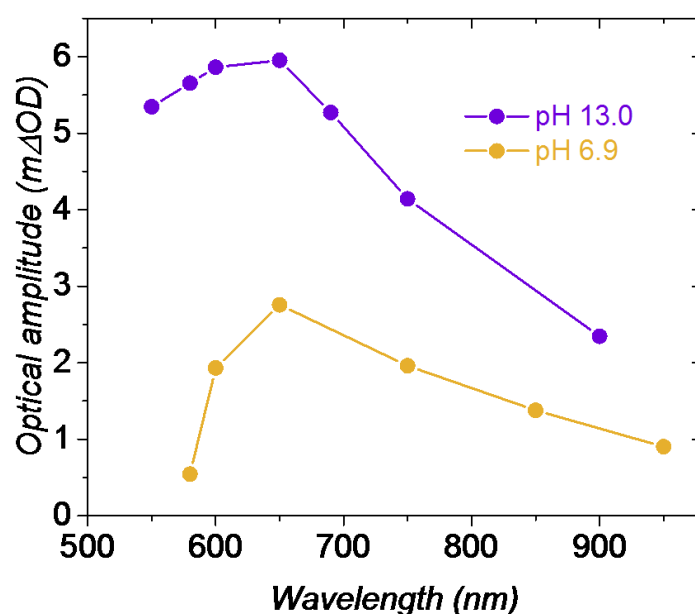


Figure 3-9. Spectra fingerprints of the APCVD $\alpha\text{-Fe}_2\text{O}_3$ photoanode measured at two different pH electrolytes, neutral (yellow) and alkaline (purple, same data as Figure 3-4) upon 5 s 365 nm continuous LED illumination at high applied potential (1.5 V vs RHE).

The observed effect of both, an increasing pH (see Figure 3-10.a) and isotopic labelling at equivalent pD values (see Figure 3-10.b), by means of LI-SEC measurements, appear to be important in the kinetics of the reaction rather than in the mechanism (see Figures A-2 and A-3). Figure 3-10.a shows the water oxidation rate law analysis as a function of increasing the electrolyte pH. From this Figure, it is apparent that the two already observed regimes of reaction are present at all the studied pH values suggesting that the reaction pathway does not change with the pH. However, it can be observed that the intercept (*i.e.*, rate constant)

moves to higher values (upwards), corresponding to an increase in the rate constant upon increasing the pH.

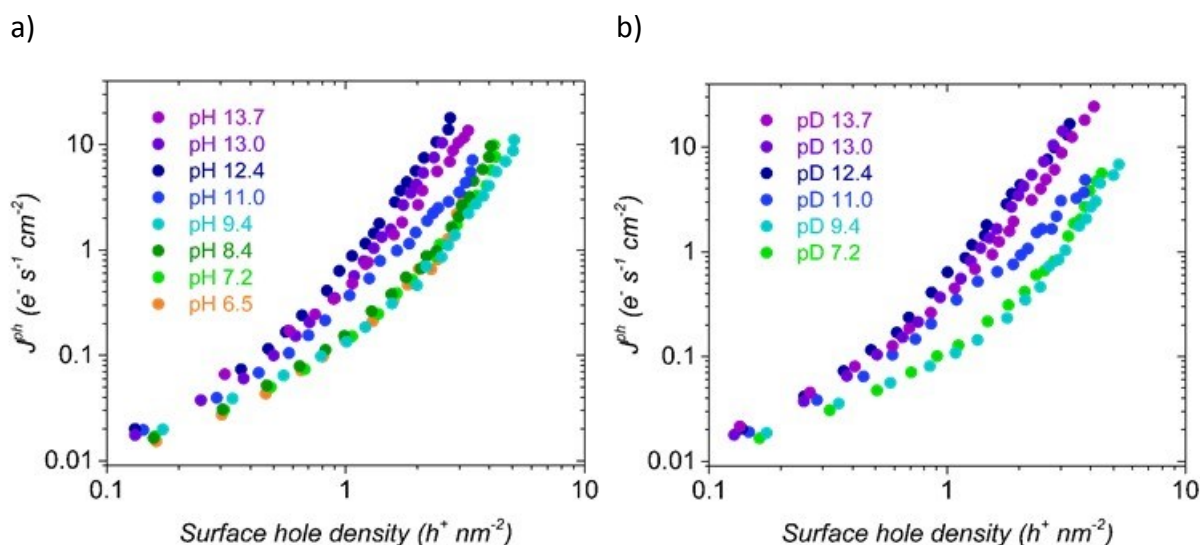


Figure 3-10. Rate law analysis for the water oxidation reaction on the APCVD α -Fe₂O₃ photoanode, measured at 650 nm under 1.5 V vs RHE in a range of a) electrolyte pH values from 6.5 to 13.7 and b) electrolyte pD values from 7.2 to 13.7, as a function of 5 s on/5 s off pulsed 365 nm illumination (~ 1 to $\sim 35 mW cm^{-2}$).

The isotopic labelling study shown in Figure 3-10.b, exhibits a similar trend compared to the pH dependence study. The 1st and 3rd order regimes are observed, whilst upon decreasing the concentrations of D⁺ in the electrolyte, with pD values varying from 7.2 to 13.7, the rate constant of D₂O oxidation increases. I note here that the pD values were calculated from the corresponding acid-base dissociation constant⁶¹ for the buffer solutions described in the Experimental section of this chapter. It is also apparent from the *JV* data, shown in Figure 3-8, and the kinetic data in Figure 3-10.a and b, that the reaction becomes faster and a higher photocurrent is extracted, with a threshold of pH ~ 11 , upon surface deprotonation (PZC $\sim 8.8-10$) consistent also with the spectral change observation.

Figure 3-10 shows, as expected, the distinctive 1st and 3rd order reaction regimes, with a threshold at $\sim 1 h^+ nm^{-2}$, for both hydrogenated and deuterated electrolytes. However, it can also be noticed that the rate laws do not overlap at all pH or pD values suggesting the kinetics of the reaction are affected by the electrolyte pH. Therefore, it can be concluded that the water oxidation mechanisms, for both reaction regimes, undergo the same pathway at the pH or pD values reported herein with a merely kinetic effect that might be sensitive to the protonation state of the hematite surface.

3.4. Discussion

3.4.1. Temperature and pH dependence and isotopic labelling studies

The kinetic behaviour of the holes accumulated at the surface of APCVD α -Fe₂O₃ photoanodes was studied by means of rate law analyses (see Equation 3-3) as a function of surface hole density (*i.e.*, light intensity). These kinetics were studied upon varying the temperature, pH and isotopic labelling, as described in *Chapter 2*, and reported for TiO₂ and BiVO₄, elsewhere.^{28,49,50} The water oxidation rate law analysis on α -Fe₂O₃ photoanodes was first reported by Le Formal *et. al.*,⁴⁶ showing a slope value (β) transitioning from 1 to 3 upon increasing the hole accumulation at the surface as shown in Figure 3-6. These order of reaction values are associated with the number of holes that need to be accumulated to overcome the rate determining step of the water oxidation reaction. It must be noted that the orders of reaction reported herein must not be confused with the molecularity of a reaction. The molecularity of a given reaction is the theoretical number of species (atoms or molecules) that collide for a reaction to proceed, whereas, the order of reaction is an experimental factor that correlates the rate of a reaction with the concentration of the reagents,⁶² as will be further discussed below.

The observed transitioning, from 1st to 3rd reaction order, behaviour in all the experiments herein (Figure 3-7.b and Figure 3-10.a and b) suggest a change in the water oxidation rate determining step (rds) and therefore a change in its activation energy. This order of reaction transitioning behaviour has been observed in water oxidation molecular catalysts. For example, Shaffer *et. al.*⁶³ reported a change in the water oxidation rds from a 1st to a 2nd order as a function of the reported Ru catalyst concentration and was associated with a change in the catalytic mechanism. Thus, the change in the water oxidation order of reaction observed in the rate law analyses herein, is assigned to a change in the reaction mechanism. Remarkably, this behaviour is maintained in the temperature range reported herein, which suggests that the kinetics of water oxidation might vary but the mechanisms remain constant.

A quantitative analysis of the kinetic data presented in Figure 3-7.b as a function of temperature yields to the Arrhenius plot shown in Figure 3-11.a and b. Such Arrhenius analyses were performed in two different ways to confirm these results. Firstly, the water oxidation rate constants for both reaction regime were calculated from the intercept of the linear fittings of the data presented in Figure 3-7.b, based on the Equation 3-4 (*i.e.* rate law).

$$J^{ph} = k_{WO} \cdot p_s^\beta \quad \text{Equation 3-4}$$

Alternatively, replacing the rate constant term according to the Arrhenius analysis, Equation 3-4 can be rewritten as:

$$J^{ph} = A \cdot e^{-Ea/k_B T} \cdot p_s^\beta \rightarrow \ln(J^{ph}) = \frac{-Ea}{k_B T} + \ln(A) + \ln(p_s^\beta) \quad \text{Equation 3-5}$$

where Ea is the activation energy and k_B is the Boltzman constant. It is apparent that to calculate the activation energy from Equation 3-5, p_s^β has to be a constant value.

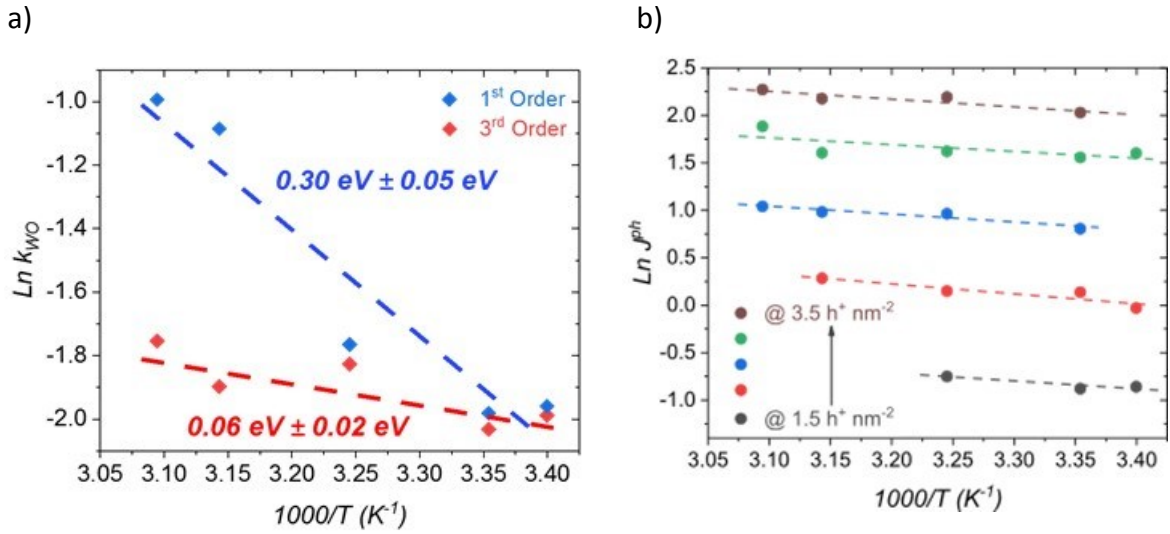


Figure 3-11. Arrhenius plot of the water oxidation reaction, on the APCVD α -Fe₂O₃ photoanode, a) plotting the rate constants for the observed 1st and 3rd reaction order providing the activation energies for both regimes. The rate constants were calculated from the intercept of the steady-state rate law analyses at a range of temperatures from 21 to 50 °C shown in Figure 3-7, measured at 1.5 V vs RHE. The dashed lines indicate the fitting to extract the activation energy values and b) using the photocurrent density values (J^{ph}) at a fixed surface hole density for the 3rd order of reaction using Equation 3-5.

Figure 3-11.a shows, for the 1st order regime, when only one hole arriving to the surface is required to overcome the rate determining step, an activation energy of 300 ± 50 meV is found, which is in agreement with previously reported values for hematite photoanodes under similar conditions of applied potential and low photon flux.^{64–66} Using Equation 3-5 for surface hole densities between 0.1 and $1 \text{ h}^+ \text{ nm}^{-2}$, an activation energy of 310 ± 40 meV is obtained, confirming the validity of both methods.

Upon increasing surface hole accumulation, for the 3rd order regime, the activation energy is reduced ~ 5 times ($Ea = 60 \pm 20$ meV, from Figure 3-11.a and 70 ± 10 meV from analysis in Figure 3-11.b). This reduction in the activation energy from the 1st to the 3rd order mechanism

is indicative of the catalytic behaviour from the $\alpha\text{-Fe}_2\text{O}_3$ surface towards water oxidation. Consequently, when the surface hole density is high enough, a more favourable catalytic pathway would be accessed on the hematite surface.

Turning now to discuss the effect of the electrolyte pH on the kinetics and mechanisms for water oxidation, in Figure 3-12.a is shown the extracted rate constants as a function of pH, for both 1st and 3rd order regimes. From this figure, it is apparent that the kinetics of the reaction until pH 9.4 for both, 1st and 3rd order mechanisms, remain unaffected by changes in the electrolyte pH. However, for pH values higher than 9.5 the water oxidation rate constant increases constantly for the 1st order regime whereas it peaks at a pH value of 12.4 for the 3rd order regime. The observed transition from constant to faster kinetics at pH 9.4 coincides, as mentioned before, with the reported point of zero charge (pzc) of hematite (8.8-10),^{58–60,67} which suggests that proton removal from the surface takes place during the catalytic cycle for both order regimes.⁴⁷ Thus, a deprotonated surface is essential to facilitate the catalytic reaction. The reason why the rate constant value peaks at pH 12.4, is tentatively assigned to a catalytic site competition between H_2O ($\sim 53\text{ M}$) and OH^- (increasing from $\sim 1 \times 10^{-7}\text{ M}$ to $\sim 1\text{ M}$) substrates. Although the better nucleophilic characteristics the OH^- groups present in the electrolyte, H_2O is in excess in the electrolyte. In addition to that, this kinetic behaviour appears to be unaffected by H/D isotopic exchange as shown in Figure 3-12.a, inset.

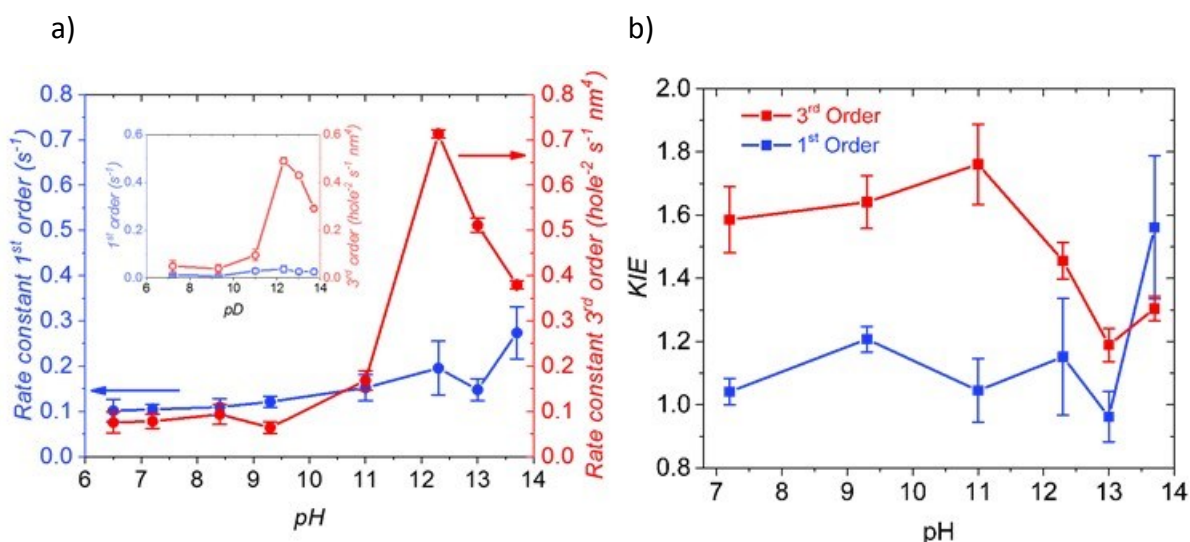


Figure 3-12. Kinetic analysis for the oxidation of water on the APCVD $\alpha\text{-Fe}_2\text{O}_3$ photoanode, under 1.5 V vs RHE in a range of pH values between 6.5 to 13.7. a) pH and pD (inset) dependence of the water oxidation rate constants for the 1st (blue) and 3rd (red) order regimes and b) the corresponding and comparative kinetic isotope effect for the 1st (blue) and 3rd (red) order regimes.

Figure 3-12.b shows the calculated kinetic isotope effect (KIE) on the water oxidation reaction for both, 1st and 3rd order regimes, as a function of the pH. It is apparent that the observed KIE for the 1st order regime (blue in Figure 3-12.b) appears to be flat, with only one point showing a higher KIE, but also with a high uncertainty. This constant behaviour contrasts with the drop from a KIE of ~ 1.6 to ~ 1.2 observed for the 3rd order reaction regime (red in Figure 3-12.b) at a pH value that coincides with the deprotonation of the surface. The observed KIE ~ 1.6 corresponds to a secondary KIE (the expected primary KIE is ~ 10.7) for O-H bonds. This KIE value is indicative that, the rds does not involve the breaking of an O-H bond but rather an O-H bond reorganisation could be involved in another stage of the water oxidation mechanism, as discussed below.

Table 2-1, displayed in *Chapter 2*, shows the predicted primary and secondary KIE values for an O-H bond breaking as 10.73 and 2.72, with the later corresponding to a bending mode, that is almost twice as high than the experimental value. As such, the constant KIE value of ~ 1.6 for the oxidation of water under the 3rd order regime on a protonated hematite surface, suggests a weak secondary kinetic isotope effect that can be assigned to the contribution of two processes. Firstly, to early events, during the catalytic cycle, of deprotonation and secondly, to a proton still present in the transition state during the rds. This is due to the KIE value drops to ~ 1.2 instead of 1.0, which indicates that the kinetics of the rds are reduced by the presence of a D atom, which might cause bond bending limitations.

A further comparison between the 3rd order water oxidation rate constants with the onset of catalysis is shown in Figure 3-13. It is apparent that, similarly to the rate constants, the photocurrent onset follows a constant behaviour upon increasing the OH^- concentration up to a pH ~ 9.4 . This constant behaviour, corresponds to a change in 59 mV per pH unit, *i.e.*, a Nernstian behaviour.⁶² This indicates that at pH values where the $\alpha\text{-Fe}_2\text{O}_3$ surface is still protonated a proton coupled electron transfer (PCET) takes place and might limit the surface holes accumulation process; however, it is not involved in the rds as the KIE observed is a weak secondary effect, as discussed previously. The catalytic onset, upon surface deprotonation, decreases to more negative potentials by a factor of ~ 100 mV per pH unit and coincides with the increase in the 3rd order rate constant.

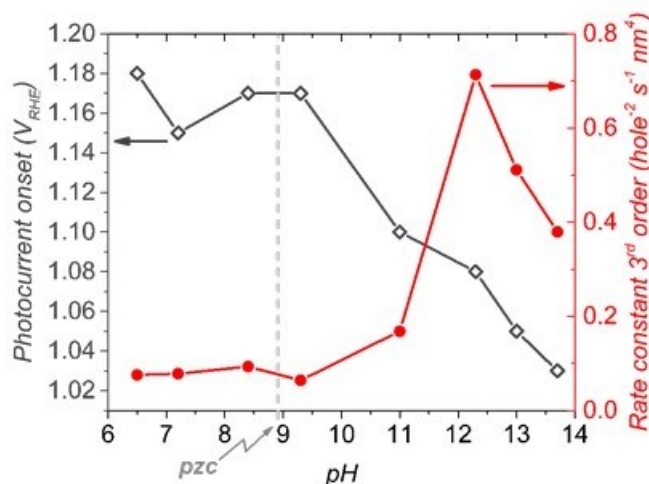


Figure 3-13. Comparative pH dependence between the photocurrent onsets and the 3rd order rate constants for the oxidation of water on the APCVD α -Fe₂O₃ photoanode, under 1.5 V vs RHE. The photocurrents onsets were calculated from the J^{ph} -V curves in Figure 3-8. The dotted line corresponds to the reported point of zero charge (pzc) for α -Fe₂O₃.

3.4.2. Mechanistic implications

Water oxidation on α -Fe₂O₃ photoanodes has been shown herein to transition from a 1st reaction order mechanism to a 3rd order one upon increasing the density of holes accumulated at the surface. These surface holes have been observed, by *in operando* infrared spectroscopy by Zandi and Hamman,⁴⁵ to have the form of Fe^{IV}=O species and are the species monitored by LI-SEC means herein. The two observed distinct order of reactions are tentatively assigned to two different reaction mechanisms, where the 1st order pathway exhibits an $E_a = 300$ meV. At low densities of Fe^{IV}=O species accumulated at the α -Fe₂O₃ photoanode surface, no O-H bond breaking takes place in the rds of this 1st order mechanism, which is in agreement with previous knowledge about water oxidation mechanisms on metal-oxide photoanodes such as hematite and titania.^{45,68–71} It has been hypothesised that the peroxide species formed at the photoanode surface could be released as H₂O₂ which can undergo in a subsequent decomposition⁶⁸ at these alkaline conditions generating O₂ and further experiments would be required to conclude on this.

Turning now to discuss the remarkable 3rd order rate determining step (rds) at high hole accumulation (< 1 h⁺ nm⁻² herein), including 1 sun illumination conditions. This rds is, similarly to the 1st order kinetics, insensitive to changes in pH and isotopic labelling, but its kinetics, although in different proportion, are accelerated upon surface deprotonation. It is apparent that this is the preferential pathway, at high Fe^{IV}=O species accumulation, for oxidation of water as its activation energy (60 meV) is lower than the 1st order E_a . Additionally, the

observed KIE implies that O-H bond breaking does not occur at the rds, with a possible PCET mechanism limiting the hole accumulation in early stages of the catalysis.

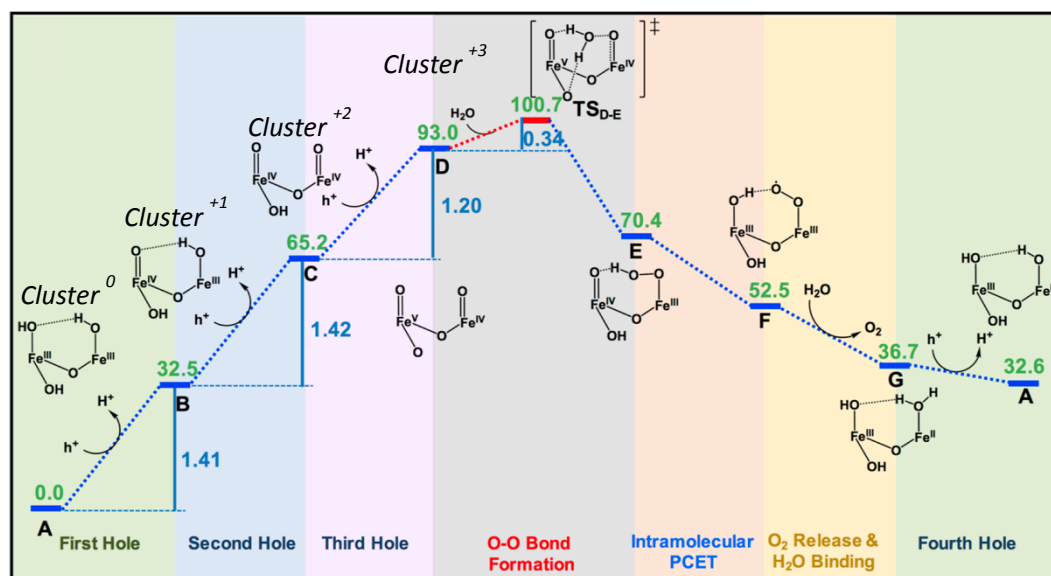


Figure 3-14. Representation of the proposed possible water oxidation mechanism on the APCVD $\alpha\text{-Fe}_2\text{O}_3$ photoanode, under ~ 1 sun illumination at 1.5 V vs RHE conditions, suggested by DFT calculations. (Relative free energies are given in green in the unit of kcal/mol and free energy changes are given in blue in the unit of eV; rate-determining steps are shown in red). Dash lines indicate hydrogen bonds and dotted lines indicate partially formed bonds at transition states. This is a modified figure from the submitted manuscript “*Multihole catalysis of water oxidation on hematite photoanodes: Insights from in operando spectroelectrochemistry and density functional theory*”, with DFT calculations undertaken by Dr. Ke Yang, Pablo Garrido and Professor Victor Batista at Yale University.

DFT calculations, performed elsewhere as noted above, served to rationalize the experimental findings and to propose a possible water oxidation mechanism on the $\alpha\text{-Fe}_2\text{O}_3$ photoanode, at a molecular level, shown in Figure 3-14. In this figure, the mechanism starts with the accumulation of two photogenerated holes. This is the formation of adjacent $\text{Fe}^{\text{IV}}=\text{O}$ species, *via* subsequent electron transfer (or PCET at pH values below the PZC) forming a bimetallic cluster doubly oxidised (Cluster^0 to Cluster^{2+} in Figure 3-14). A subsequent oxidative step takes place when a third surface hole diffuses to the cluster (Cluster^{3+} in Figure 3-14), followed by a water nucleophilic attack and a subsequent O-O bond formation during the rate determining step in accordance with the low KIE observed, as no O-H bond breaking is involved. After the O-O bond formation, the rest of the reaction is energetically downhill, from the fourth hole transfer to oxygen release. These DFT calculations, predicted activation enthalpy of 50 meV and similar potentials for the initial three oxidation steps (equilibrium

steps). This might suggest that the 1st, 2nd and 3rd hole transfers to the reaction cluster could be limited by the ability of holes to diffuse to such cluster. These subsequent oxidations lead the cluster to increase its ‘global’ oxidation state to accumulate enough oxidative power to oxidise water. This process will be referred as to redox levelling process hereafter.

Recently, Zhao and co-workers,⁴⁸ have reported a mechanistic study of water oxidation on a nanorod α -Fe₂O₃ photoanode by attenuated total reflectance infrared spectroscopy (ATR-IR) and electrochemical impedance spectroscopy (EIS) under photoelectrochemical water oxidation conditions. In this study, the authors propose that upon increasing the electrolyte pH, the water oxidation reaction transitions from a 1st to a reaction order of 2.5 as a function of surface hole density. This order of reaction at high pH (~ 2.5) can be compared to the 3rd order reported herein. The difference can be attributed in part to the small range of hole densities reported, but also can be attributed partly to the raw data conversion to surface hole density. The authors use impedance spectroscopy (EIS) to measure resistance and capacitances using an equivalent circuit still in debate.^{52,55,72} It is important to consider that the interpretation of EIS data is not straightforward and the selection of an appropriate model to fit the data is fundamental.

Interestingly, Zhao and co-workers⁴⁸ observed a FT-IR signal at $\sim 1100\text{ cm}^{-1}$, which is assigned to the stretch vibration of a peroxo species ($\text{Fe}^{\text{III}}\text{-O-H}\cdots\text{O}^{\bullet}\text{-O-Fe}^{\text{III}}$) that is similar to the proposed transition state during the rate determining step (rds) of the reaction shown in Figure 3-14. I note here that, although the authors propose such peroxo species including Fe^{III} atoms, that signal at $\sim 1100\text{ cm}^{-1}$ focuses on the peroxo vibration, the presence of Fe^{IV}=O species can be observed at $\sim 900\text{ cm}^{-1}$, previously reported by Zandi and Hamann.⁴⁵ Therefore, the given spectroscopic evidence elsewhere,^{45,48} concomitant with the presented rate law analyses and DFT calculations allow to propose a possible reconciled mechanism for water oxidation on hematite shown in Figure 3-14.

A similar mechanism for water oxidation on Co₃O₄ spinel, has recently been suggested to take place upon a water nucleophilic attack on two adjacent Co^{IV}=O species forming a cluster which would resemble the *Cluster*⁺² proposed in Figure 3-14. Based on DFT calculations and rapid-scan FT-IR measurements, Frei *et. al.*,^{73,74} suggest that a transitioning, from ‘slow’ to ‘fast’, mechanism takes place according to the ability of the reaction cluster to accumulate more than one oxidising equivalents (Co^{IV}=O species). This transitioning behaviour resembles

the 1st to 3rd order mechanism transitioning, reported herein, according to the accumulation of surface holes. Comparison with other catalytic systems

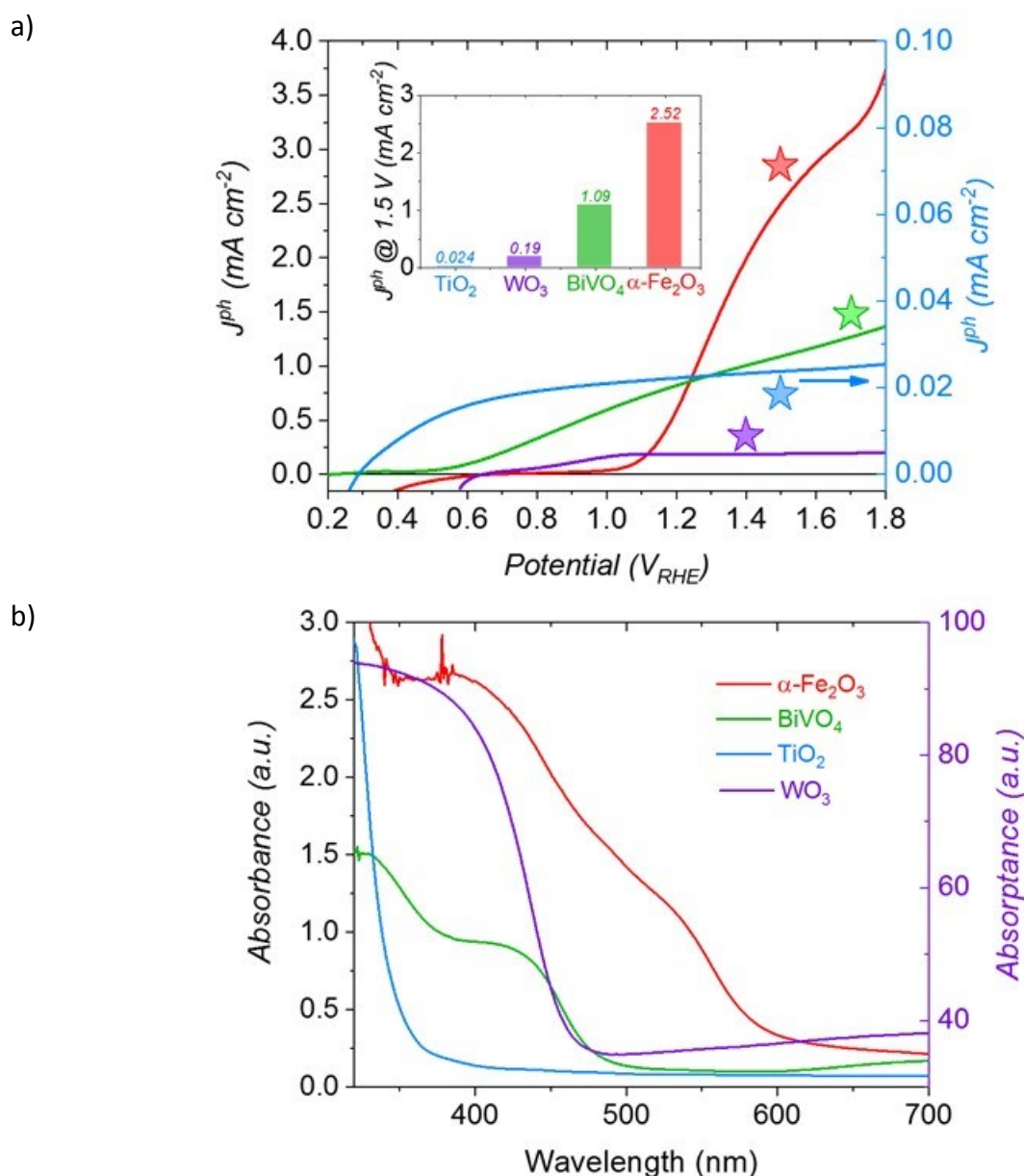


Figure 3-15. Comparative analysis of water oxidation on four of the most studied metal-oxide photoanodes, α -Fe₂O₃ (red), BiVO₄ (green), TiO₂ (blue) and WO₃ (purple). a) Photocurrent/potential (J^{ph} -V) response of the four studied photoanodes, ~1 sun illumination conditions. The star indicates the applied potential at which the rate law analyses were carried out. Inset: J^{ph} achieved for each held photoanode at 1.5 V vs RHE and b) UV-Vis spectra of the four photoanodes. Measurement conditions: WO₃, diffuse reflectance system, pH 3; BiVO₄, transmittance system, pH 7; α -Fe₂O₃, transmittance system, pH 13; TiO₂, transmittance system pH 13.

In the last section of this Chapter, I turn to compare the kinetic performance of four of the most studied metal-oxides photoanodes: α -Fe₂O₃, studied and discussed in detail in previous sections, BiVO₄ (prepared and measured by Dr. Yimeng Ma, Imperial College London), TiO₂ (prepared and measured by Dr. Andreas Kafizas, Imperial College London) and WO₃ (prepared

by Dr. Timothy Rosser, University of Cambridge and measured by Dr. Laia Francàs Imperial College London). Comparative J - V curves and water oxidation rate law analyses of the four different metal-oxide photoanodes, are shown in Figure 3-15.a and Figure 3-16.a, respectively. From the comparative J - V , it is apparent that α -Fe₂O₃ has the latest (more positive) photocatalysis onset potential whereas TiO₂ exhibits the earliest. This is often associated with the flat-band potential as well as the photovoltage exhibited by the photoanode at 1 sun, with the latter being correlated to the kinetic competition between recombination suppression and charge transfer.^{38,52,75–78} The photocurrent densities observed increased in ~2 orders of magnitude from TiO₂ to α -Fe₂O₃ (see Figure 3-15.a, inset), which shows that upon recombination suppression conditions, J^{ph} accounts for their difference in light absorption shown in Figure 3-15.b.

Figure 3-16.a shows the comparative rate law analyses for water oxidation on α -Fe₂O₃, BiVO₄, TiO₂ and WO₃. It is apparent from this figure that the reaction kinetics increase in the following order: α -Fe₂O₃ < BiVO₄ < TiO₂ < WO₃. More quantitatively, the reaction kinetics, expressed as ‘turn-over frequencies’ (TOF) per hole at the surface, increase from a TOF of 0.125 s⁻¹ at low irradiation intensity on hematite to a TOF to 60 s⁻¹ at high irradiation intensity for tungsten oxide (Figure 3-16.b).

The kinetics of water oxidation probe to increase with the more oxidative valence band edge (see inset Figure 3-16.a) as the surface holes have a higher free energy to perform the reaction. From a molecular point of view, faster reaction kinetics might be related with a more reactive chemical nature of the surface holes in each semiconductor. For example, surface holes in hematite have been shown to be Fe^{IV}=O species, whereas in titania, surface holes have been discussed to have a radical nature, either in terminal Ti-OH or bridging Ti-O-Ti species. As such, the localisation of the charge in a metal centre or more in the oxygen as a radical species can have an important impact in the kinetics of reaction.^{79–82}

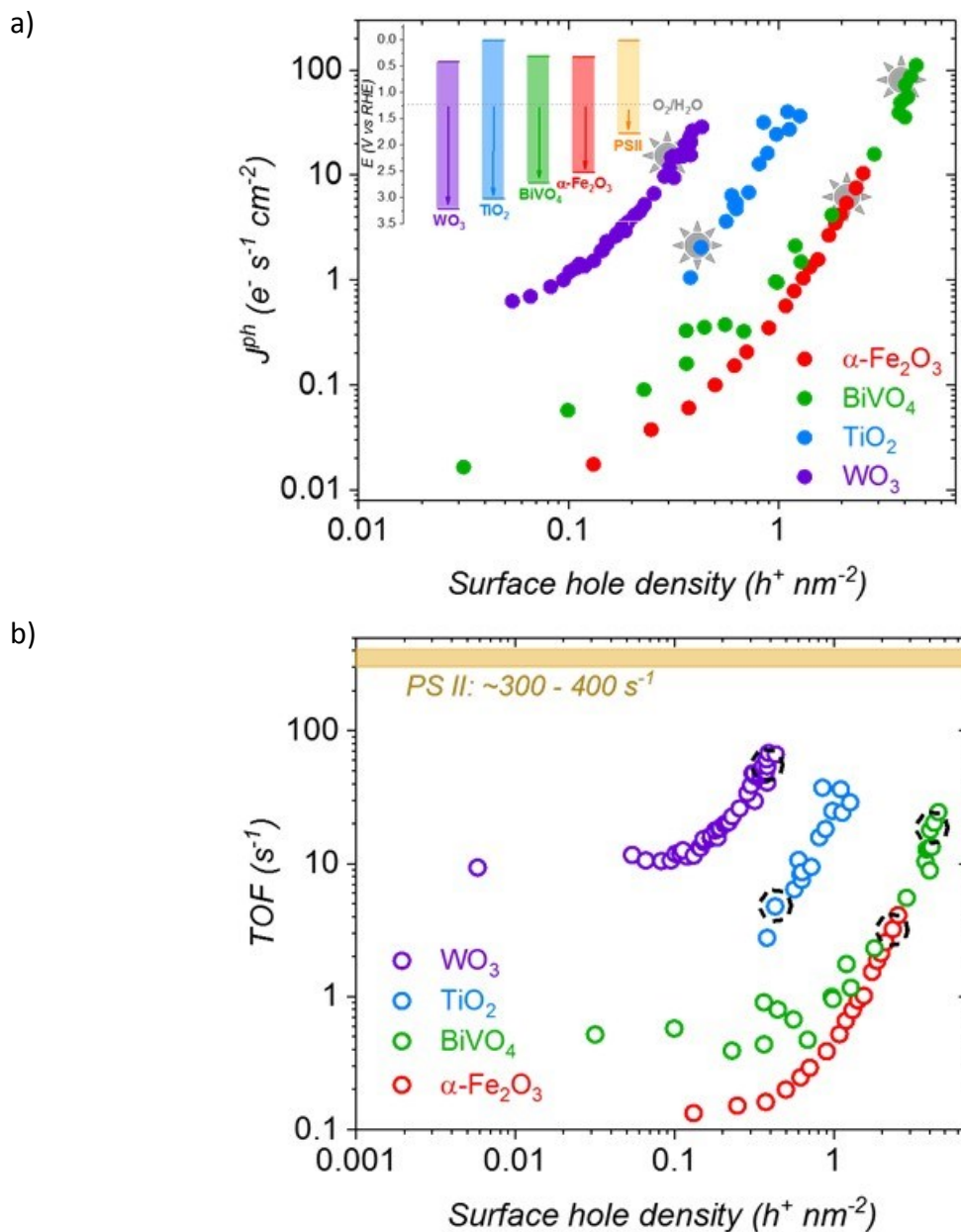
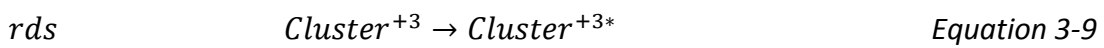
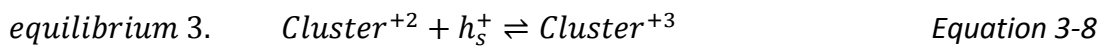
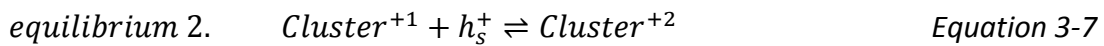
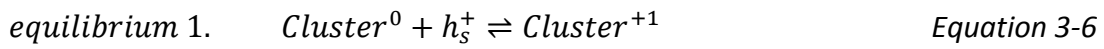


Figure 3-16. Comparative kinetic analysis of water oxidation on four of the most studied metal-oxide photoanodes, $\alpha\text{-Fe}_2\text{O}_3$ (red), BiVO_4 (green), TiO_2 (blue) and WO_3 (purple). a) Rate law analyses for the water oxidation reaction on the four studied photoanodes, the suns indicate ~ 1 sun illumination conditions. Inset: Conduction and valence band edges for the four photoanodes studied herein with respect to the water oxidation redox potential and compared to the equivalent redox potentials for PSII and b) turn-over frequencies (TOF), calculated from the data presented in a), for water oxidation as a function of the irradiation intensity. Measurement conditions: WO_3 , diffuse reflectance system, pH 3, applied potential 1.4 V vs RHE; BiVO_4 , transmittance system, pH 7 at 1.7 V vs RHE; $\alpha\text{-Fe}_2\text{O}_3$, transmittance system, pH 13 at 1.5 V vs RHE; TiO_2 , transmittance system pH 13 at 1.5 V vs RHE. In all cases 365 nm LED irradiation was used from 0.5% to 300% one sun and measurements were performed at 25 °C

On the other hand, although the kinetics of water oxidation differs between the studied photoanodes, Figure 3-16.a shows striking common mechanistic features. It is apparent from these data that two of the studied photoanodes ($\alpha\text{-Fe}_2\text{O}_3$, and BiVO_4) undergoes in a

transition from a 1st to a 3rd order of reaction with TiO₂ showing a 3rd order at the studied range of hole accumulation. I note here that WO₃ does not reach a 3rd reaction order but shows a gradient of 2.5. This can be explained by its non-unity Faradaic efficiency for water oxidation,⁸³ due to different competition reactions taking place and therefore contributing to the rate law data. It is striking that under 1 sun illumination conditions the studied photoanodes undergo a 3rd order mechanism suggesting a similar rate determining step of the water oxidation reaction. This common rds could be related to the O-O bond formation in a triply oxidised cluster of reaction, whose kinetics depend on the holes oxidative power (*i.e.*, valence band edge) and can be generally drawn by the following equations, based on the mechanism for hematite in Figure 3-14:



with h_s^+ representing a surface hole. In the presented general mechanism, the reaction cluster at the semiconductor surface undergoes in a redox levelling process by subsequent oxidations until the O-O bond is formed in the rate determining step (rds). The reaction finishes (not shown) with the transfer of the 4th hole (energetically downhill) releasing oxygen. The kinetics of the overall water oxidation reaction, assuming relatively similar equilibrium constants for Equations 3-6 to 3-9, are then determined by the kinetics of the rds which are proportional to the density of surface holes cubed as follows:

$$r_1 = k_1 \cdot [\text{Cluster}^0] \cdot p_s \quad \text{and} \quad r_{-1} = k_{-1} \cdot [\text{Cluster}^{+1}] \quad \text{Equation 3-10}$$

where r_1 and k_1 correspond to the rate and the rate constant for the forward reaction, respectively and r_{-1} and k_{-1} correspond to the rate and the rate constant for the backward reaction, respectively, applied for the first equilibrium step (Equation 3-6). In steady-state conditions, the equilibrium is reached thus $r_1 = r_{-1}$, therefore Equation 3-10 can be rewritten as follows:

$$[\text{Cluster}^{+1}] = k_{eq.1} \cdot [\text{Cluster}^0] \cdot p_s = k_{eq.1} \cdot p_s \quad \text{Equation 3-11}$$

with $k_{eq,1}$ as the equilibrium constant defined as the forward/backward rate constants ratio (k_1/k_{-1}). The density of $Cluster^0$ species at the surface is considered to be unity as it is the reaction media. For the 2nd and 3rd equilibrium steps, the following equations can then be written:

$$[Cluster^{+2}] = k_{eq,2} \cdot [Cluster^{+1}] \cdot p_s = k_{eq,2} \cdot k_{eq,1} \cdot p_s^2 \quad \text{Equation 3-12}$$

$$[Cluster^{+3}] = k_{eq,3} \cdot [Cluster^{+2}] \cdot p_s = k_{eq,3} \cdot k_{eq,1} \cdot k_{eq,2} \cdot p_s^3 \quad \text{Equation 3-13}$$

For the rate determining step, the kinetics are determined by:

$$r = k_{rds} \cdot [Cluster^{+3}] = k_{WO} \cdot p_s^3 \quad \text{Equation 3-14}$$

Where k_{WO} is the product of the equilibrium constants and the rds rate constant and corresponds to the observed rate constant for water oxidation in the studies rate law analyses presents in this *Chapter*. As such, the water oxidation rate is proportional to the surface hole density cubed. This possible general mechanism is depicted schematically in Figure 3-17.

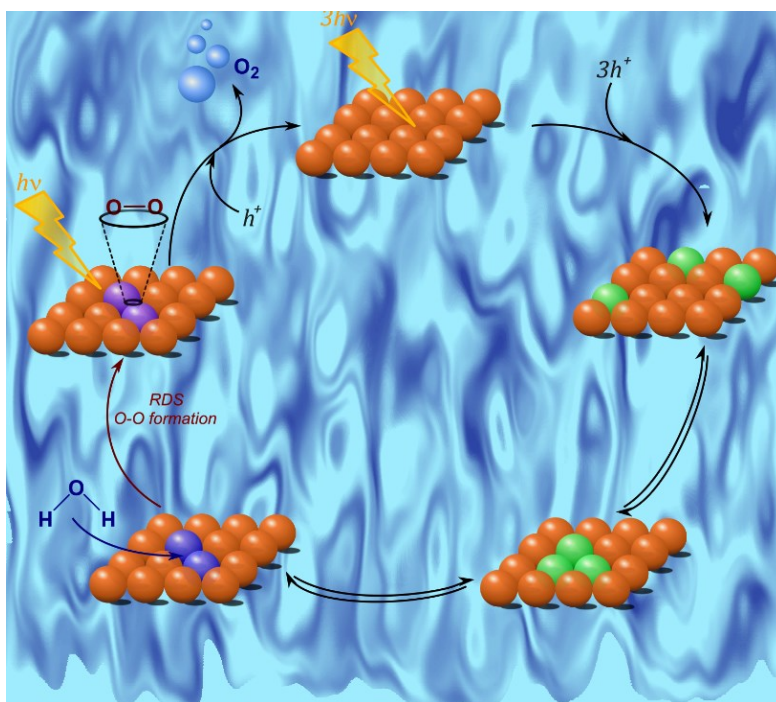


Figure 3-17. Schematic general representation of the water oxidation catalytic cycle in a metal-oxide photoanode, where 3 photogenerated surface holes, $3h^+$ (green dots) accumulate in the reaction cluster. Subsequently they equilibrate with the triply oxidised cluster (blue dots) followed by a water nucleophilic attack (WNA). The rate determining step (rds) is reached and the O-O bond formation takes place (violet dots) followed by the 4th hole transfer and oxygen molecule release.

The proposed water oxidation reaction mechanism (specific for hematite in Figure 3-14 and general for metal-oxide photoanodes in Equations 3-6 to 3-9 and Figure 3-17) also shares striking similarities with the reaction mechanism of the oxygen evolution centre (OEC) in the PSII in plants (see Figure 3-1.b), besides the structural complexity of the latter. This structural characteristic is potentially a key factor in the faster water oxidation kinetics reported for OEC compared to the observed experimentally herein (TOF per hole ~ 1 -2 orders of magnitude under 1 sun irradiation) as shown in Figure 3-16.b.^{36,84} The general water oxidation mechanism in the OEC (S-state cycle), depicted in Figure 3-1, exhibits the accumulation of oxidative equivalents by subsequent oxidations of three Mn^{3+} to Mn^{4+} in the OEC cluster. This redox levelling process is strikingly similar to the accumulation of photogenerated holes in the hematite surface according to the mechanism shown in Figure 3-14. Although, the rds of the water oxidation reaction in the OEC is well accepted to be the O-O bond formation, it is not entirely clear yet⁸⁵ if the reaction, either to proceed via an oxo-oxyl radical coupling⁸⁶⁻⁸⁹ or via a water nucleophilic attack.^{1,90-92} However, it is clear the important role of the μ -oxo bridges linking the Mn atoms in the OEC cluster, as they participate in the redox levelling process, regulating the deprotonation and the binding of the cluster. It is apparent, therefore, that for water oxidation in the OEC as well as in $\alpha\text{-Fe}_2\text{O}_3$, the accumulation of multiple oxidising equivalents in metal centres is key to help the deprotonation of the water substrate as the cluster becomes more acidic. This characteristic could be extended to the rest of the metal-oxide photoanodes studied herein as they undergo in equivalent water oxidation mechanisms.

It is important to note that, water oxidation on metal-oxide photoanodes do not function in the same way as on the OEC in PSII. The mechanism proposed in Figure 3-14 undergoes in the formation of a peroxo species, recently experimentally observed by Zhao *et. al.*,⁴⁸ which contrasts with the proposed rds in the OEC.^{1,89,93,94} More important, water oxidation in the studied metal-oxide photoanodes require a larger driving force (see comparative valence band positions in Figure 3-16.a, inset) and proceeds with turn-over frequencies ~ 1 -2 orders of magnitude lower than the OEC in PSII.

This general mechanism requiring accumulation of oxidative species around a metal-containing cluster, has also been observed in other systems. For example, as discussed previously, water oxidation mechanisms on Co_3O_4 ^{73,74} spinel and the proposed herein for α -

Fe₂O₃ both include the formation of a cluster with two metal centres. These M(OH)-O-M(OH) species can adsorb a water molecule, accumulate oxidative charges by sequential PCET and ultimately oxidise water. Strikingly, these M(OH)-O-M(OH) species are also present in highly active homogeneous Ir and Fe based catalytic systems^{95,96} for water oxidation. Similar clusters have been observed, for methane oxidation, in biological systems such as the Fe(IV)₂ diamond-core structure of carboxylate-rich, non-heme diiron enzymes.^{97–99} As such, the water oxidation reaction could be understood as an equivalent reaction across the studied materials and some homogeneous examples.

3.5. Conclusions

The oxygen evolution reaction in natural systems can provide guidelines to understand and subsequent design of better catalytic systems for artificial water oxidation. I report in this chapter a possible water oxidation reaction mechanism, specific for α -Fe₂O₃ and general for other metal-oxide photoanodes, which shares remarkable similitudes with a catalytic system of great biological and structural complexity, such as the oxygen evolution centre in the photosystem II that has evolved for millions of years.

Experimental rate law analyses concomitant with DFT calculations allow to propose two different mechanisms of water oxidation on metal-oxide photoanodes according to the photon flux. I report herein that these photoanodes have a catalytic function to oxidise water when reducing the activation energy upon increasing the density of surface accumulated holes. At commercial conditions, *i.e.*, ~1 sun, I propose a water nucleophilic attack mechanism, whose rate determining step is overcome upon the lateral diffusion of 3 photogenerated holes to a 'dimeric' cluster of reaction, with an activation energy of 60 meV on hematite photoanodes. A key step in this mechanism is the coupled oxidation and deprotonation events, occurring also in the OEC in PSII, that allow the reaction cluster to undergo in a redox levelling process before the rate determining step of the reaction.

3.6. References

1. Barber, J. 'Photosystem II: the water splitting enzyme of photosynthesis and the origin of oxygen in our atmosphere'. *Q. Rev. Biophys.* **49**, 14–1 (2017).
2. Cardona, T. in *eLS* 1–10 (John Wiley & Sons, 2017). doi:10.1002/9780470015902.a0002034.pub3
3. Barber, J. Photosystem II: the engine of life. *Q. Rev. Biophys.* **36**, 71–89 (2003).
4. Zhu, S. & Wang, D. Photocatalysis: Basic Principles, Diverse Forms of Implementations and Emerging Scientific Opportunities. *Adv. Energy Mater.* 1700841 (2017). doi:10.1002/aenm.201700841
5. Berardi, S. *et al.* Molecular artificial photosynthesis. *Chem. Soc. Rev.* **43**, 7501–7519 (2014).
6. Walter, M. G. *et al.* Solar Water Splitting Cells. *Chem. Rev.* **110**, 6446–6473 (2010).
7. Lewis, N. S. & Nocera, D. G. Powering the planet: chemical challenges in solar energy utilization. *Proc. Natl. Acad. Sci. U. S. A.* **103**, 15729–35 (2006).
8. Kato, M., Cardona, T., Rutherford, A. W. & Reisner, E. Photoelectrochemical Water Oxidation with Photosystem II Integrated in a Mesoporous Indium–Tin Oxide Electrode. *J. Am. Chem. Soc.* **134**, 8332–8335 (2012).
9. Askerka, M., Brudvig, G. W. & Batista, V. S. The O₂ -Evolving Complex of Photosystem II: Recent Insights from Quantum Mechanics/Molecular Mechanics (QM/MM), Extended X-ray Absorption Fine Structure (EXAFS), and Femtosecond X-ray Crystallography Data. *Acc. Chem. Res.* **50**, 41–48 (2017).
10. Peter, L. M. in *Photoelectrochemical Solar Fuel Production: From Basic Principles to Advanced Devices* (2016). doi:10.1007/978-3-319-29641-8_1
11. Grätzel, M. Photoelectrochemical cells. *Nature* **414**, 338–344 (2001).
12. Roger, I., Shipman, M. A. & Symes, M. D. Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting. *Nat. Rev. Chem.* **1**, (2017).
13. Moniz, S. J. A., Shevlin, S. A., Martin, D. J., Guo, Z.-X. & Tang, J. Visible-Light Driven Heterojunction Photocatalysts for Water Splitting-A Critical Review. *Energy Environ. Sci.* **8**, 731 (2015).
14. van de Krol, R., Liang, Y. & Schoonman, J. Solar hydrogen production with nanostructured metal oxides. *J. Mater. Chem.* **18**, 2311–2320 (2008).
15. van de Krol, R. & Grätzel, M. *Photoelectrochemical Hydrogen Production*. (Springer, 2012). doi:10.1007/978-1-4614-1380-6
16. Pendlebury, S. R. *et al.* Ultrafast Charge Carrier Recombination and Trapping in Hematite Photoanodes under Applied Bias. *J. Am. Chem. Soc.* **136**, 9854–9857 (2014).
17. Vura-Weis, J. *et al.* Femtosecond M 2,3-Edge Spectroscopy of Transition-Metal Oxides: Photoinduced Oxidation State Change in α -Fe₂O₃. *J. Phys. Chem. Lett* **4**, (2013).
18. Yamanaka, K.-I. & Morikawa, T. Charge-Carrier Dynamics in Nitrogen-Doped TiO₂ Powder Studied by Femtosecond Time-Resolved Diffuse Reflectance Spectroscopy. *J. Phys. Chem. C* **116**, 1286–1292 (2012).
19. Barroso, M., Pendlebury, S. R., Cowan, A. J. & Durrant, J. R. Charge carrier trapping,

- recombination and transfer in hematite (α -Fe₂O₃) water splitting photoanodes. *Chem. Sci.* **4**, 2724–2734 (2013).
20. Ravensbergen, J. *et al.* Unraveling the carrier dynamics of BiVO₄: A femtosecond to microsecond transient absorption study. *J. Phys. Chem. C* **118**, 27793–27800 (2014).
 21. Sachs, M., Pastor, E., Kafizas, A. & Durrant, J. R. Evaluation of Surface State Mediated Charge Recombination in Anatase and Rutile TiO₂. *J. Phys. Chem. Lett.* **7**, 3742–3746 (2016).
 22. Kafizas, A. *et al.* Where Do Photogenerated Holes Go in Anatase:Rutile TiO₂? A Transient Absorption Spectroscopy Study of Charge Transfer and Lifetime. *J. Phys. Chem. A* **120**, 715–723 (2016).
 23. Kafizas, A., Godin, R. & Durrant, J. R. in *Semiconductors for Photocatalysis* **97**, 3–46 (2017).
 24. Pesci, F. M., Cowan, A. J., Alexander, B. D., Durrant, J. R. & Klug, D. R. Charge Carrier Dynamics on Mesoporous WO₃ during Water Splitting. *J. Phys. Chem. Lett.* **2**, 1900–1903 (2011).
 25. Cristino, V. *et al.* Some aspects of the charge transfer dynamics in nanostructured WO₃ films. *J. Mater. Chem. A* **4**, 2995–3006 (2016).
 26. Peter, L. M. Dynamic aspects of semiconductor photoelectrochemistry. *Chem. Rev.* **90**, 753–769 (1990).
 27. Cowan, A. J. & Durrant, J. R. Long-lived charge separated states in nanostructured semiconductor photoelectrodes for the production of solar fuels. *Chem. Soc. Rev.* **42**, 2281–2293 (2013).
 28. Francàs, L., Mesa, C. A., Pastor, E., Le Formal, F. & Durrant, J. R. in *Advances in Photoelectrochemical Water Splitting: Theory, Experiment and Systems Analysis* (eds. Tilley, S. D., Lany, S. & van de Krol, R.) in press (Royal Society of Chemistry, 2018).
 29. Liu, C., Dasgupta, N. P. & Yang, P. Semiconductor Nanowires for Artificial Photosynthesis. *Chem. Mater.* **26**, 415–422 (2014).
 30. Pendlebury, S. R. *et al.* Correlating long-lived photogenerated hole populations with photocurrent densities in hematite water oxidation photoanodes. *Energy Environ. Sci.* **5**, 6304–6312 (2012).
 31. Upul Wijayantha, K. G., Saremi-Yarahmadi, S. & Peter, L. M. Kinetics of oxygen evolution at α -Fe₂O₃ photoanodes: a study by photoelectrochemical impedance spectroscopy. *Phys. Chem. Chem. Phys.* **13**, 5264 (2011).
 32. Peter, L. M., Wijayantha, K. G. U. & Tahir, A. A. Kinetics of light-driven oxygen evolution at α -Fe₂O₃ electrodes. *Faraday Discuss.* **155**, 309–322 (2012).
 33. Peter, L. M. & Wijayantha, K. G. U. Photoelectrochemical Water Splitting at Semiconductor Electrodes: Fundamental Problems and New Perspectives. *ChemPhysChem* **15**, 1983–1995 (2014).
 34. Cummings, C. Y., Marken, F., Peter, L. M., Wijayantha, K. G. U. & Tahir, A. A. New Insights into Water Splitting at Mesoporous α -Fe₂O₃ Films: A Study by Modulated Transmittance and Impedance Spectroscopies. *J. Am. Chem. Soc.* **134**, 1225–1234 (2012).
 35. Dau, H. *et al.* The Mechanism of Water Oxidation: From Electrolysis via Homogeneous to Biological Catalysis. *ChemCatChem* **2**, 724–761 (2010).
 36. Duan, L. *et al.* A molecular ruthenium catalyst with water-oxidation activity comparable to that

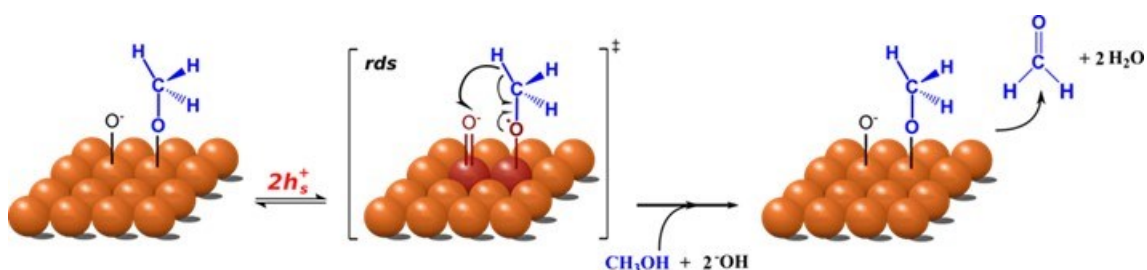
- of photosystem II. *Nat. Chem.* **4**, 418–423 (2012).
37. Kärkäs, M. D. & Åkermark, B. Water oxidation using earth-abundant transition metal catalysts: opportunities and challenges. *Dalt. Trans.* **45**, 14421–14461 (2016).
 38. Iandolo, B., Orn Wickman, B., Zorić, I. & Hellman, A. The rise of hematite: origin and strategies to reduce the high onset potential for the oxygen evolution reaction. *J. Mater. Chem. A* **3**, 16896 (2015).
 39. Grave, D. A., Yatom, N., Ellis, D. S., Toroker, M. C. & Rothschild, A. The “Rust” Challenge: On the Correlations between Electronic Structure, Excited State Dynamics, and Photoelectrochemical Performance of Hematite Photoanodes for Solar Water Splitting. *Adv. Mater.* 1706577 (2018). doi:10.1002/adma.201706577
 40. Takashima, T., Ishikawa, K. & Irie, H. Detection of Intermediate Species in Oxygen Evolution on Hematite Electrodes Using Spectroelectrochemical Measurements. *J. Phys. Chem. C* **120**, 24827–24834 (2016).
 41. Cummings, C. Y., Marken, F., Peter, L. M., Tahir, A. A. & Wijayantha, K. G. U. Kinetics and mechanism of light-driven oxygen evolution at thin film α -Fe₂O₃ electrodes. *Chem. Commun.* **48**, 2027 (2012).
 42. Peter, L. M., Upul Wijayantha, K. G. & Tahir, A. A. Kinetics of light-driven oxygen evolution at α -Fe₂O₃ electrodes. *Faraday Discuss.* **155**, 309–322 (2012).
 43. Zandi, O. & Hamann, T. W. Enhanced Water Splitting Efficiency Through Selective Surface State Removal. *J. Phys. Chem. Lett.* **5**, 1522–1526 (2014).
 44. Zandi, O. & Hamann, T. W. The potential versus current state of water splitting with hematite. *Phys. Chem. Chem. Phys.* **17**, 22485–22503 (2015).
 45. Zandi, O. & Hamann, T. W. Determination of photoelectrochemical water oxidation intermediates on hematite electrode surfaces using operando infrared spectroscopy. *Nat. Chem.* **8**, (2016).
 46. Le Formal, F. *et al.* Rate Law Analysis of Water Oxidation on a Hematite Surface. *J. Am. Chem. Soc.* **137**, 6629–6637 (2015).
 47. Zhang, Y. *et al.* Pivotal Role and Regulation of Proton Transfer in Water Oxidation on Hematite Photoanodes. *J. Am. Chem. Soc.* **138**, 2705–2711 (2016).
 48. Zhang, Y. *et al.* Rate-Limiting O–O Bond Formation Pathways for Water Oxidation on Hematite Photoanode. *J. Am. Chem. Soc.* **ASAP**, (2018).
 49. Ma, Y. *et al.* Rate Law Analysis of Water Oxidation and Hole Scavenging on a BiVO₄ Photoanode. *ACS Energy Lett.* 618–623 (2016). doi:10.1021/acsenergylett.6b00263
 50. Kafizas, A. *et al.* Water Oxidation Kinetics of Accumulated Holes on the Surface of a TiO₂ Photoanode: A Rate Law Analysis. *ACS Catal.* **7**, 4896–4903 (2017).
 51. Kay, A., Cesar, I. & Grätzel, M. New Benchmark for Water Photooxidation by Nanostructured α -Fe₂O₃ Films. *J. Am. Chem. Soc.* **128**, 15714–15721 (2006).
 52. Le Formal, F. *et al.* Back Electron–Hole Recombination in Hematite Photoanodes for Water Splitting. *J. Am. Chem. Soc.* **136**, 2564–2574 (2014).
 53. Ma, Y., Le Formal, F., Kafizas, A., Pendlebury, S. R. & Durrant, J. R. Efficient suppression of back electron/hole recombination in cobalt phosphate surface-modified undoped bismuth

- vanadate photoanodes. *J. Mater. Chem. A* **3**, (2015).
54. Peter, L. *Kinetics and Mechanisms of Light-Driven Reactions at Semiconductor Electrodes : Principles and Techniques. Photoelectrochemical Water Splitting: Materials, Processes and Architectures* (RCS Publishing, 2013). doi:10.1039/9781849737739-00019
 55. Klahr, B., Gimenez, S., Fabregat-Santiago, F., Hamann, T. & Bisquert, J. Water Oxidation at Hematite Photoelectrodes: The Role of Surface States. *J. Am. Chem. Soc.* **134**, 4294–4302 (2012).
 56. Mesa, C. A. *et al.* Kinetics of Photoelectrochemical Oxidation of Methanol on Hematite Photoanodes. *J. Am. Chem. Soc.* **139**, 11537–11543 (2017).
 57. Cornell, R. M. & Schwertmann, U. *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses.* (WILEY-VCH Verlag, 2003). doi:10.1002/3527602097
 58. Kosmulski, M. pH-dependent surface charging and points of zero charge. IV. Update and new approach. *J. Colloid Interface Sci.* **337**, 439–448 (2009).
 59. Lützenkirchen, J. *et al.* Surface potential at the hematite (001) crystal plane in aqueous environments and the effects of prolonged aging in water. *Geochim. Cosmochim. Acta* **120**, 479–486 (2013).
 60. Chatman, S., Zarzycki, P., Preočanin, T. & Rosso, K. M. Effect of surface site interactions on potentiometric titration of hematite (α -Fe₂O₃) crystal faces. *J. Colloid Interface Sci.* **391**, 125–134 (2013).
 61. Gary, R. *et al.* Second Dissociation Constant of Deuteriophosphoric Acid in Deuterium oxide from 5 to 50°. Standardization of a pD Scale. *J. Phys. Chem.* **68**, 3806–3809 (1964).
 62. Atkins, P. *Physical Chemistry.* (Oxford University Press, 2001).
 63. Shaffer, D. W., Xie, Y., Szalda, D. J. & Concepcion, J. J. Manipulating the Rate-Limiting Step in Water Oxidation Catalysis by Ruthenium Bipyridine–Dicarboxylate Complexes. *Inorg. Chem.* **55**, 12024–12035 (2016).
 64. Cowan, A. J. *et al.* Activation Energies for the Rate-Limiting Step in Water Photooxidation by Nanostructured α -Fe₂O₃ and TiO₂. *J. Am. Chem. Soc.* **133**, 10134–10140 (2011).
 65. Glasscock, J. A., Barnes, P. R. F., Plumb, I. C. & Savvides, N. Enhancement of Photoelectrochemical Hydrogen Production from Hematite Thin Films by the Introduction of Ti and Si. *J. Phys. Chem. C* **111**, 16477–16488 (2007).
 66. Miller, E. L., Paluselli, D., Marsen, B. & Rocheleau, R. E. Low-temperature reactively sputtered iron oxide for thin film devices. *Thin Solid Films* **466**, 307–313 (2004).
 67. Chatman, S., Zarzycki, P. & Rosso, K. M. Surface potentials of (001), (012), (113) hematite (α -Fe₂O₃) crystal faces in aqueous solution. *Phys. Chem. Chem. Phys.* **15**, 13911–13921 (2013).
 68. Cowan, A. J., Tang, J., Leng, W., Durrant, J. R. & Klug, D. R. Water Splitting by Nanocrystalline TiO₂ in a Complete Photoelectrochemical Cell Exhibits Efficiencies Limited by Charge Recombination. *J. Phys. Chem. C* **114**, 4208–4214 (2010).
 69. Liao, P., Keith, J. A. & Carter, E. A. Water Oxidation on Pure and Doped Hematite (0001) Surfaces: Prediction of Co and Ni as Effective Dopants for Electrocatalysis. *J. Am. Chem. Soc.* **134**, 13296–13309 (2012).
 70. Hellman, A. & Pala, R. G. S. First-Principles Study of Photoinduced Water-Splitting on Fe₂O₃. *J.*

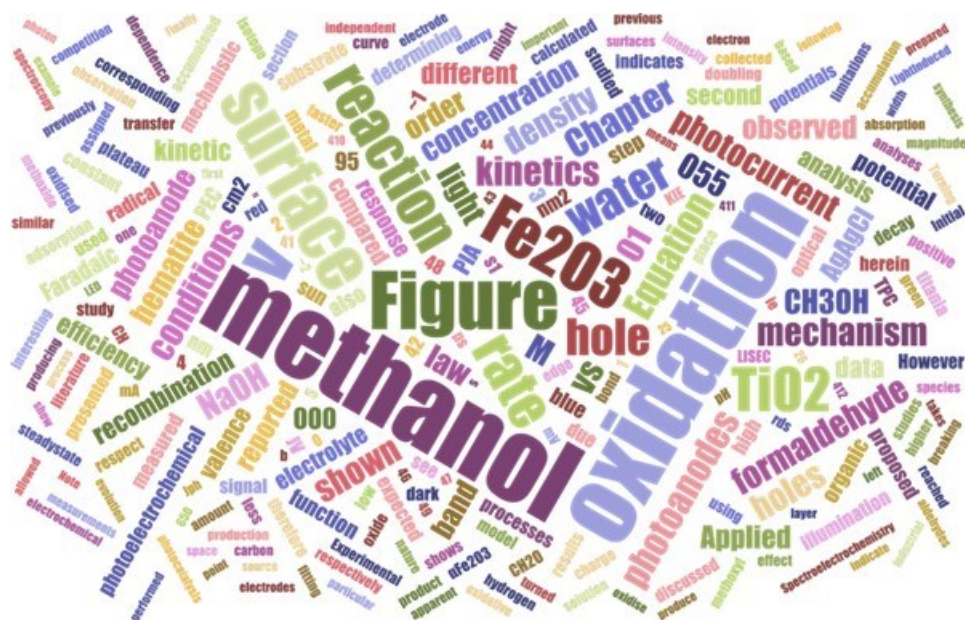
- Phys. Chem. C* **115**, 12901–12907 (2011).
71. Hu, J., Zhao, X., Chen, W., Su, H. & Chen, Z. Theoretical Insight into the Mechanism of Photoelectrochemical Oxygen Evolution Reaction on BiVO₄ Anode with Oxygen Vacancy. *J. Phys. Chem. C* **121**, 18702–18709 (2017).
 72. Klahr, B., Gimenez, S., Fabregat-Santiago, F., Bisquert, J. & Hamann, T. W. Electrochemical and photoelectrochemical investigation of water oxidation with hematite electrodes. *Energy Environ. Sci.* **5**, 7626–7636 (2012).
 73. Zhang, M., De Respinis, M. & Frei, H. Time-resolved observations of water oxidation intermediates on a cobalt oxide nanoparticle catalyst. *Nat. Chem.* **6**, 362–367 (2014).
 74. Zhang, M. & Frei, H. Water Oxidation Mechanisms of Metal Oxide Catalysts by Vibrational Spectroscopy of Transient Intermediates. *Annu. Rev. Phys. Chem.* **68**, 209–31 (2017).
 75. Sivula, K., Le Formal, F. & Grätzel, M. Solar Water Splitting: Progress Using Hematite (α -Fe₂O₃) Photoelectrodes. *ChemSusChem* **4**, 432–449 (2011).
 76. Bedoya-Lora, F. E. *et al.* Effects of low temperature annealing on the photo-electrochemical performance of tin-doped hematite photo-anodes. *Electrochim. Acta* **251**, 1–11 (2017).
 77. Iandolo, B. *et al.* Correlating flat band and onset potentials for solar water splitting on model hematite photoanodes. *RCS Adv.* **5**, 61021–61030 (2015).
 78. Le Formal, F., Sivula, K. & Grätzel, M. The Transient Photocurrent and Photovoltage Behavior of a Hematite Photoanode under Working Conditions and the Influence of Surface Treatments. *J. Phys. Chem. C* **116**, 26707–26720 (2012).
 79. Kafizas, A. *et al.* Water Oxidation Kinetics of Accumulated Holes on the Surface of a TiO₂ Photoanode: A Rate Law Analysis. *ACS Catal.* **7**, 4896–4903 (2017).
 80. Micic, O. I., Zhang, Y., Cromack, K. R., Trifunac, A. D. & Thurnauer, M. C. Trapped Holes on TiO₂ Colloids Studied by Electron Paramagnetic Resonance. *J. Phys. Chem.* **97**, 1211–1283 (1993).
 81. Kisumi, T., Tsujiko, A., Murakoshi, K. & Nakato, Y. Crystal-face and illumination intensity dependences of the quantum efficiency of photoelectrochemical etching, in relation to those of water photooxidation, at n-TiO₂ (rutile) semiconductor electrodes. *J. Electroanal. Chem.* **545**, 77–107 (2003).
 82. Zigah, D., Rodríguez-López, J. & Bard, A. J. Quantification of photoelectrogenerated hydroxyl radical on TiO₂ by surface interrogation scanning electrochemical microscopy. *Phys. Chem. Chem. Phys.* **14**, 12764–12772 (2012).
 83. Rosser, T. E., Gross, M. A., Lai, Y.-H. & Reisner, E. Precious-metal free photoelectrochemical water splitting with immobilised molecular Ni and Fe redox catalysts. *Chem. Sci.* **7**, 4024–4035 (2016).
 84. Schulze, M., Kunz, V., Frischmann, P. D. & Würthner, F. A supramolecular ruthenium macrocycle with high catalytic activity for water oxidation that mechanistically mimics photosystem II. *Nat. Chem.* **8**, 576–583 (2016).
 85. Barber, J. A mechanism for water splitting and oxygen production in photosynthesis. *Nat. Plants* **3**, (2017).
 86. Siegbahn, P. E. M. Theoretical Studies of O–O Bond Formation in Photosystem II. *Inorg. Chem.* **47**, 1779–1786 (2008).

87. Siegbahn, P. E. M. O-O Bond Formation in the S4 State of the Oxygen-Evolving Complex in Photosystem II. *Chem. - A Eur. J.* **12**, 9217–9227 (2006).
88. Siegbahn, P. E. M. Water oxidation mechanism in photosystem II, including oxidations, proton release pathways, O—O bond formation and O₂ release. *Biochim. Biophys. Acta* **1827**, 1003–1019 (2013).
89. Li, X. & Siegbahn, P. E. M. Water Oxidation for Simplified Models of the Oxygen-Evolving Complex in Photosystem II. *Chem. - A Eur. J.* **21**, 18821–18827 (2015).
90. Pecoraro, V. L., Baldwin, M. J., Caudle, M. T., Hsieh, W.-Y. & Law, N. A. A proposal for water oxidation in photosystem II. *Pure Appl. Chem.* **70**, 925–929 (1998).
91. Vrettos, J. S., Limburg, J. & Brudvig, G. W. Mechanism of photosynthetic water oxidation: combining biophysical studies of photosystem II with inorganic model chemistry. *Biochim. Biophys. Acta* **1503**, 229–245 (2001).
92. Sproviero, E. M., Gascó, J. A., Mcevoy, J. P., Brudvig, G. W. & Batista, V. S. Quantum Mechanics/Molecular Mechanics Study of the Catalytic Cycle of Water Splitting in Photosystem II. *J. Am. Chem. Soc.* **130**, 3428–3442 (2008).
93. Klauss, A., Haumann, M. & Dau, H. Seven Steps of Alternating Electron and Proton Transfer in Photosystem II Water Oxidation Traced by Time-Resolved Photothermal Beam Deflection at Improved Sensitivity. *J. Phys. Chem. B* **119**, 2677–2689 (2015).
94. Vinyard, D. J. & Brudvig, G. W. Progress Toward a Molecular Mechanism of Water Oxidation in Photosystem II. *Annu. Rev. Phys. Chem.* **68**, 101–16 (2017).
95. Yang, K. R. *et al.* Solution Structures of Highly Active Molecular Ir Water-Oxidation Catalysts from Density Functional Theory Combined with High- Energy X-ray Scattering and EXAFS Spectroscopy. *J. Am. Chem. Soc.* **138**, 5511–5514 (2016).
96. Gamba, I., Codolà, Z., Lloret-Fillol, J. & Costas, M. Making and breaking of the O-O bond at iron complexes. *Coord. Chem. Rev.* **334**, 2–24 (2017).
97. Tinberg, C. E. & Lippard, S. J. Dioxygen Activation in Soluble Methane Monooxygenase. *Acc. Chem. Res.* **280**, 280–288 (2011).
98. Shu, L. *et al.* An Fe₂^{IV}O₂ Diamond Core Structure for the Key Intermediate Q of Methane Monooxygenase. *Science (80-.)*. **275**, 515–518 (1997).
99. Friedle, S., Reisner, E. & Lippard, S. J. Current challenges of modeling diiron enzyme active sites for dioxygen activation by biomimetic synthetic complexes. *Chem. Soc. Rev.* **39**, 2768–2779 (2010).

Chapter 4. Kinetic and mechanistic study of methanol oxidation on α -Fe₂O₃ and TiO₂ photoanodes



TOC Figure



Word cloud for this *Chapter*

In this chapter, water, as an electron source for hydrogen evolution, is substituted for a simple organic substrate to overcome the kinetic limitations and complex mechanism PEC water oxidation undergoes on metal-oxide photoanodes. Herein, a mechanism of reaction is proposed for the photoelectrochemical oxidation of methanol on two different metal oxide photoelectrodes, hematite ($\alpha\text{-Fe}_2\text{O}_3$) and titania (TiO_2). Methanol, as a model organic substrate, is shown to be oxidised to formaldehyde with $\sim 100\%$ Faradaic efficiency following kinetics of second order in surface hole density in both $\alpha\text{-Fe}_2\text{O}_3$ and TiO_2 photoanodes. The experimental mechanistic studies presented herein show that the reaction is independent of the space charge layer width but exhibits slower kinetics on the hematite surface compared to titania. The rate determining step of this reaction proposed in this Chapter is the breaking of a C-H bond, supported by light-induced spectroelectrochemistry by isotopic labelling. These results provided insights into the nature of the electron transfer of an organic substrate oxidation as an alternative source of electrons for proton reduction.

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

“Kinetics of photoelectrochemical oxidation of methanol on hematite photoanodes”, J. Am. Chem. Soc., **2017**, 139, 11537–11543.

4.1. Introduction

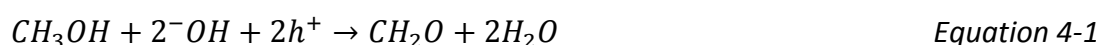
Solar driven H₂ production from photoelectrochemical (PEC) water splitting in artificial photosynthetic systems is kinetically limited by the water oxidation reaction¹ as introduced in *Chapter 1*. Literature has established, for the particular case of hematite (α -Fe₂O₃) and titania (TiO₂) photoanodes, that the oxygen evolution reaction takes place within the *ms* – *s* timescale by means different techniques such as: transient absorption spectroscopy (TAS) by our group^{2–4}, electrochemical impedance spectroscopy (EIS)⁵ and intensity-modulated photocurrent spectroscopy (IMPS).^{6–8} This reaction is known to require 4 photogenerated holes to complete. However, in *Chapter 3*, it was reported that its rate determining step (rds) depends on the accumulation and cooperative function of 3 surface holes for different metal-oxide photoanodes. The kinetics of water oxidation were also reported, in *Chapter 3*, to be hampered by the complex mechanism of reaction. These kinetic limitations can be diminished or even avoided by substituting water for substrates easier to oxidise, such as organic molecules.

Nowadays the electrochemical or photoelectrochemical destruction of organic pollutants and synthesis of high value-added compounds is attracting particular interest. For example, PEC water detoxification has emerged as a promising alternative as one of the ‘advanced oxidation process’ technologies for water and wastewater treatment. In this field, TiO₂ is considered most interesting photocatalytic material with due to its stability, low cost and high efficiency for a wide range of water pollutants degradation, ranging from organics^{9–11} to bacteria such *E. coli*.¹² However, although potentially interesting, studying such non-selective processes is out of the scope of this thesis.

On the other hand, driving selective oxidation reactions (*i.e.*, targeting a particular product) can lead to the synthesis of value-added products concomitant with hydrogen production in a complete PEC device. There are different interesting oxidative processes to study that would be of industrial interest, some examples are presented here: (1) Photoelectrochemical oxidation of alkenes has been reported to produce industrially demanded aldehydes and epoxides used as precursors in the pharmaceutical industry;^{13,14} (2) different alcohols have been shown to be selectively oxidised in heterogeneous and homogeneous photocatalysis, producing specific aldehydes of higher added-value compared to the alcohol precursor;^{15–17} (3) an interesting example is the rapidly growing industrial by-product, glycerol, that has been

proven to be oxidised to produce dihydroxyacetone (DHA), which is ~200 fold more valuable than crude or purified glycerol;¹⁸ or (4) the photocatalytic conversion of biomass into useful ketones or aldehydes while producing hydrogen.¹⁹ All these examples prove that this approach is an interesting pathway of overcoming not only the water oxidation kinetic limitations, but also could potentially promote the feasibility of a hydrogen economy. For such processes to be controlled it is important to understand their kinetics and reaction mechanisms.

To study the catalytic action of two of the most studied metal-oxide photoanodes, such as $\alpha\text{-Fe}_2\text{O}_3$ and TiO_2 , on selective organic oxidation reactions, methanol has been selected as a model organic substrate. Under strong and non-selective oxidative conditions, methanol is expected to produce initially formaldehyde, then formic acid and finally carbon dioxide. (see Equations 4-1 to 4-3)



The mechanism of this reaction has been studied in literature mainly on metallic electrodes for methanol fuel cell applications.^{20–22} Methanol has been used primarily as a hole scavenger to increase the yield of hydrogen production in PEC systems using metal oxide semiconductors, such as titania^{20,23} and hematite.²⁴ However, the key kinetic and mechanistic aspects of the reaction remaining still not well understood.

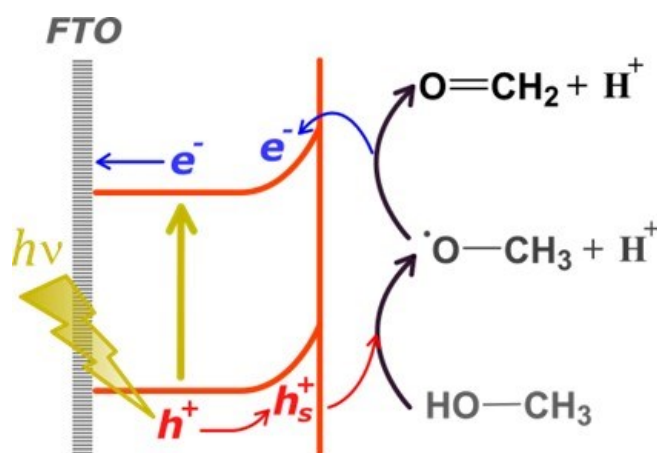


Figure 4-1. A common proposed mechanism in literature for methanol oxidation on metal oxide surfaces, within photocurrent doubling conditions.

In the literature, methanol oxidation has been reported with low Faradaic efficiencies for formaldehyde production.²⁵ Some studies indicate that the oxidation mechanism starts with adsorption of the substrate to the metal oxide semiconductor surface as methoxide species. This adsorption is followed by a first oxidation producing a $\text{CH}_3\text{O}\bullet$ radical and a subsequent oxidation by a valence band hole, releasing formaldehyde.²⁶ In other studies,²⁷ it is reported that the methoxyl radical injects an electron to the conduction band of the semiconductor giving rise to a photocurrent doubling mechanism, as depicted in Figure 1-1. However, the key kinetic and thermodynamic parameters affecting the rate determining step of this reaction under PEC operating conditions (1 sun) are still not yet well understood and are the focus of this chapter. Light-induced spectroelectrochemistry (LI-SEC) is used to study the rate law analysis of methanol oxidation under different bias conditions comparing the kinetics and mechanism of reaction on $\alpha\text{-Fe}_2\text{O}_3$ and TiO_2 photoanodes.

4.2. Experimental

4.2.1. (Photo)electrochemical (PEC) response

PEC responses of nanostructured $\alpha\text{-Fe}_2\text{O}_3$ prepared by APCVD as detailed in Chapter 2 and mesoporous TiO_2 were evaluated under dark and ~ 1 sun illumination conditions, initially in 0.1 M NaOH, pH 13.0 electrolyte. The illumination source used for these experiments was a 365 nm LED, with the power controlled by the current passing through it. This allowed the photon flux to be tuned until appropriate plateau photocurrents equivalent to AM 1.5 illumination conditions were reached. These photocurrents have been reported previously for these photoanodes ($\sim 3 \text{ mA cm}^{-2}$ for hematite and $\sim 0.1 \text{ mA cm}^{-2}$ for titania).^{28–30} The PEC performance of the studied photoanodes was evaluated subsequently adding methanol. Different concentrations (by volume) of CH_3OH solutions were prepared ranging from 4% to 98% in 0.1M NaOH.

All the applied potentials presented in this *Chapter*, are referred to the silver|silver chloride (Ag/AgCl) electrode. This is due to converting a measured potential vs the Ag/AgCl electrode to a potential vs the reversible hydrogen electrode (RHE) might not be accurate in aqueous-organic solutions by using the Nernst equation:

$$E_{\text{RHE}}(V) = E_{\text{Ag/AgCl}}^0 + E'_{\text{Ag/AgCl}} + 0.059 \cdot \text{pH} \quad \text{Equation 4-4}$$

The non-accurate conversion is due to the pH measurement in the highly concentrated methanol electrolytes. A pH measurement depends, among many factors, on the relative permittivity (ϵ) of the electrolyte, which would influence the activity of the ions in solution. Solvent mixtures of CH₃OH in H₂O show ϵ values ranging from ~80 to ~36 for mixtures between 0% and 95% by weight,³¹ with a threshold value of $\epsilon = 35$ considered as a lower limit for the activity to concentration approximation in the pH calculations.³² I note that the independence of the kinetics and mechanism of the oxidation of methanol experimentally observed in this chapter, indicate that the conversion of the electrode values is not a fundamental point to be addressed herein.

4.2.2. Rate law analysis

Rate law analyses were performed by means of light-induced spectroelectrochemistry (LI-SEC), using the same 365 nm LED illumination source as for the PEC performance measurements. Photoinduced absorption (PIA) and transient photocurrent (TPC) responses of the photoanodes were measured as a function of light intensity, therefore as a function of surface hole density, in 0.1 M NaOH and 95% CH₃OH in 0.1M NaOH for the case of hematite and 4% CH₃OH in 0.1 M NaOH for titania. The α -Fe₂O₃ photoanode was held at a high applied potential (0.55 V vs Ag/AgCl) thereby avoiding back or 'surface' electron-hole recombination and at 0.00 V and -0.80 V vs Ag/AgCl for α -Fe₂O₃ and TiO₂, respectively, to study possible competition with water oxidation and with recombination. Further mechanistic studies were carried out by isotopic exchange. Deuterated methanol (CD₃OD), 99% deuterium, was used to prepare the 95% CD₃OD in 0.1 M NaOD in D₂O electrolyte.

4.2.3. Formaldehyde quantification

The expected oxidation product, formaldehyde, was detected and quantified by spectrophotometry thanks to the violet colour formaldehyde develops upon reaction with 4-amino-5-hydrazino-1,2,4-triazole-3-thiol (Purpald) $\geq 99\%$, Sigma-Aldrich, following a method developed by Jacobsen *et al.*³³

Formaldehyde was produced on α -Fe₂O₃ photoanode by setting a bulk photoelectrolysis (chronoamperometry) in a 100 mL PEC cell applying 0.55 V vs Ag/AgCl and under continuous ~1 sun illumination conditions. Three aliquots were taken from the reaction cell after 13, 31.6 and 47.6 minutes of the beginning of the reaction. The aliquots of, 10, 5 and 5 mL respectively,

were mixed with 10 mL 1M NaOH and 0.1 g purpald and diluted to a final volume of 25 mL after 30 min air bubbling to promote reaction. The quantification took place by measuring the UV-Vis spectra and following the absorbance at 549 nm of the resulting violet coloured solution. The concentration was subsequently calculated by interpolation from a calibration curve (0 – 5 ppm) prepared from a 37% W ACS reagent formaldehyde solution. I note that this method is sensitive to other small aldehydes such as acetaldehyde, propionaldehyde, butyraldehyde, and benzaldehyde at different wavelengths. However, the only aldehyde expected from the oxidation of methanol is formaldehyde. The amount of formaldehyde (CH₂O) expected, as a function of time, from the reaction was calculated from the chronoamperometry as shown in Equation 4-5.

$$\text{mol CH}_2\text{O expected}_{(t)} = \frac{\int_0^t J^{ph} \cdot dt}{nF} \quad \text{Equation 4-5}$$

where the numerator denotes the area under the chronoamperometric curve, n the number of electrons transferred per CH₂O molecule formed and F the Faraday constant (96485.3 C mol⁻¹). Once the amount of expected product was calculated, the Faradaic efficiency (FE) of the reaction was estimated as shown in Equation 4-6.

$$FE = \frac{\text{mol CH}_2\text{O quantified}_{(t)}}{\text{mol CH}_2\text{O expected}_{(t)}} \cdot 100 \quad \text{Equation 4-6}$$

4.3. Results

4.3.1. (Photo)electrochemical response

The photoelectrochemical response (J - V) of the APCVD α -Fe₂O₃ in water and with the addition of different concentrations of methanol is shown in Figure 4-2. The presented J - V curves in water (black and red lines, respectively in Figure 4-2) are in agreement with dark and light driven water oxidation by nanocrystalline hematite previously reported by Grätzel and co-workers.^{28,29} Upon addition of methanol to the electrolyte, the onset of photocatalysis decreases by ~300 mV, from ~0.1 V to ~-0.2 V (indicated with the horizontal arrow in Figure 4-2), in accordance with previous hole scavenging studies on hematite, since the methanol requires less oxidative potential to be oxidised.^{24,34,35} This more facile methanol oxidation, also results in an increase in the photocurrent from ~2.7 mA cm⁻² to ~3.9 mA cm⁻² (for the 95% CH₃OH in 0.1 M NaOH electrolyte), indicated with the vertical arrow in Figure 4-2.

In Figure 4-2 the PEC response of the hematite photoanode as a function of methanol concentration can also be observed. The plateau photocurrent exhibited by $\alpha\text{-Fe}_2\text{O}_3$ increases as the concentration of methanol increases until a plateau is reached at $\sim 90\%$ concentration. This might indicate that diffusion towards and/or adsorption of methanol on the photoanode surface might limit the reaction until a concentration of 90% of CH_3OH is reached. Consequently, the kinetic and mechanistic analysis on hematite is performed using an electrolyte containing 95% CH_3OH in 0.1 M NaOH is selected.

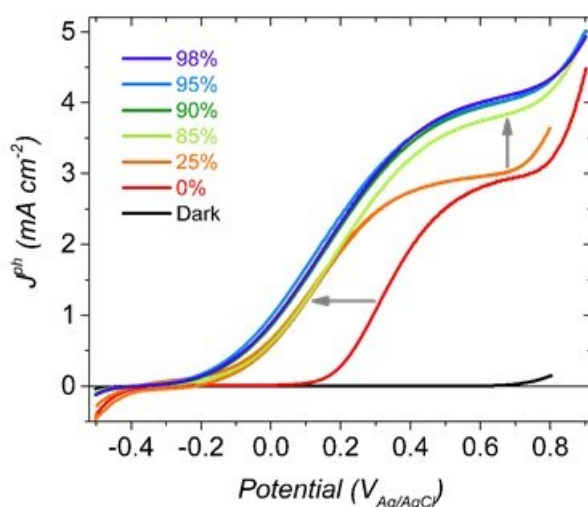
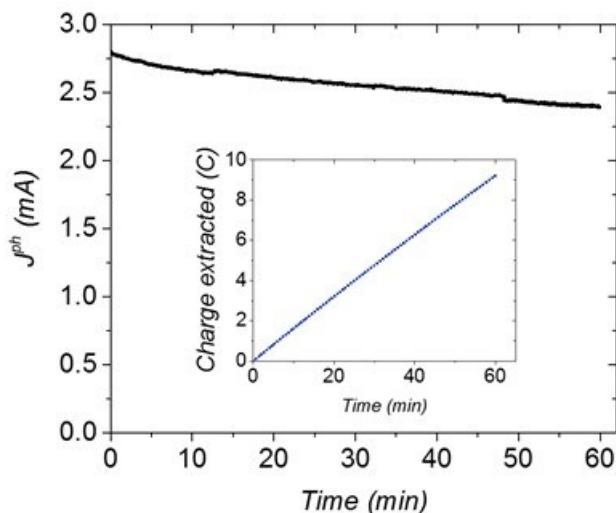


Figure 4-2. Current/potential (J - V) response of the $\alpha\text{-Fe}_2\text{O}_3$ photoanode under dark (black line) and ~ 1 sun front illumination (electrode/electrolyte) conditions measured in 0.1 M NaOH with varying concentration of methanol by volume as follows: 0% (red), 25% (orange), 85% (light green), 90% (dark green), 95% (blue) and 98% (purple). The vertical arrow indicates the increasing plateau photocurrent densities achieved by the increasing concentration of methanol in the electrolyte. The horizontal arrow indicates the decrease in the required applied potential to obtain catalytic currents.

4.3.2. Formaldehyde quantification

Methanol is expected to produce formaldehyde as first oxidation product in the 2-electron reaction shown in Equation 4-1. The current/time (chronoamperometric) response of the $\alpha\text{-Fe}_2\text{O}_3$ photoanode in 95% CH_3OH in 0.1 M NaOH electrolyte under ~ 1 sun illumination conditions is shown in Figure 4-3.a. From this curve the estimation of the expected CH_2O amount produced as a function of time (see Equation 4-5) was calculated by integrating the area under the curve to obtain the extracted charge (see Figure 4-3.a, inset). The formation of CH_2O was monitored and quantified *via* a spectrophotometric titration as detail in the experimental section. The calibration curve corresponding to the formaldehyde quantification is shown in Figure 4-3.b.

a)



b)

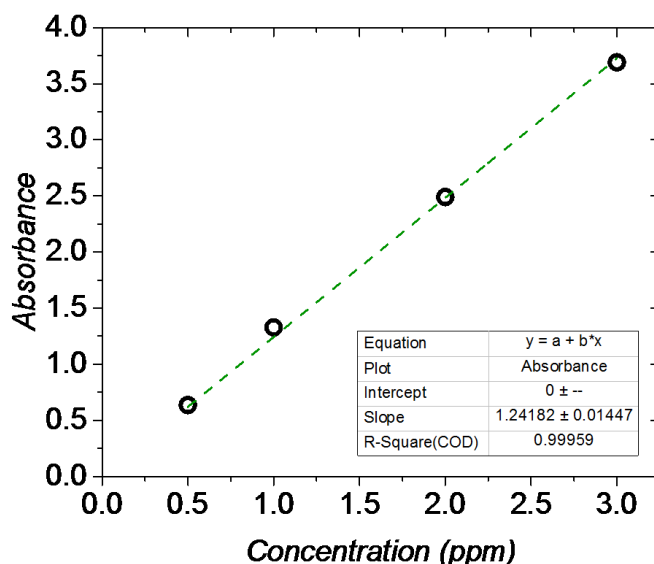


Figure 4-3. a) Current/time (chronoamperometric) response of the α - Fe_2O_3 photoanode in 95% CH_3OH in 0.1 M NaOH under continuous ~ 1 sun front illumination conditions at 0.55 V vs Ag/AgCl (inset: charge extracted calculated from the area under the chronoamperometric curve vs time) and b) calibration curve for the spectrophotometric detection of CH_2O . Absorbance measured at 549 nm as a function of the CH_2O concentration prepared by dilution from a standard (200 ppm) solution.

Figure 4-4 shows the amount of formaldehyde expected (line) compared to the amount of formaldehyde measured (triangles). We estimate a Faradaic Efficiency of 96%, confirming that formaldehyde is the only oxidation product and that formic acid and carbon dioxide were not formed significantly under these experimental conditions. The last point of this figure, 60 min reaction, shows a considerable deviation of the calculated (line) CH_2O evolution. This might be due to a significant reduction in the concentration of methanol after 1 hour reaction yielding to a lack of substrate to react with surface holes and possible competition with water oxidation.

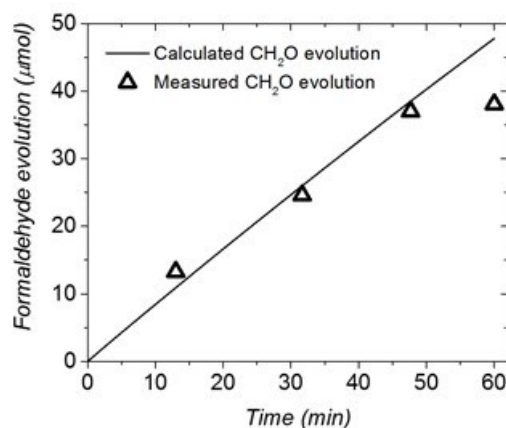


Figure 4-4. Formaldehyde evolution, calculated with 100% Faradaic efficiency (line) and measured (triangles), following the described spectrophotometric titration

4.3.3. Rate law analysis

Light-induced spectroelectrochemistry (LI-SEC) is used to study the kinetics and the rate determining step (rds) of the PEC oxidation of methanol to formaldehyde on the α - Fe_2O_3 photoanodes. As described previously in *Chapter 2*, the optical (PIA) signal monitors the density of surface accumulated holes whereas the electrochemical one (TPC) corresponds to the assay of the rate of reaction. The PIA signal was acquired probing at the valence band hole absorption maxima as shown in *Chapter 3*, at 650 nm for α - Fe_2O_3 photoanodes.³⁶

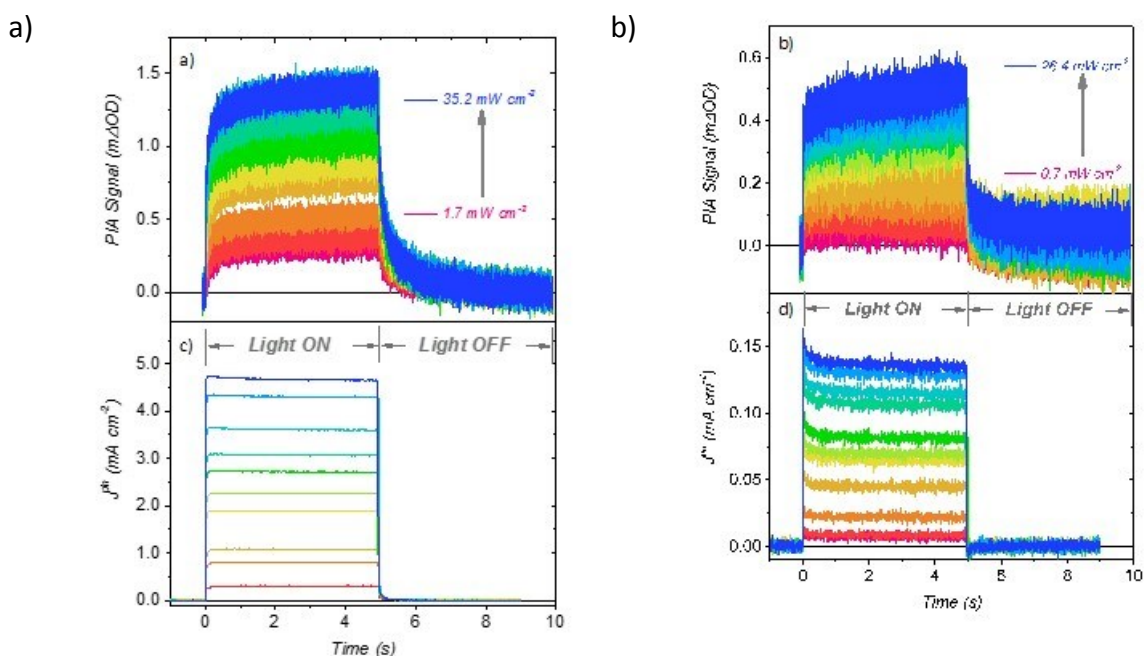


Figure 4-5. Oxidation of 95% CH_3OH in 0.1 M NaOH on α - Fe_2O_3 as a function of 5 s on/5 s off pulsed 356 nm illumination (~ 1 to $\sim 35 \text{ mW cm}^{-2}$). PIA signal of surface valence band hole density (p_s) probed at 650 nm under a) 0.55 V and b) 0.00 V vs Ag/AgCl and simultaneous assay of TPC under c) 0.55 V and d) 0.00 V vs Ag/AgCl.

Figure 4-5 shows the photo-induced absorption (Figure 4-5.a for 0.55 V and Figure 4-5.b for 0.00 V) and the transient photocurrent, corresponding to the rate of reaction (Figure 4-5.c for 0.55V and Figure 4-5.d for 0.00 V), of methanol oxidation on α -Fe₂O₃. The oxidation of methanol was studied at two different applied potentials, 0.55 V (left) and 0.00 V (right) vs Ag/AgCl, to compare the effect on the catalysis of reducing the space charge layer width in the hematite photoanode. Additionally, data at 0.00 V was collected to rule out a possible kinetic competition between water and methanol oxidation reactions. This applied potential was selected due to the negligible water oxidation photocurrent (red in Figure 4-2) observed.

The behaviour of the PIA and TPC signals exhibit the characteristic rise, plateau and decays, already discussed in *Chapter 3*. The PIA signals between 0.55 V (left) and 0.00 V (right) differ in the plateau value (*i.e.*, hole accumulation) and decay dynamics (discussed below) for similar photon flux. In the particular case of the optical decays, when the LED is turned off, can be assigned to the reaction of holes with the electrolyte only when no back electron-hole recombination processes are present. Such back electron-hole recombination processes have been observed by means of TPC measurements as negative spikes upon turning the light off.^{37–40} Absence of back electron-hole recombination is observed in the TPC at 0.55 V, data shown in Figure 4-5.b (left), compared to the data collected at 0.00 V (Figure 4-5.b, right), where some negative spikes are observed at 5 s. Such recombination losses reduce the efficiency of the system to oxidise methanol obtaining less photocurrent with similar light intensities, in other words, a higher light intensity is required to accumulate comparable hole densities at the surface of the α -Fe₂O₃ photoanode (see both left and right Figure 4-5). To further confirm the presence of recombination losses, Figure 4-6 shows the normalised (at ~ 0.5 mΔOD) optical signal for the dissipative surface hole consumption. In this figure it is apparent that when the light is turned off, the similar density of surface holes is consumed faster (see light grey decay in Figure 4-6) at 0.00 V. This confirms that, when the applied potential is not positive enough, back electron-hole recombination is present during methanol oxidation at 0.00 V.

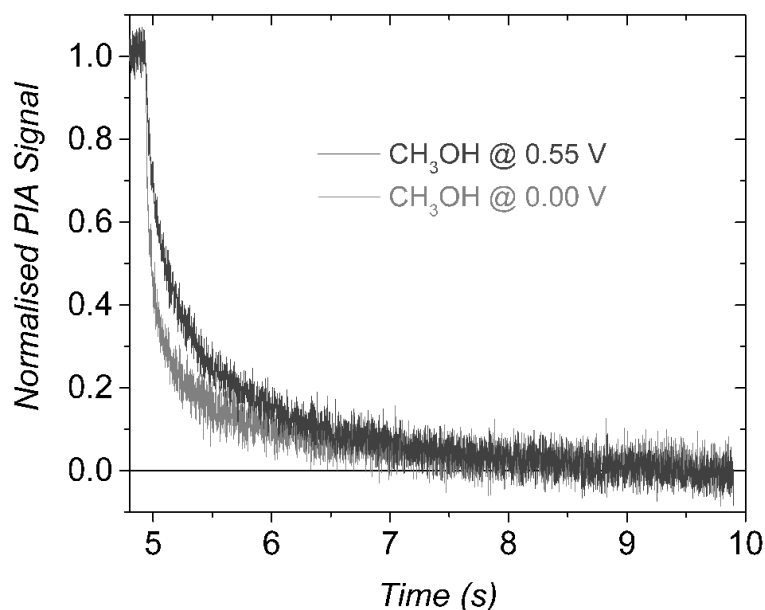


Figure 4-6. Oxidation of 95% CH₃OH in 0.1 M NaOH on α -Fe₂O₃. Optical signal decays (when light was turned off) under 0.00 V (light grey) and 0.55 V (dark grey) vs Ag/AgCl. Qualitative indication of surface hole recombination participating in the consumption of holes at low applied potentials. The signals chosen for normalisation were the closest to ~ 0.5 mΔOD, 5 mW cm⁻² (light orange) in Figure 4-5.a and 26.4 mW cm⁻² (dark blue) in Figure 4-5.b.

In order to gain further mechanistic information, analogous PIA and TPC data were taken (see Figure A-4 in the appendix) to study the kinetic effect of H/D isotope substitution. For this purpose, the electrolyte used was 95% CD₃OH (d₄-methanol) in a heavy aqueous (D₂O as solvent) solution of 0.1 M NaOD on α -Fe₂O₃. The optical signals observed in this figure show qualitatively a higher hole accumulation at comparable light intensities. This indicates that more holes can be accumulated in the presence of isotopically labelled methanol suggesting the possibility of a slower hole transfer to the electrolyte. This will be further discussed in the mechanistic implications section of this *Chapter*.

4.3.4. Comparison with TiO₂ photoanodes

In *Chapter 3*, faster rate constants for water oxidation were observed upon more positive valence band positions of the photoanodes. As such, the valence band position for methanol, as model organic substrate, is evaluated by comparing the kinetic and mechanistic studied on hematite to titania photoanodes. In this chapter and the corresponding publication,⁴¹ the synthesis and all the measurements using TiO₂ as photoanode were performed and kindly provided by Dr. Andreas Kafizas (Imperial College London).

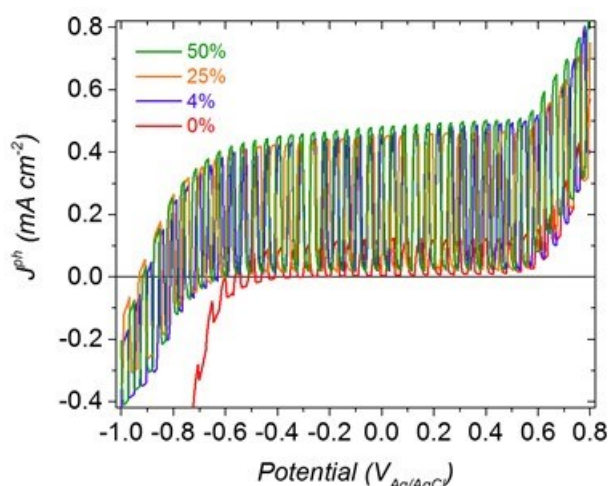


Figure 4-7. Current/potential (J - V) response of the TiO_2 photoanode under chopped ~ 1 sun front illumination (electrode/electrolyte) conditions measured in 0.1 M NaOH with varying concentration of methanol as follows: 0% (red), 4% (purple), 25% (orange) and 50% (green).

The J - V response, shown in Figure 4-7, of the TiO_2 photoanode in 0.1 M NaOH ($\sim 0.1 \text{ mA cm}^{-2}$) is consistent with previous reports.³⁰ Similarly to hematite, the onset of photocatalysis of methanol oxidation on titania requires $\sim 350 \text{ mV}$ less potential than water oxidation, taking the onset as the applied potential producing an oxidative current of $10 \mu\text{A cm}^{-2}$. Interestingly, the kinetics of methanol oxidation on TiO_2 reaches the 'saturation' point, where no diffusion/adsorption limitations are present, at a concentration of 4% CH_3OH in 0.1M NaOH.

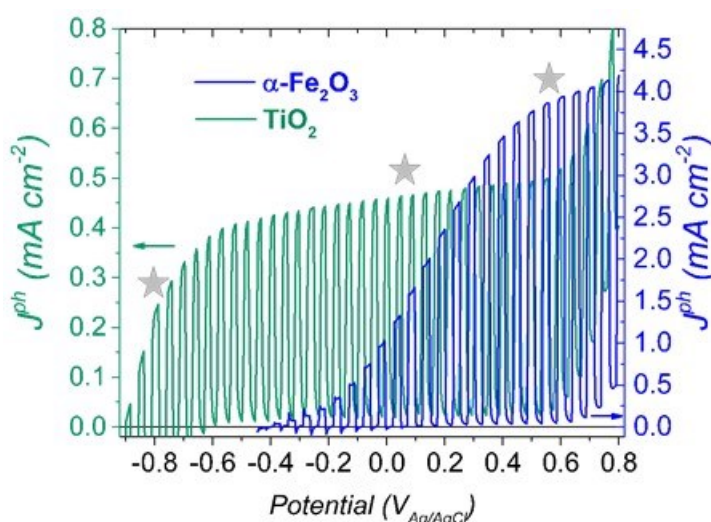


Figure 4-8. Current/potential (J - V) response of the $\alpha\text{-Fe}_2\text{O}_3$ (blue) and TiO_2 (green) photoanodes in 95% and 4% CH_3OH in 0.1 M NaOH respectively, under chopped ~ 1 sun front illumination conditions. The stars indicate the applied potentials at which the photo-induced absorption spectroscopy studies were carried out.

Comparative J - V curves for methanol oxidation on $\alpha\text{-Fe}_2\text{O}_3$ (blue) and TiO_2 (green) are shown in Figure 4-8. Nanocrystalline $\alpha\text{-Fe}_2\text{O}_3$ produces circa 1 order of magnitude more photocurrent ($\sim 4 \text{ mA cm}^{-2}$) than TiO_2 ($\sim 0.4 \text{ mA cm}^{-2}$) at high applied potentials. This

remarkable difference is most likely caused by the ability of hematite to absorb more AM1.5 light than titania due to its smaller bandgap (2.1 and 3.1 eV, respectively). Turning to onset of photocatalysis, TiO₂ requires ~500 mV less positive potential compared to α -Fe₂O₃, most likely due to their difference in valence band edge positions (2.1 and 2.6 V vs RHE at pH 14, respectively).^{42,43}

Analogous PIA and TPC data to those shown in Figure 4-5 for α -Fe₂O₃ were collected at -0.80 V vs Ag/AgCl on TiO₂ in 4% CH₃OH in 0.1 M NaOH (see Figure A-5 in the appendix), by means of LI-SEC measurements, measuring the PIA signal of the TiO₂ photoanode at 500 nm as reported elsewhere.⁴⁴ I note that the concentration at which the photocurrent, *i.e.* rate of reaction, is independent of the amount of methanol in the electrolyte, is lower for TiO₂ than for α -Fe₂O₃, as observed in the *J-V* curves in Figure 4-2 and Figure 4-8. This data, although with higher signal/noise ratio, was useful to compare how the accumulated holes react in different metal oxides surfaces.

Methanol, as model organic substrate, is shown herein to oxidise with ~300 mV less overpotential than water on a nanostructured α -Fe₂O₃ photoanodes. Compared to water oxidation, methanol produces ~50% more plateau photocurrent with a remarkable almost unity Faradaic efficiency. Additionally, it has been shown that back electron-hole recombination processes accelerate the decay dynamics of PIA optical signal upon turning the light off. Further LI-SEC data will be used in the discussion section for rate law analyses. Finally, methanol oxidation on α -Fe₂O₃ is compared with TiO₂ photoanodes producing significantly less photocurrent but requiring ~500 mV less overpotential. These data collected allowed the assay of the accumulation, steady-state, reaction and back electron-hole recombination of the α -Fe₂O₃ and TiO₂ photoanodes while monitoring the rate of reaction as a function of surface hole density under different conditions of band bending, valence band edge and H/D isotope substitution.

4.4. Discussion

4.4.1. (Photo)electrochemical response

The photoelectrochemical response (*J-V*) of the studied α -Fe₂O₃ and TiO₂ photoanodes was examined at first for the water oxidation reaction (0.1 M NaOH) to corroborate these results with the usual *J-V* curves reported in literature.^{28–30} It is apparent, for both α -Fe₂O₃

and TiO₂ photoanodes, that the achieved plateau photocurrents (J_{lim}) are limited by a mass transfer process. Figure 4-9 shows how the plateau photocurrent, *i.e.* the rate of reaction, increases as the methanol concentration increased in the electrolyte. This linear dependency (up to ~90% for α -Fe₂O₃ and ~4% for TiO₂) is most likely due to diffusion limitations of methanol to reach the surface of the photoanode as shown in Equation 4-7.⁴⁵

$$J_{lim} = e \cdot C_{MeOH} \cdot \left(\frac{D_{MeOH}}{\pi \cdot t} \right)^{1/2} \quad \text{Equation 4-7}$$

where e is the elementary charge ($1.6 \cdot 10^{-9}$ A s), C_{MeOH} is the concentration of methanol in the bulk of the solution and D_{MeOH} is the diffusion coefficient of methanol in 0.1 M NaOH. Note that this equation was developed for rotating disks electrodes and that the analysis of all the parameters of it is out of the scope of this chapter.

Figure 4-9 also shows that the concentration at which the photocurrent is not diffusion limited, *i.e.* when a ‘photocurrent-saturating’ concentration is reached, differed for both photoanodes, at least by one order of magnitude (~90% for α -Fe₂O₃ and ~4% for TiO₂). This difference might be due to different interaction mechanisms between CH₃OH, H₂O and the photoanode surface. Methanol and water undergoes competitive adsorption mechanism on TiO₂ and α -Fe₂O₃ surfaces. However, methanol adsorption appears to be more favourable on hematite surfaces, where CH₃OH has been reported to be chemisorbed (as methoxide).⁴⁶

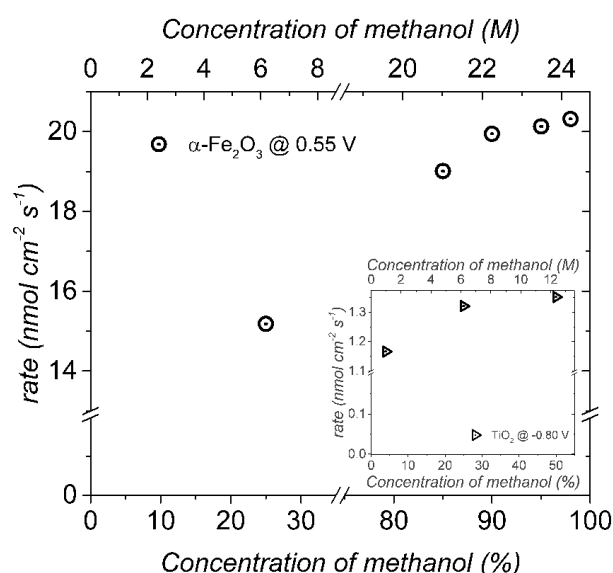


Figure 4-9. Rate of methanol oxidation measured at 0.55 V for α -Fe₂O₃ and -0.80 V vs Ag/AgCl for TiO₂ (inset) as a function of methanol concentration in 0.1 M NaOH.

4.4.2. Rate law analysis

Turning now to a more quantitative analysis of the PIA and TPC data presented in the previous section, a rate law analysis is presented. Equation 4-8 corresponds to the rate law for the oxidation of 95% CH₃OH in aqueous 0.1 M NaOH. This was based on the rate law analysis describing the kinetics of water oxidation on different metal oxides (α -Fe₂O₃, BiVO₄ and TiO₂), described in *Chapter 2* and applied in *Chapter 3* and reported previously by our group.^{36,47-49} This model considers the change of the surface hole density (p_s) over the time ($\frac{dp_s}{dt}$) as the sum of the incoming flux of holes towards the surface (J_{holes}), *i.e.* photocurrent (J^{ph}), and 2 hole consuming processes, namely back electron-hole recombination ($-k_{SR} \cdot p_s^\gamma$) and reaction with the electrolyte ($-k_{MO} \cdot p_s^\alpha$ for methanol oxidation and $-k_{WO} \cdot p_s^\beta$ for water oxidation if in competition).

$$\frac{dp_s}{dt} = J_{holes} - k_{WO} \cdot p_s^\beta - k_{MO} \cdot p_s^\alpha - k_{SR} \cdot p_s^\gamma \quad \text{Equation 4-8}$$

where k_{WO} , k_{MO} and k_{SR} correspond to the water and methanol oxidation and back electron-hole recombination observed rate constants, respectively. The hole consuming processes exhibit a power law dependence on the density of accumulated holes with α , β and γ as the rate orders.

In order to simplify the kinetic model presented in Equation 4-8, PIA and TPC data were collected on α -Fe₂O₃ at a high positive applied potential (0.55 V vs Ag/Cl) where no back electron-hole recombination was present (as shown in Figure 4-5, left and Figure 4-8), therefore the $-k_{SR} \cdot p_s^\gamma$ term could be approximated to 0. In addition to this, Figure 4-10.a compares the dynamics of the surface holes on hematite under these strong applied potential conditions. From the faster decay dynamics exhibited by CH₃OH (blue) compared to H₂O (red) is apparent that hole transfer to water in presence of methanol is minimal and can be ignored. As such, the term $-k_{WO} \cdot p_s^\beta$, in Equation 4-8, corresponding to the water oxidation kinetics, can also be approximated to 0. Therefore Equation 4-8 can be simplified to:

$$\frac{dp_s}{dt} = J_{holes} - k_{MO} \cdot p_s^\alpha \quad \text{Equation 4-9}$$

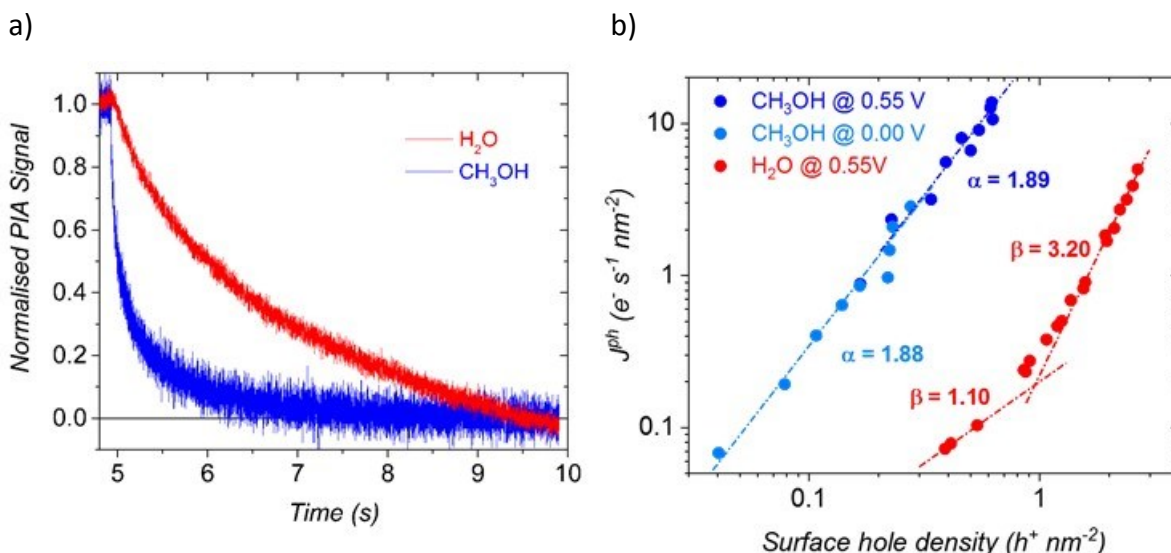


Figure 4-10. Kinetic comparison between water – 0.1 M NaOH – (red) and methanol – 95% CH₃OH in 0.1 M NaOH – (blue) oxidation kinetics of reaction on α -Fe₂O₃, a) Normalised PIA decay at ~ 1.5 *m*ΔOD measured at 650 nm under 0.55 V vs Ag/AgCl and b) rate law analysis for water and methanol oxidation measured at 650 nm under 0.55 V and 0.00 V vs Ag/AgCl.

Under conditions of a high positive applied potential, the rate law analysis developed in *Chapter 2* can be extended to the oxidation of organic substrates with methanol as substrate model. As such, for steady-state conditions, Equation 4-9 can be rewritten logarithmically as, with J_{holes} as the photocurrent (J^{ph}):

$$\log(J^{ph}) = \alpha \cdot \log(p_s) + \log(k_{MO}) \quad \text{Equation 4-10}$$

where the slope of the plot is the order of reaction (α) with respect to the surface hole density and the intercept refers to the observed methanol oxidation rate constant. This logarithmic plot is shown in Figure 4-10.b exhibiting a reaction of 2nd order with respect to the density of accumulated holes at the surface, which differs from the 1st to 3rd transitioning mechanism discussed in *Chapter 3* (this will be further discussed in the Mechanistic implications section of this *Chapter*). It is apparent from this plot that the intercept, therefore the rate constant for methanol oxidation (dark blue data points) is ~ 2 orders of magnitude higher than that for water oxidation (red data points) confirming that water does not compete with methanol to be oxidised under these highly oxidative conditions.

In addition to that, as previously mentioned, data was also collected at 0.00 V (where water oxidation does not proceed as shown in Figure 4-2) to evaluate the effect of the space charge layer width in the mechanism as well as to further confirm the absence of competition between water and methanol oxidation at high positive potentials such as 0.55 V. These data

is shown Figure 4-10.b (light blue dots). In this figure the linear fitting of the two sets of data (0.55 V and 0.00 V) overlap indicating that the methanol oxidation reaction kinetics on α -Fe₂O₃ are virtually identical at matched surface hole densities. This observation also indicates that the steady-state approximation of the rate law analysis in Equation 4-10, addresses uniquely the kinetics of reaction, even under back electron-hole recombination conditions. The second-order rate constant, obtained from Equation 4-10, is $33 \text{ h}^+ \text{ nm}^{-2} \text{ s}^{-1}$ for both applied potentials. This remarkable observation takes place despite differences in the voltage applied to, and therefore band bending at, the semiconductor/electrolyte junction. This indicates that the rate constant of this reaction is independent of the band-bending or the photoanode Fermi level. Consequently, the rate of methanol oxidation depends solely upon the density of surface holes that the metal oxide is able to accumulate. Furthermore, this observation implies that these surface holes react with an energy offset determined by the valence band edge (VBE), reflecting the semiconducting nature of the α -Fe₂O₃ photoanode and opposite to metallic electrodes for which the kinetics of reaction depend upon the free energy of the electrode which is controlled by the applied potential.^{42,50}

The observed second order kinetic behaviour is further confirmed by two different analyses of the optical data for α -Fe₂O₃ data measured at 0.55 V vs Ag/AgCl, namely an initial rates law and the fitting of a decay to second order kinetics (see Figure 4-11). The initial rates law analysis uses the optical decay when the light is turned off, hence no photocurrent flows through the system ($J^{ph} = 0$) at a 0.55 V when no back electron-hole recombination takes place, therefore Equation 4-8 can be rewritten logarithmically as:

$$\log\left(-\frac{dp_s}{dt}\right) = \alpha \cdot \log(p_s) + \log(k_{MO}) \quad \text{Equation 4-11}$$

where $\frac{dp_s}{dt}$ is the initial slope of the optical decays. The gradient in Figure 4-11.a is ~ 2 , supporting the second order dependence of methanol oxidation with respect to the surface hole density with an observed rate constant of $23 \text{ h}^+ \text{ nm}^{-2} \text{ s}^{-1}$. Additionally, the signal corresponding to a surface hole density of $0.23 \text{ h}^+ \text{ nm}^{-2}$ in steady-state was fitted to a second order kinetic decay as follows (Figure 4-11.b):

$$(p_s)_t = \frac{1}{(p_s)_0^{-1} + k_{MO} \cdot t} \quad \text{Equation 4-12}$$

where $(p_s)_0$ is the steady-state (initial) surface hole density obtaining a fitted rate constant of $26 \text{ h}^+ \text{ nm}^{-2} \text{ s}^{-1}$. Both initial rates law (Equation 4-11) and the fitting to second order kinetics (Equation 4-12) exhibits similar rate constant values (23 and $26 \text{ h}^+ \text{ nm}^{-2} \text{ s}^{-1}$) confirming the validity of the experimental results.

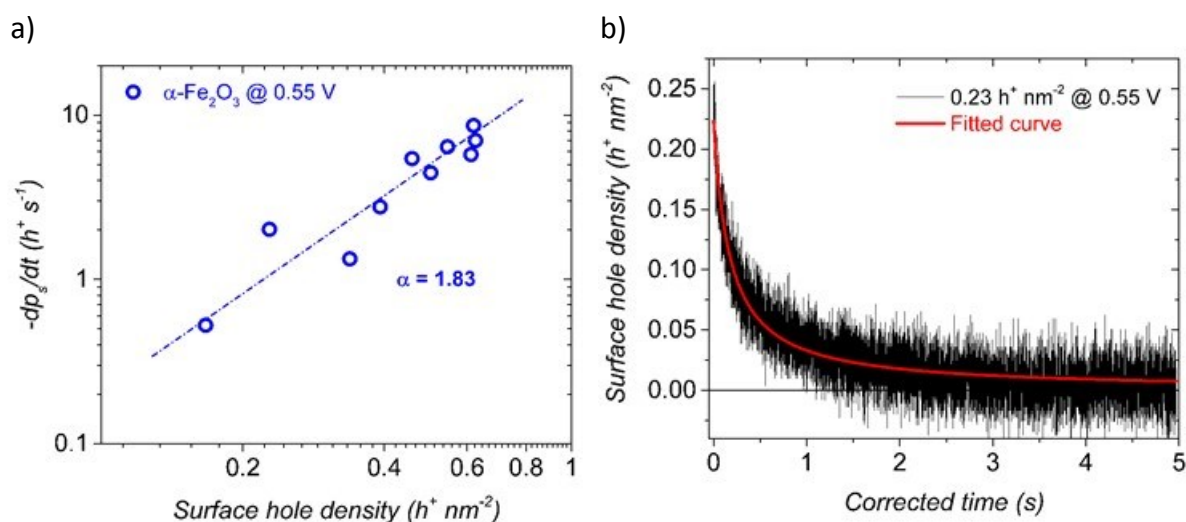


Figure 4-11. Methanol oxidation on $\alpha\text{-Fe}_2\text{O}_3$ at 0.55 V vs Ag/AgCl kinetic analysis based uniquely on the optical signal, a) Initial rates law analysis, negative gradient of PIA signal ($\frac{dp_s}{dt}$) within the first 30 ms as a function of the surface hole density (p_s) and b) surface hole density decay when light was turned off for a steady-state (p_s) of $0.23 \text{ h}^+ \text{ nm}^{-2}$ (black) and its corresponding fitting to second order kinetics (red)

A kinetic isotope effect (KIE) study was performed to further investigate the second order rate determining step of methanol oxidation on $\alpha\text{-Fe}_2\text{O}_3$. For this purpose isotopically labelled d_4 -methanol (CD_3OD) was used as substrate as opposed to CH_3OH . As expected, a second order dependency of the reaction rate with respect to the density of surface holes is observed (see Figure 4-12). However, a KIE of ~ 20 (with $k_{\text{CH}_3\text{OH}} = 33 \text{ h}^+ \text{ nm}^{-2} \text{ s}^{-1}$ and $k_{\text{CD}_3\text{OD}} = 1.35 \text{ h}^+ \text{ nm}^{-2} \text{ s}^{-1}$) is obtained, corresponding to a 20-fold reduction in the reaction rate at equivalent hole densities. Such observation implies that the ‘turn-over frequency’ per hole decreases from $\sim 20 \text{ s}^{-1}$ to $\sim 1 \text{ s}^{-1}$ in the presence of d_4 -methanol at ~ 1 sun irradiation conditions, which indicates, as known in literature,⁵¹ that the rate determining step of the reaction involves a C-H bond breaking.

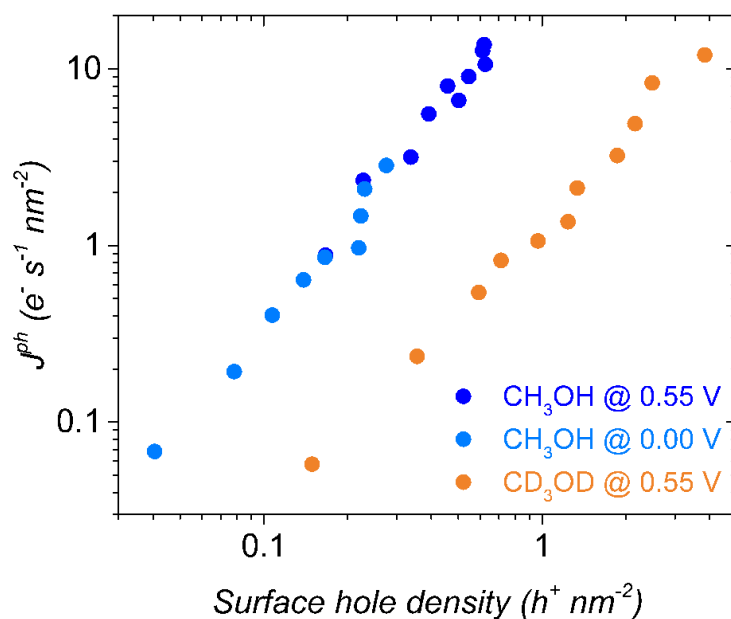


Figure 4-12. Rate law analysis, J^{ph} vs p_s for the oxidation of CD_3OD in aqueous (D_2O) 0.1 M NaOD on $\alpha\text{-Fe}_2\text{O}_3$ at 0.55 V (orange) compared to the rate law for the oxidation of CH_3OH on $\alpha\text{-Fe}_2\text{O}_3$ at 0.00 V (light blue) and 0.55 V (dark blue).

4.4.3. Comparison with TiO_2 photoanodes

Turning now to discuss the comparison between hematite and anatase photoanodes, Figure 4-13 shows the photocurrent density (J^{ph}) as a function of the surface hole density (p_s) for the oxidation of methanol on $\alpha\text{-Fe}_2\text{O}_3$ and TiO_2 correcting for surface roughness on both photoanodes. It is apparent from the presented data for TiO_2 that the gradient of J^{ph} vs p_s is ~ 2 , similarly to $\alpha\text{-Fe}_2\text{O}_3$ at 0.00 V and 0.55 V, evidencing a common second order dependence of methanol oxidation with respect to the surface hole density. This observation indicates that the rate determining step of the methanol oxidation reaction has some parallels for these two oxides despite the different nature of the surface holes in both photoanodes ($\text{Fe}^{\text{IV}}=\text{O}$ for $\alpha\text{-Fe}_2\text{O}_3$ ⁵² and $\text{Ti}^{\text{IV}}\text{-O}\bullet$ for TiO_2 ^{53,54}, further discussed in the mechanistic implications section).

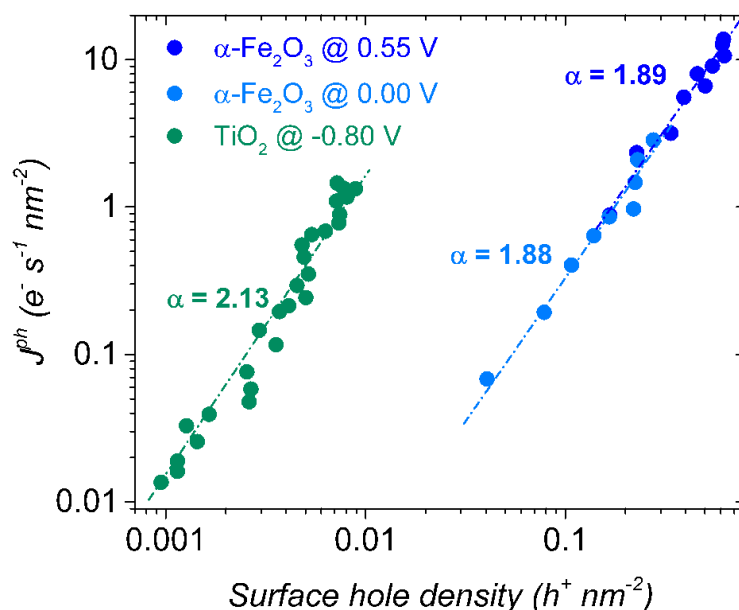


Figure 4-13. Rate law analysis, J^{ph} vs p_s for the oxidation of CH_3OH on $\alpha-Fe_2O_3$ at 0.00 V (light blue) and 0.55 V (dark blue) vs Ag/AgCl and on TiO_2 at -0.80 V (green) vs Ag/AgCl applied potentials. The dotted lines represent a linear fitting with gradient 2.

Additionally, it is shown that TiO_2 oxidises methanol with a second-order rate constant ~ 500 times faster than $\alpha-Fe_2O_3$ (are $15000 h^{+^{-1}} nm^{-2} s^{-1}$ for TiO_2 compared to $33 h^{+^{-1}} nm^{-2} s^{-1}$ for $\alpha-Fe_2O_3$), which can be assigned most simply to the more positive valence band edge of TiO_2 compared to that of $\alpha-Fe_2O_3$ (2.6 and 2.1 V vs NHE at pH 14, respectively).^{42,43} The difference in their VBE would provide the holes accumulated at the surface of TiO_2 a larger energy offset with respect to the oxidation potential (ΔG) to drive the reaction. Furthermore, the methanol adsorption differences discussed in the Photoelectrochemical response section might also be important in the observed kinetics of the reaction, although such a physicochemical study was out of the scope of this chapter.

4.4.4. Mechanistic implications

The results reported herein show evidence that, (1) methanol is photoelectrochemically oxidised to formaldehyde with almost unity Faradaic efficiency on $\alpha-Fe_2O_3$ and (2), the reaction follows a 2nd order dependence on the surface hole density of $\alpha-Fe_2O_3$ and TiO_2 ; (3) the reaction kinetics are independent of the band-bending but depend upon the valence band edge of the metal oxide and finally (4) the rate determining step of methanol oxidation involves a C-H bond breaking. Based on this evidence and the available literature, in this section I discuss a plausible mechanism for the methanol oxidation reaction.

Firstly, the reported Faradaic efficiency herein (96 %) for CH₂O photosynthesis using an earth-abundant based photocatalyst is higher compared to the reported Faradaic efficiency of electrochemical methanol oxidation on Pt electrodes (81%)²² or in a photochemical process using TiO₂ (30%).²⁷ Additionally, these photosynthetic processes, taking place at room temperature, could be considered for further studies towards CH₂O industrial production under high light intensities. Such industrial processes normally include the use of a Ag or Fe-Mo-based catalysts working at 500 – 600 °C for 85 – 90% yield or ~300 °C for 99% yield, respectively.^{55,56}

Methanol oxidation has been reported to take place on metal oxide surfaces with low Faradaic efficiencies. However, these studies were normally carried out at low methanol concentration or low photon fluencies. For example, Wahl et. al.,²⁷ reported a Faradaic efficiency of 30% for the oxidation of 0.4% methanol in 0.1 M NaOH on TiO₂. Such concentration conditions are below the ‘saturating-photocurrent’ region according to Figure 4-7 and might be one of the most critical factors for the higher (almost unity) Faradaic efficiency observed herein. Therefore, the mechanism discussed in this section corresponds for the oxidation of methanol in saturation conditions, which is second order with respect to the density of accumulated holes at the surface of both, α -Fe₂O₃ and TiO₂. This observation suggests that the rate determining step for the oxidation of methanol requires 2 holes to cooperate or ‘accumulate’ to oxidise methanol to formaldehyde on hematite and titania, with ~2 orders of magnitude faster kinetics for the latter assigned to its deeper valence band edge.

The oxidation of methanol to formaldehyde in some metal oxides, such as TiO₂ and ZnO, in literature has been proposed to proceed via a photocurrent doubling (in which one absorbed photon produces two conduction band electrons) mechanism.^{22,27,57,58} This mechanism, shown in Figure 1-1, begins when a molecule of methanol is adsorbed on the photoanode surface followed by a hole transfer to the adsorbed methoxide forming a methoxy radical. The second oxidation step occurs by an electron injection from the radical into the conduction band of the semiconductor, releasing formaldehyde. However, this photocurrent doubling mechanism has been observed only under low light intensity conditions. Furthermore, Schoenmakers et. al.,⁵⁹ have reported a transition in the quantum efficiency of methanol oxidation on ZnO from 2 to 1 when increasing the light intensity 4 orders of magnitude from ~0.005 to 5 suns. This indicates that a photocurrent doubling

mechanism can dominate at low light intensities. However, at operating conditions (1 Sun) no photocurrent doubling is expected, consistent with the observed second order dependence of methanol oxidation on $\alpha\text{-Fe}_2\text{O}_3$ and TiO_2 photoanodes in agreement with previous studies.^{25,60}

Focusing now on the kinetic isotope effect (KIE) caused by H/D substitution, before reaching the transition state in the rds of the reaction, methanol undergoes adsorption forming a methoxide species releasing a proton. Subsequently, a hole transfer takes place to form a methoxyl radical. This radical then interacts with a second surface hole in the rds with a kinetic isotope effect of ~ 20 , which was most obviously assigned to a C-H bond breaking. This is an exceptionally high KIE value compared to, for example, the calculated KIE of ~ 7 (see Table 2-1) for a C-H bond stretching mode, indicating that important structural rearrangements take place during the transition state. This unusual KIE could be assigned to a carbon rehybridization from sp^3 to sp^2 of the surface bound methoxyl radical due to a loss of the stretching and bending modes,⁶¹ thus promoting important differences in the zero-point energy of this transition state, therefore increasing the KIE by H/D substitution.

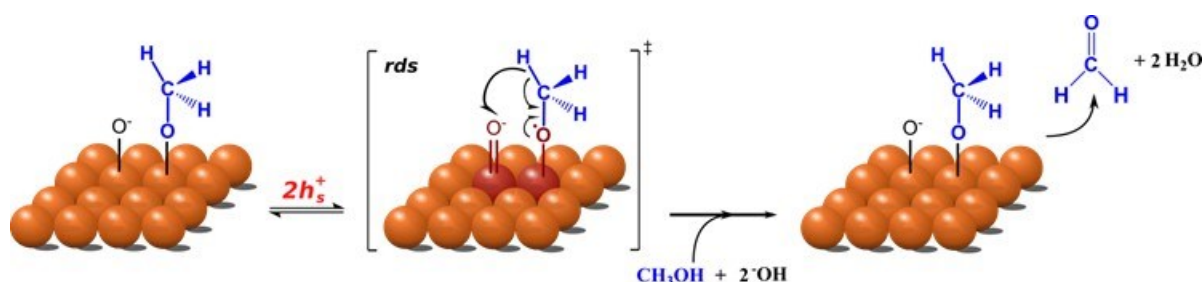


Figure 4-14. Plausible methanol oxidation mechanism on $\alpha\text{-Fe}_2\text{O}_3$, in which the cooperative function of two surface holes (h_s^+) results in a C-H bond breaking during the rate determining step with carbon rehybridization.⁴¹ The surface and valence band (VB) of the $\alpha\text{-Fe}_2\text{O}_3$ photoanode are also represented.

Methanol is oxidised to formaldehyde with ~ 1 Faradaic efficiency on hematite with the rate determining step reached after methanol adsorption (as methoxide) and the accumulation of two valence band holes at the surface. Upon a hole transfer to the adsorbed methoxide, a methoxyl radical ($\text{CH}_3\text{O}\bullet$) is produced reacting with a second neighbouring surface hole. To propose the plausible mechanism shown in Figure 4-14, a non-interaction between methoxyl radicals was assumed based on a reported ‘saturating’ methanol-adsorbed surface density ($\sim 2 \times 10^{13} \text{ molecules cm}^{-2}$) on hematite by Carlos-Cuellar et. al.⁶² This coverage

corresponds to approximately one methoxy species every 5 nm^2 , sufficiently apart not to interact between them during the rds. I note here that, different hematite films, with different surface exposed facets and roughness factors among other characteristics, could lead to different methanol surface coverage. However, a possible interaction between two methoxyl radicals is likely not to involve two holes at the rate limiting step, therefore a second order reaction would not be observed in Figure 4-10. This allows a tentative assignment of the rds as the methoxyl radical oxidation by another surface hole in a reaction cluster similar to the proposed for water oxidation in *Chapter 3*. The proposed mechanism is based on the observed second-order kinetics, in which a C-H bond breaks while the carbon is rehybridized, as depicted in Figure 4-14. This mechanism is consistent with previous proposed mechanisms under different working conditions (*e.g.*, methanol concentration and light intensity) and might complement the proposed photocurrent doubling mechanisms.^{22,25–27,34,57–60} Recently, Hamann and co-workers,⁵² assigned the $\text{Fe}^{\text{IV}}=\text{O}$ species to the surface holes in $\alpha\text{-Fe}_2\text{O}_3$, which diffuse to the catalytic cluster to form the reactive species shown in Figure 4-14. This mechanism can also operate under back electron-hole recombination conditions as suggested by the rate law at different applied potentials. Finally, a broadly similar mechanism should operate on TiO_2 , as the second-order kinetics indicates. This mechanism operates with faster kinetics as the holes in TiO_2 are more energetic due to its deeper valence band. In literature, the nature of a surface hole in TiO_2 has been proposed to be a $\bullet\text{OH}$ radical formed either in a terminal $\text{Ti}^{\text{IV}}\text{-OH}$ ^{53,63} groups or in a bridging $\text{Ti}^{\text{IV}}\text{-O-Ti}^{\text{IV}}$ groups.^{54,64,65} This radical nature of titania surface holes may also be correlated with the faster kinetics observed in anatase compared with hematite photoanodes.

4.5. Conclusions

The oxidation of organic substrates can serve to overcome the kinetic limitations of mechanistically complex photoelectrochemical water oxidation in the water splitting process, as studied in *Chapter 3*. This can potentially be carried out while degrading organic pollutants or a high value-added product is synthesised. As such, in this *Chapter* the kinetics and mechanism of the oxidation of methanol, as model organic substrate, are studied. I report the photosynthesis of formaldehyde, from methanol, in aqueous/organic solutions at room temperature (25°C) under ~ 1 sun irradiation with a Faradaic efficiency of unity. The

unprecedented Faradaic efficiency shown herein allow to suggest the possibility of a hydrogen production concomitant with the selective synthesis of high added-value chemicals.

Experimental rate law analyses allowed the mechanistic investigation of the observed second order kinetics of methanol oxidation with respect to the surface hole density. Applied potential dependence and isotope labelling experiments allowed the proposal of a plausible mechanism for the oxidation of methanol specifically on α -Fe₂O₃, but sharing parallels with TiO₂ photoanodes. From the plausible methanol oxidation reaction proposed herein, some parallels with the proposed water oxidation mechanism, studied in *Chapter 3*, can be drawn suggesting the importance of the undertaken molecular point of view. As such, the kinetics presented herein were shown to be independent of the space charge layer width, but sensitive to the valence band edge of the photoanode.

4.6. References

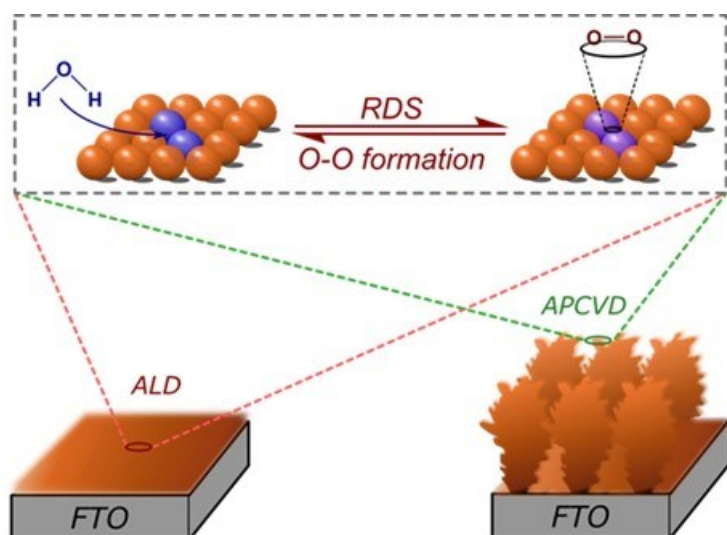
1. Peter, L. M. Semiconductor electrochemistry. in *Photoelectrochemical Solar Fuel Production: From Basic Principles to Advanced Devices* (2016). doi:10.1007/978-3-319-29641-8_1
2. Barroso, M., Pendlebury, S. R., Cowan, A. J. & Durrant, J. R. Charge carrier trapping, recombination and transfer in hematite (α -Fe₂O₃) water splitting photoanodes. *Chem. Sci.* **4**, 2724–2734 (2013).
3. Cowan, A. J. & Durrant, J. R. Long-lived charge separated states in nanostructured semiconductor photoelectrodes for the production of solar fuels. *Chem. Soc. Rev.* **42**, 2281–2293 (2013).
4. Pendlebury, S. R. *et al.* Correlating long-lived photogenerated hole populations with photocurrent densities in hematite water oxidation photoanodes. *Energy Environ. Sci.* **5**, 6304–6312 (2012).
5. Upul Wijayantha, K. G., Saremi-Yarahmadi, S. & Peter, L. M. Kinetics of oxygen evolution at α -Fe₂O₃ photoanodes: a study by photoelectrochemical impedance spectroscopy. *Phys. Chem. Chem. Phys.* **13**, 5264 (2011).
6. Peter, L. M., Wijayantha, K. G. U. & Tahir, A. A. Kinetics of light-driven oxygen evolution at α -Fe₂O₃ electrodes. *Faraday Discuss.* **155**, 309–322 (2012).
7. Peter, L. M. & Wijayantha, K. G. U. Photoelectrochemical Water Splitting at Semiconductor Electrodes: Fundamental Problems and New Perspectives. *ChemPhysChem* **15**, 1983–1995 (2014).
8. Cummings, C. Y., Marken, F., Peter, L. M., Wijayantha, K. G. U. & Tahir, A. A. New Insights into Water Splitting at Mesoporous α -Fe₂O₃ Films: A Study by Modulated Transmittance and Impedance Spectroscopies. *J. Am. Chem. Soc.* **134**, 1225–1234 (2012).
9. Chong, M. N., Jin, B., Chow, C. W. K. & Saint, C. Recent developments in photocatalytic water treatment technology: A review. *Water Res.* **44**, 2997–3027 (2010).
10. Mills, A. & Le Hunte, S. An overview of semiconductor photocatalysis. *J. Photochem. Photobiol. A Chem.* **108**, 1–35 (1997).
11. Quesada-Cabrera, R., Mills, A. & O’rourke, C. Action spectra of P25 TiO₂ and a visible light absorbing, carbon-modified titania in the photocatalytic degradation of stearic acid. *Appl. Catal. B Environ.* **150**, 338–344 (2014).
12. Rincón, A. G. & Pulgarin, C. Photocatalytical inactivation of E. coli: effect of (continuous–intermittent) light intensity and of (suspended–fixed) TiO₂ concentration. *Appl. Catal. B Environ.* **44**, 263–284 (2003).
13. Palmisano, G. *et al.* Advances in selective conversions by heterogeneous photocatalysis. *Chem. Commun* **46**, 7074–7089 (2010).
14. Fagnoni, M., Dondi, D., Ravelli, D. & Albini, A. Photocatalysis for the Formation of the C–C Bond. *Chem. Rev.* **107**, 2725–2756 (2007).
15. Yang, J. *et al.* Selective oxidation of alcohols on hydrogen titanate nanotubes under visible light irradiation: relationship between nanostructure and catalytic activity. *Catal. Sci. Technol.* **6**, 7604–7614 (2016).
16. ten Brink, G.-J., Arends, I. W. C. E. & Sheldon, R. A. Green, catalytic oxidation of alcohols in water. *Science (80-)*. **287**, 1636–1639 (2000).

17. Kasap, H. *et al.* Solar-Driven Reduction of Aqueous Protons Coupled to Selective Alcohol Oxidation with a Carbon Nitride–Molecular Ni Catalyst System. *J. Am. Chem. Soc.* **138**, 9183–9192 (2016).
18. Katryniok, B. *et al.* Selective catalytic oxidation of glycerol: perspectives for high value chemicals. *Green Chem.* **13**, 1960–1979 (2011).
19. Ruberu, T. P. A., Nelson, N. C., Slowing, I. I. & Vela, J. Selective Alcohol Dehydrogenation and Hydrogenolysis with Semiconductor-Metal Photocatalysts: Toward Solar-to-Chemical Energy Conversion of Biomass-Relevant Substrates. *J. Phys. Chem. Lett.* **3**, 2798–2802 (2012).
20. Antoniadou, M. & Lianos, P. Production of electricity by photoelectrochemical oxidation of ethanol in a PhotoFuelCell. *Appl. Catal. B Environ.* **99**, 307–313 (2010).
21. Iwasita, T. Methanol and CO electrooxidation. in *Handbook of Fuel Cells – Fundamentals, Technology and Applications* (eds. Vielstich, W., Gasteiger, H. & Lamm, A.) **2**, (John Wiley & Sons, 2003).
22. Batista, E. A., Malpass, G. R. P., Motheo, A. J. & Iwasita, T. New mechanistic aspects of methanol oxidation. *J. Electroanal. Chem.* **571**, 273–282 (2004).
23. Kafizas, A. *et al.* Where Do Photogenerated Holes Go in Anatase:Rutile TiO₂ ? A Transient Absorption Spectroscopy Study of Charge Transfer and Lifetime. *J. Phys. Chem. A* **120**, 715–723 (2016).
24. Pendlebury, S. R. *et al.* Dynamics of photogenerated holes in nanocrystalline α -Fe₂O₃ electrodes for water oxidation probed by transient absorption spectroscopy. *Chem. Commun.* **47**, 716–718 (2011).
25. Micka, K. & Gerischer, H. Anodic photooxidation of formic acid and methanol at a zinc oxide electrode and the influence of anions. *J. Electroanal. Chem.* **38**, 397–402 (1972).
26. Shen, M. & Henderson, M. A. Identification of the Active Species in Photochemical Hole Scavenging Reactions of Methanol on TiO₂. *J. Phys. Chem. Lett.* **2**, 2707–2710 (2011).
27. Wahl, A. *et al.* Photoelectrochemical studies pertaining to the activity of TiO₂ towards photodegradation of organic compounds. *J. Electroanal. Chem.* **396**, 41–51 (1995).
28. Kay, A., Cesar, I. & Grätzel, M. New Benchmark for Water Photooxidation by Nanostructured α -Fe₂O₃ Films. *J. Am. Chem. Soc.* **128**, 15714–15721 (2006).
29. Cornuz, M., Grätzel, M. & Sivula, K. Preferential Orientation in Hematite Films for Solar Hydrogen Production via Water Splitting. *Chem. Vap. Depos.* **16**, 291–295 (2010).
30. Cowan, A. J. *et al.* Activation Energies for the Rate-Limiting Step in Water Photooxidation by Nanostructured α -Fe₂O₃ and TiO₂. *J. Am. Chem. Soc.* **133**, 10134–10140 (2011).
31. Albright, P. S. & Gosting, L. J. Dielectric Constants of the Methanol-Water System from 5 to 55°. *J. Am. Chem. Soc.* **68**, 1061–1063 (1946).
32. Rondinini, S. pH measurements in non-aqueous and aqueous–organic solvents – definition of standard procedures. *Anal. Bioanal. Chem.* **374**, 813–816 (2002).
33. Jacobsen, N. W. & Dickinson, R. G. Spectrometric assay of aldehydes as 6-mercapto-3-substituted-s-triazolo(4,3-b)-tetrazines. *Anal. Chem.* **46**, 298–299 (1974).
34. Klahr, B., Gimenez, S., Zandi, O., Fabregat-Santiago, F. & Hamann, T. Competitive Photoelectrochemical Methanol and Water Oxidation with Hematite Electrodes. *ACS Appl.*

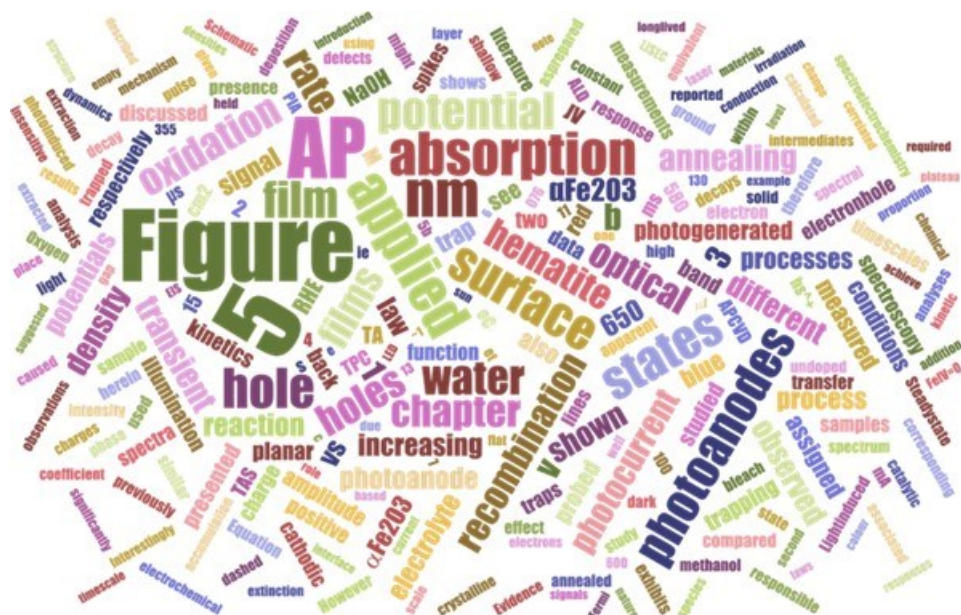
- Mater. Interfaces* **7**, 7653–7660 (2015).
35. Léger, J. M. Mechanistic aspects of methanol oxidation on platinum-based electrocatalysts. *J. Appl. Electrochem.* **31**, 767–771 (2001).
 36. Le Formal, F. *et al.* Rate Law Analysis of Water Oxidation on a Hematite Surface. *J. Am. Chem. Soc.* **137**, 6629–6637 (2015).
 37. Cummings, C. Y., Marken, F., Peter, L. M., Tahir, A. A. & Wijayantha, K. G. U. Kinetics and mechanism of light-driven oxygen evolution at thin film α -Fe₂O₃ electrodes. *Chem. Commun.* **48**, 2027 (2012).
 38. Le Formal, F. *et al.* Back Electron–Hole Recombination in Hematite Photoanodes for Water Splitting. *J. Am. Chem. Soc.* **136**, 2564–2574 (2014).
 39. Ma, Y., Le Formal, F., Kafizas, A., Pendlebury, S. R. & Durrant, J. R. Efficient suppression of back electron/hole recombination in cobalt phosphate surface-modified undoped bismuth vanadate photoanodes. *J. Mater. Chem. A* **3**, (2015).
 40. Peter, L. *Kinetics and Mechanisms of Light-Driven Reactions at Semiconductor Electrodes : Principles and Techniques. Photoelectrochemical Water Splitting: Materials, Processes and Architectures* (RCS Publishing, 2013). doi:10.1039/9781849737739-00019
 41. Mesa, C. A. *et al.* Kinetics of Photoelectrochemical Oxidation of Methanol on Hematite Photoanodes. *J. Am. Chem. Soc.* **139**, 11537–11543 (2017).
 42. Nozik, A. J. & Memming, R. Physical Chemistry of Semiconductor–Liquid Interfaces. *J. Phys. Chem.* **100**, 13061–13078 (1996).
 43. Chen, S. & Wang, L.-W. Thermodynamic Oxidation and Reduction Potentials of Photocatalytic Semiconductors in Aqueous Solution. *Chem. Mater.* **24**, 3659–3666 (2012).
 44. Wang, X. *et al.* Transient Absorption Spectroscopy of Anatase and Rutile: The Impact of Morphology and Phase on Photocatalytic Activity. *J. Phys. Chem. C* **119**, 10439–10447 (2015).
 45. Memming, R. *Semiconductor Electrochemistry*. (WILEY-VCH Verlag, 2001).
 46. Wang, C.-Y., Groenzin, H. & Shultz, M. J. Comparative Study of Acetic Acid, Methanol, and Water Adsorbed on Anatase TiO₂ Probed by Sum Frequency Generation Spectroscopy. *J. Am. Chem. Soc.* **127**, 9736–9744 (2005).
 47. Ma, Y. *et al.* Rate Law Analysis of Water Oxidation and Hole Scavenging on a BiVO₄ Photoanode. *ACS Energy Lett.* 618–623 (2016). doi:10.1021/acsenenergylett.6b00263
 48. Kafizas, A. *et al.* Water Oxidation Kinetics of Accumulated Holes on the Surface of a TiO₂ Photoanode: A Rate Law Analysis. *ACS Catal.* **7**, 4896–4903 (2017).
 49. Francàs, L., Mesa, C. A., Pastor, E., Le Formal, F. & Durrant, J. R. Rate Law Analysis of Water Splitting Photoelectrodes. in *Advances in Photoelectrochemical Water Splitting: Theory, Experiment and Systems Analysis* (eds. Tilley, S. D., Lany, S. & van de Krol, R.) in press (Royal Society of Chemistry, 2018).
 50. Bard, A. J. & Faulkner, L. R. *Electrochemical methods : fundamentals and applications*. (John Wiley & Sons, Inc., 2001).
 51. Atkins, P. *Physical Chemistry*. (Oxford University Press, 2001).
 52. Zandi, O. & Hamann, T. W. Determination of photoelectrochemical water oxidation intermediates on haematite electrode surfaces using operando infrared spectroscopy. *Nat.*

- Chem.* **8**, (2016).
53. Nakamura, R., Okamura, T., Ohashi, N., Imanishi, A. & Nakato, Y. Molecular Mechanisms of Photoinduced Oxygen Evolution, PL Emission, and Surface Roughening at Atomically Smooth (110) and (100) n-TiO₂ (Rutile) Surfaces in Aqueous Acidic Solutions. *J. Am. Chem. Soc.* **127**, 12975–12983 (2005).
 54. Howe, R. F. & Grätzel, M. EPR Study of hydrated anatase under UV irradiation. *J. Phys. Chem* **91**, 3906–3909 (1987).
 55. Inclusive Science and Engineering. Formaldehyde from Methanol Process. *Science, Engineering & Technology for Business, Research and Industries* (2012). Available at: <http://www.inclusive-science-engineering.com/formaldehyde-from-methanol-process/>. (Accessed: 16th October 2017)
 56. Millar, G. J. & Collins, M. Industrial Production of Formaldehyde Using Polycrystalline Silver Catalyst. *Ind. Eng. Chem. Res.* **56**, 9247–9265 (2017).
 57. Fermín, D. J., Ponomarev, E. A. & Peter, L. M. Dynamics of photo-processes at the n-TiO₂/aqueous electrolyte interface. in *Proceedings of the Symposium on Photoelectrochemistry* (ed. Rajeshwar, K.) **97**, (The Electrochemical Society, 1997).
 58. Zhou, C. *et al.* Site-specific photocatalytic splitting of methanol on TiO₂(110). *Chem. Sci.* **1**, 575–580 (2010).
 59. H. Schoenmakers, G., Vanmaekelbergh, D. & J. Kelly, J. The mechanism of current-doubling reactions at ZnO photoanodes. *J. Chem. Soc. Faraday Trans.* **93**, 1127–1132 (1997).
 60. Nomikos, G. N., Panagiotopoulou, P., Kondarides, D. I. & Verykios, X. E. Kinetic and mechanistic study of the photocatalytic reforming of methanol over Pt/TiO₂ catalyst. *Appl. Catal. B Environ.* **146**, 249–257 (2014).
 61. Anslyn, E. V. & Dougherty, D. A. *Modern Physical Organic Chemistry*. (University Science Books, 2006).
 62. Carlos-Cuellar, S. *et al.* Heterogeneous Uptake Kinetics of Volatile Organic Compounds on Oxide Surfaces Using a Knudsen Cell Reactor: Adsorption of Acetic Acid, Formaldehyde, and Methanol on α -Fe₂O₃, α -Al₂O₃, and SiO₂. *J. Phys. Chem. A* **107**, 4250–4261 (2003).
 63. Zigah, D., Rodríguez-López, J. & Bard, A. J. Quantification of photoelectrogenerated hydroxyl radical on TiO₂ by surface interrogation scanning electrochemical microscopy. *Phys. Chem. Chem. Phys.* **14**, 12764–12772 (2012).
 64. Micic, O. I., Zhang, Y., Cromack, K. R., Trifunac, A. D. & Thurnauer, M. C. Trapped Holes on TiO₂ Colloids Studied by Electron Paramagnetic Resonance. *J. Phys. Chem* **97**, 1211–1283 (1993).
 65. Kisumi, T., Tsujiko, A., Murakoshi, K. & Nakato, Y. Crystal-face and illumination intensity dependences of the quantum efficiency of photoelectrochemical etching, in relation to those of water photooxidation, at n-TiO₂ (rutile) semiconductor electrodes. *J. Electroanal. Chem.* **545**, 77–107 (2003).

Chapter 5. Photogenerated holes surface recombination and trapping vs. reaction: kinetic competition in $\alpha\text{-Fe}_2\text{O}_3$ photoanodes



TOC Figure



Word cloud for this *Chapter*

In this chapter, the effect of annealing an ALD synthesised hematite photoanode on recombination, trapping and hole transfer to the electrolyte is studied by means of transient absorption spectroscopy, transient photocurrent and spectro(photo)electrochemical measurements. Annealing thin, planar hematite films is shown to reduce the density of trap states and therefore reducing electron trapping processes increasing the fraction of photogenerated holes arriving to the photoanode surface. It is also shown that reaction kinetics are insensitive to the presence of such trap states, often regarded as intermediates for water oxidation, providing evidence that the accumulation of photogenerated holes at the surface is key to achieve oxygen evolution.

Most of the results of this chapter are included in these publications in preparation *“Towards a general water oxidation mechanism of reaction on hematite photoanodes”* and *“The role of surface states on the water oxidation catalysis on planar hematite photoanodes”*.

5.1. Introduction

α -Fe₂O₃ is often regarded in literature as one of the most promising photoanode materials for water oxidation. However, different nanostructures have been reported in literature for these photoanodes with efficiencies and photocurrent density values yet to be improved to reach the theoretical limit of 12.5 mA cm^{-2} for a thick and highly absorbing hematite (with $\sim 2.0 \text{ mA cm}^{-2}$ being the theoretical limit for the thin undoped hematite films used herein, using a band gap of 2.0 eV and an absorptance $\sim 30\%$).¹ Among those nanostructures, dendrites, nanoparticles, nanorods and nanotubes have been synthesised via electrochemical or chemical methods, reaching plateau current densities up to 1.5 mA cm^{-2} .^{2–5} Different chemical vapour deposition methods have delivered hematite photoanodes reaching plateau photocurrents up to 4 mA cm^{-2} with high surface areas compared to planar films producing up to 1 mA cm^{-2} .^{6–10} To study surface process on uniform and conformal films the atomic layer deposition (ALD) method is ideal as this method can deposit conformal and uniform films.

In photoelectrochemical processes in hematite, understanding the surface charge transfer from the α -Fe₂O₃ photoanode to the electrolyte is paramount to achieve high conversion yields, which was the focus of *Chapters 3 and 4*. However, the light-induced events occurring before charge transfer to the electrolyte are also key to design better photoelectrode materials for solar water splitting. These events, as explained in *Chapter 1*, start after light is absorbed, generating electron/hole (e^-/h^+) pairs. Several transient absorption spectroscopy studies have reported that in hematite these charge carriers mostly undergo recombination in ultrafast timescales (up to hundreds of picoseconds) upon high excitation intensities.^{11,12} Subsequently, slow recombination, of trapped charges already separated, takes place up to millisecond timescales. These recombination processes are recognised as one of the most important factors for poor performances in the α -Fe₂O₃ photoanodes.^{13,14} These timescales are significantly faster compared to the millisecond to second timescale of water oxidation in such photoanodes, as probed by transient absorption spectroscopy (TAS),^{15–17} electrochemical impedance spectroscopy (EIS)^{18–20} and intensity-modulated photocurrent spectroscopy (IMPS).^{21–23} At comparable timescales, $ms - s$, back electron-hole recombination processes have also been observed to be in direct kinetic comparison with hole transfer to the electrolyte.^{24,25} Note that this back electron-hole recombination process is understood herein as the recombination of bulk electrons with holes within the space charge layer. and

hence, the need of applying a positive potential to suppress such recombination. This differs to the ‘surface recombination’ process sometimes referred in literature as a recombination process assisted by surface states,^{26–28} which to certain extent had also been associated with physical defects on the hematite surface (such oxygen vacancies).²⁹

Those ‘surface states’, as introduced in *Chapter 1*, have also been regarded in literature, by low-frequency data assignment from impedance spectroscopy (EIS), to be located intraband gap and to participate as intermediates in the water oxidation catalytic cycle.^{22,30–32} However, TAS^{15,33} and more recently, light-induced spectroelectrochemistry (LI-SEC), referred in literature as photo-induced absorption spectroscopy,^{34,35} have provided evidence for hole transfer from the valence band to the electrolyte. Additionally, as discussed in *Chapter 3*, the interpretation of EIS data is not always straight forward and some of such assignments can be interpreted differently. For example, Le Formal *et. al.*,^{24,36} presented evidence of low-frequency data from EIS to correlate to back electron-hole recombination, further supported by TAS and transient photocurrent (TPC) data, using a model that does not require such surface states being directly involved either in recombination or reaction. Figure 1-1 shows a schematic illustration of these two different models. Figure 1-1.a presents schematically the model where upon hole photogeneration, they accumulate at the hematite surface and are transferred to the electrolyte from the valence band. Hole transfer to the ‘surface states’ and subsequent transfer to the electrolyte is shown in Figure 1-1.b.

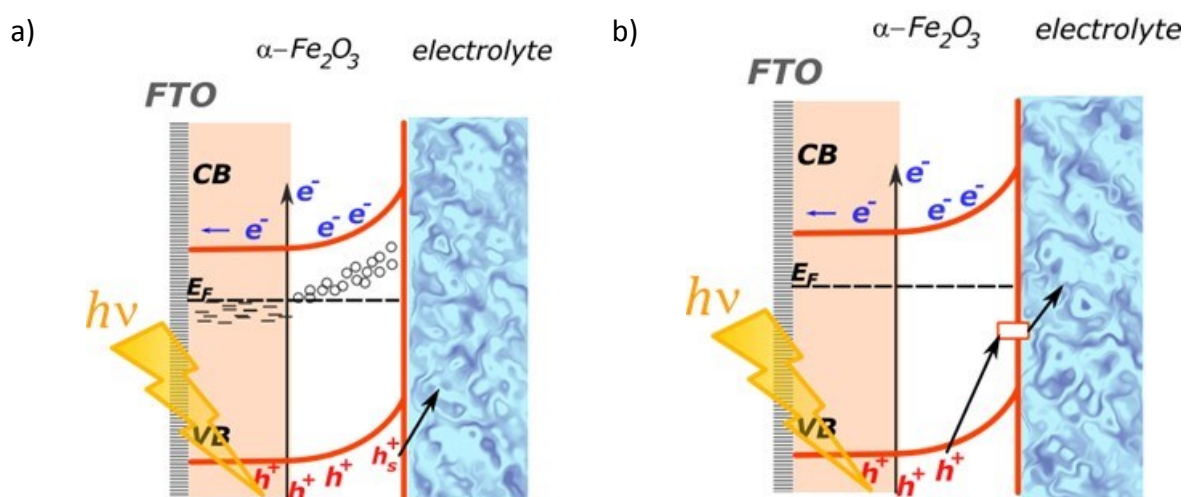


Figure 5-1. Schematic representation of the processes involving photogenerated charge carriers taking place in a hematite photoanode where a) holes are transferred to the electrolyte from the valence band and b) holes are transferred to ‘surface states’ which participate in the reaction as intermediates.

In addition to the mentioned recombination processes, TAS measurements, mainly on Si-doped hematite films, have provided evidence of a fast ($>$ nanosecond timescale) electron trapping process into shallow trap states below the conduction band. These trap states have normally been considered product of the hematite doping process.³⁷ Such traps have been shown to exhibit a characteristic positive absorption at ~ 580 nm under depletion conditions (*i.e.*, high positive applied potential) in spectroelectrochemical measurements.^{33,38} Upon illumination a ground state absorption loss is reflected in an optical bleach at ~ 580 nm in TAS spectra shown by Barroso *et. al.*^{15,33} On the other hand, these shallow traps have been suggested to mediate recombination.³⁹ Also, this spectroelectrochemical signal at 580 nm, has been assigned, supported by the already mentioned EIS data to correspond to surface states mediating water oxidation,^{21,30,40} with $\text{Fe}^{\text{IV}}=\text{O}$ as its chemical nature.⁴¹ Note that more recently, the term surface states in hematite has been more associated with photogenerated holes and reaction intermediates, although still being assigned to be intraband gap states.^{6,25,41}

Physical defects sites have been frequently related with the presence of oxygen vacancies in hematite films and at the surface and recently associated with Fermi level pinning^{6,25,42} Such defects have traditionally been controlled by the annealing process after hematite deposition. Upon iron oxide deposition, a high-temperature annealing process is normally required to achieve the desired $\alpha\text{-Fe}_2\text{O}_3$ crystalline structure. However, the annealing temperature also plays an important role removing oxygen vacancies or improving the interface between the underlying FTO contact layer and the photoactive material.⁴³ This annealing process has suggested to be also responsible for the passivation of states energetically located within the bandgap. For example, Wang and co-workers⁵ have shown that 800 °C annealing reduces surface defects leading to smaller required overpotentials. Zandi and Hamann,⁴² have proposed, for un-doped ALD $\alpha\text{-Fe}_2\text{O}_3$ photoanodes, the presence of two different, shallow (just below the conduction band) and mid band gap, types of surface traps. The authors propose that upon annealing at 800 °C the shallow states are passivated, and only mid band-gap states remain present in the film, assigning them, as introduced previously to reaction intermediates. As such, the effect of this annealing process on the dynamics of photogenerated holes is studied in this *Chapter*. For this purpose, two planar and relatively non defective $\alpha\text{-Fe}_2\text{O}_3$ photoanodes synthesised at different annealing conditions

are compared. The role of the states removed upon annealing is investigated, and in particular their role in the water oxidation reaction.

5.2. Experimental

5.2.1. Samples

In this chapter, two planar α -Fe₂O₃ photoanodes are studied, one as-prepared (AP) film after ALD deposition at 230 °C and the second film underwent annealing (AN) at 600 °C, after the ALD deposition, as detailed in *Chapter 2*. These two films were prepared and kindly provided by Dr. Ludmilla Steier (École Polytechnique Fédérale de Lausanne). These films contained an ALD deposited TiO₂ underlayer that induces doping (in very thin, few nm, films) and works as a hole blocking layer, *i.e.* it helps preventing holes near the hematite/FTO interface from recombining with electrons that have been extracted to the FTO.^{10,44,45} These ALD films were synthesised phase pure and crystalline, with thickness of ~ 20 nm, a charge carrier concentration (unaffected by the TiO₂ underlayer due to the film thickness), N_D , of $\sim 3 \times 10^{19} \text{ cm}^{-3}$. This N_D was measured by electrochemical impedance spectroscopy corresponding to a maximum space charge layer width, W_{SC} , of ~ 11 nm.

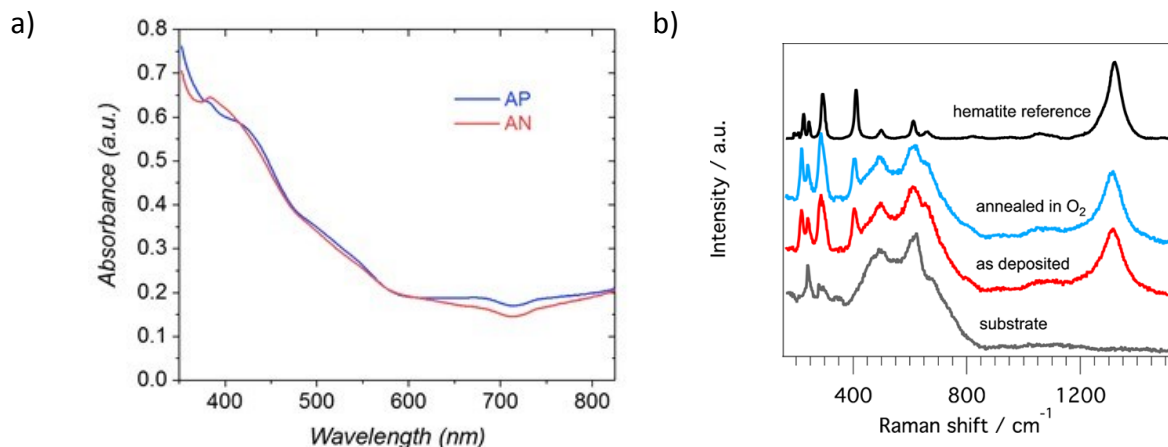


Figure 5-2. Characterisation of the hematite photoanodes employed herein, a) UV-Vis absorption spectra of the as-prepared (blue) and annealed (red) α -Fe₂O₃ photoanodes in 1 M NaOH and b) Raman spectra of both, the AP (red) and AN (blue), α -Fe₂O₃ photoanodes compared to a reference hematite spectrum and the FTO/TiO₂ substrate. This image is from the reference.¹⁰

A high temperature annealing can change a number of properties within a metal-oxide photoanode such as the crystalline structure and the oxygen vacancy content. However, from the measured UV-Vis spectra, see Figure 5-2.a, and the reported Raman spectra¹⁰ (see Figure 5-2.b), it can be concluded that these high crystalline films are hematite phase-pure and do not undergo phase transitions by the 600 °C annealing process.

5.2.2. (Photo)electrochemical response

In this chapter, the electrochemical and photoelectrochemical (PEC) performances of the two planar $\alpha\text{-Fe}_2\text{O}_3$ photoanodes, were evaluated by current-potential (J - V) responses under dark and ~ 1 sun illumination conditions. A 365 nm LED was used as illumination source for the experiments presented in this *Chapter*, as detailed in *Chapter 2* previously. The J - V responses of the studied photoanodes were evaluated first in 1 M NaOH electrolyte and subsequently in a hole scavenger solution (a solution of 95 % CH_3OH in 0.1 M NaOH).

5.2.3. Transient absorption spectroscopy and transient photocurrent

Recombination kinetics were studied by means of transient absorption (TA) spectroscopy, equipment described in *Chapter 2*, in a PEC cell, using a Pt mesh as counter electrode and Ag/AgCl as reference electrode, at different applied potentials using 1M NaOH as electrolyte. A 355 nm, 6 nm width pulse from a Nd-YAG laser was used as illumination source at $130 \mu\text{J cm}^{-2}$ irradiation intensity and a pulse rate of 0.3 Hz. Charge carrier dynamics were probed at wavelengths ranging from 550 to 800 nm. Hole and trapped states kinetics were probed at 650 and 580 nm respectively.¹⁵ Concomitantly with TA, charge extraction was studied by means of transient photocurrent measurements. This time resolved photocurrent measurements were performed in the same apparatus as for the TA measurements as described in *Chapter 2*.

5.2.4. Rate law analysis

Light-induced spectroelectrochemistry (LI-SEC) was used to study the water oxidation rate law analyses. As described in *Chapter 2*, these rate laws were performed as a function of a 365 nm LED illumination intensity, therefore as a function of surface hole density. Photoinduced absorption (PIA) and transient photocurrent (TPC) responses of the photoanodes were measured in 1 M NaOH for both films. The photoanodes were held at different applied potentials (1.15, 1.3 and 1.5 V vs RHE) to study possible competition between surface recombination and water oxidation.

5.3. Results

5.3.1. (Photo)electrochemical response

The electrochemical response in dark and under chopped light (J - V) conditions of the two, as-prepared (AP) and annealed (AN), films are shown in Figure 3-3.

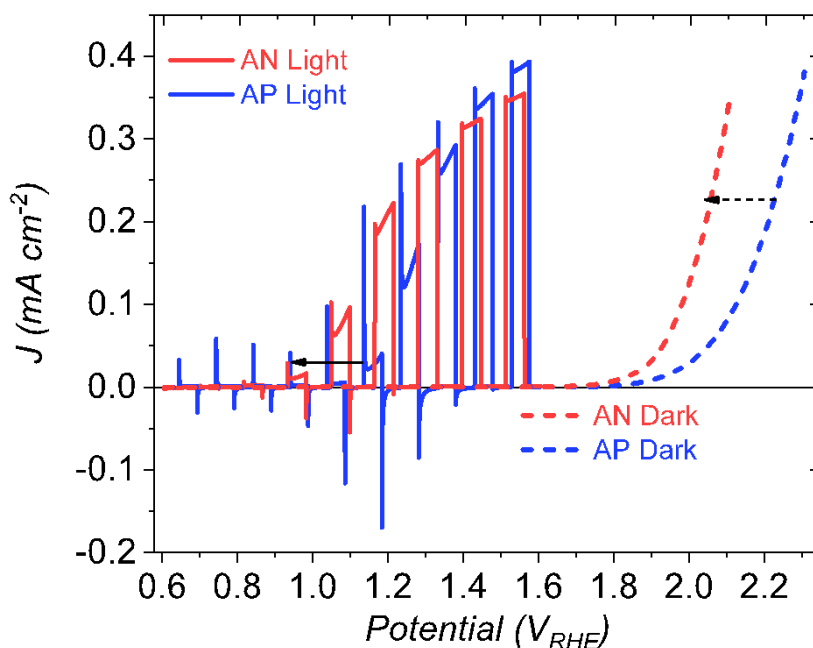


Figure 5-3. Current/potential (J - V) response of the planar α - Fe_2O_3 photoanodes, AN (red) and AP (blue), under dark (dashed lines) and chopped ~ 1 sun front illumination (electrode/electrolyte) conditions (solid lines) measured in 1 M NaOH electrolyte. The arrow indicates the ~ 200 mV shift in both, dark current and photocurrent potentials after annealing.

From Figure 3-3 it is apparent that the 600 °C annealing process causes a shift in both photocurrent and dark current onset (solid and dashed arrows in Figure 3-3, respectively) of ~ 200 mV towards more negative potentials, as reported previously by Steier *et. al.*¹⁰ A similar shift has been observed for a number of hematite films upon annealing processes at different temperatures ranging from 500 – 1000 °C and has been assigned to the elimination of some surface defects. Such defects have commonly been associated with oxygen vacancies or with the crystalline structure, as explained in the introduction, which are hypothesised to be responsible for partial Fermi level pinning.^{3,5,42,46,47} From this figure a smaller intensity of the cathodic spikes, up to ~ 1.5 V in the J - V , can also be observed in the annealed film (AN) compared to the as-prepared one (AP). These cathodic spikes have been previously assigned to back electron-hole recombination processes that compete with water oxidation as they take place in the same timescales, within the ms – s timescale.²⁴ Such back electron-hole recombination is known to stop on increasing the applied potential, but also could be overcome if the hole transfer to the electrolyte is faster (as discussed in *Chapter 4*). As such, methanol was used as hole scavenger to further examine this type of recombination on planar α - Fe_2O_3 photoanodes.

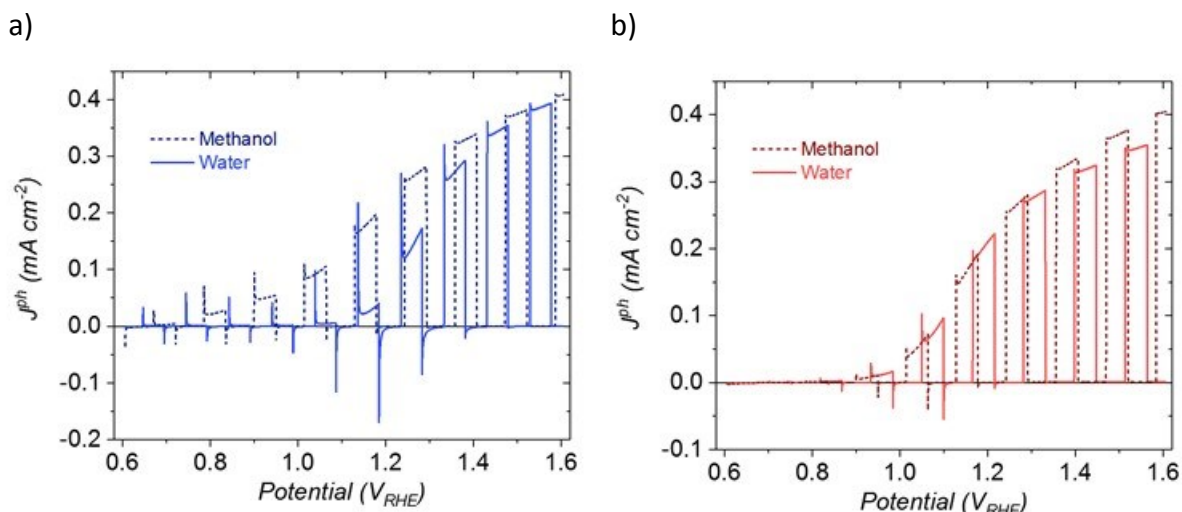


Figure 5-4. Photocurrent/potential (J^{ph} - V) response of the planar α - Fe_2O_3 photoanodes under ~ 1 sun front illumination (electrode/electrolyte) conditions measured in 1 M NaOH (solid lines) and with a hole scavenger, 95% CH_3OH in 1 M NaOH (dashed lines). a) AP (blue) and b) AN (red) samples.

Figure 5-4 shows the different effect in the J - V curves for both the AP (Figure 5-4.a) and AN films (Figure 5-4.b), respectively. Upon addition of methanol it is apparent from Figure 5-4.a that the back electron-hole recombination exhibited by the AP photoanode is significantly suppressed. On the contrary, for the AN sample, the addition of methanol does not reduce the magnitude of the cathodic spikes, which might suggest that other hole consuming process (*i.e.*, trapping or recombination) are potentially taking place in a faster timescale than methanol oxidation. Such fast hole consuming processes can be studied by means of transient absorption spectroscopy. This study is presented in the following section.

5.3.2. Transient absorption spectroscopy and transient photocurrent

To investigate charge carrier recombination and extraction processes, TAS and TPC were performed under different applied potentials. This allowed the evaluation of the effect of changing the Fermi level in the films before and after annealing.

Figure 5-5 shows the TA spectral fingerprint at two different timescales for both films. At low applied potentials (0.76 V vs RHE). Figure 5-5.a shows that both, AP and AN, films exhibit a small ground state bleach peaking ~ 580 nm and a positive absorption whose peak centres at ~ 650 nm at fast timescales (up to 100 μs), which decays before 100 ms. The 580 nm negative signal has previously been assigned¹⁶ to the loss of ground state absorption caused by the refilling of shallow trap states below the conduction band. This process is bias dependent as more shallow traps are available with increasing the band bending, reflected in a growth of the bleach amplitude (compare Figure 5-5 a and b, dashed lines). This is due to

an increased density of shallow states acting as electron traps in both samples. Additionally, the 650 nm positive signal has been assigned, in *Chapter 3* in this thesis and elsewhere, to photogenerated holes absorption.^{15,16,33–35} When the applied potential is increased from 0.76 to 1.50 V vs RHE (see Figure 5-5.b), the amplitude of this optical feature increases at all timescales, for both the AP and the AN photoanodes, as expected for an increase of the space charge layer. This increase in amplitude indicates a reduction in recombination processes.³³

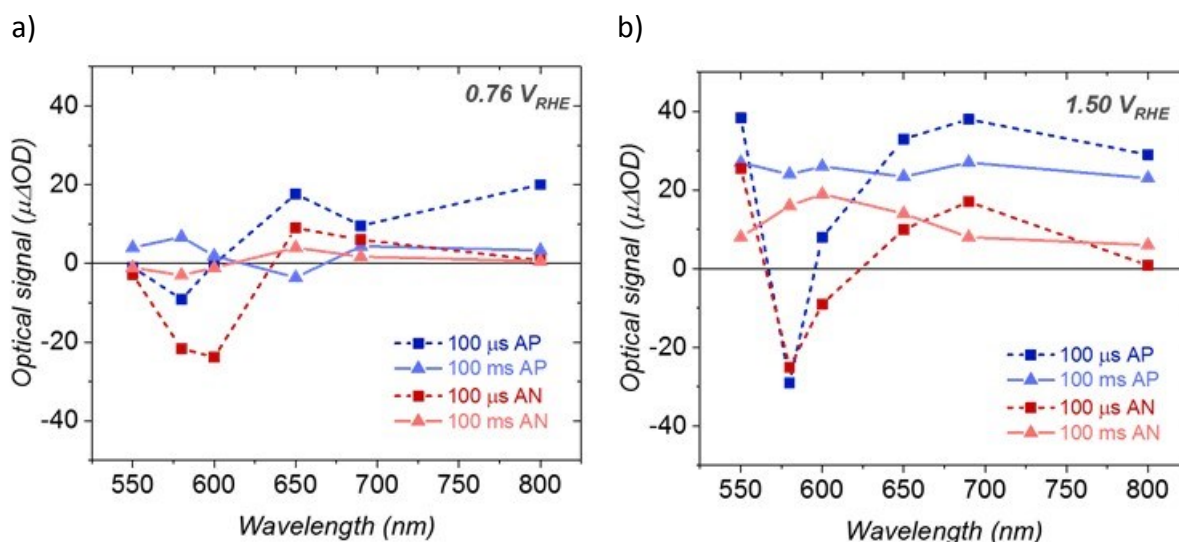


Figure 5-5. Transient absorption spectral response measured 100 μ s (squares and dashed lines) and 100 ms (triangles and solid lines) after a 130 μ J cm^{-2} 355 nm laser pulse, of the planar, AP (blue) and AN (red), α -Fe₂O₃ photoanodes at a) 0.76 V and b) 1.50 V vs RHE, respectively in 1 M NaOH electrolyte.

The long-lived (100 ms) spectra, when the potential is highly oxidative (see triangles and solid lines in Figure 5-5.b) are different between both AP and AN samples. The annealed sample (red) exhibits a spectrum that peaks at ~ 600 nm, resembling that for an APCVD α -Fe₂O₃ film shown in *Chapter 3*. Interestingly the spectrum of the as-prepared sample (blue) exhibits a flat flattened or levelled spectrum. This is assigned, and further confirmed by steady-state photoinduced absorption (PIA) optical measurements in the rate law analyses section, to a second absorption peak around ~ 700 nm.

Before further confirming the second light-induced absorption peak observed at 100 ms with the AP photoanode held at 1.5 V, the transient decays of the observed species are compared. Firstly the 650 nm positive absorption is explored, in Figure 5-6, followed by the 580 nm ground state bleach in Figure 5-7.

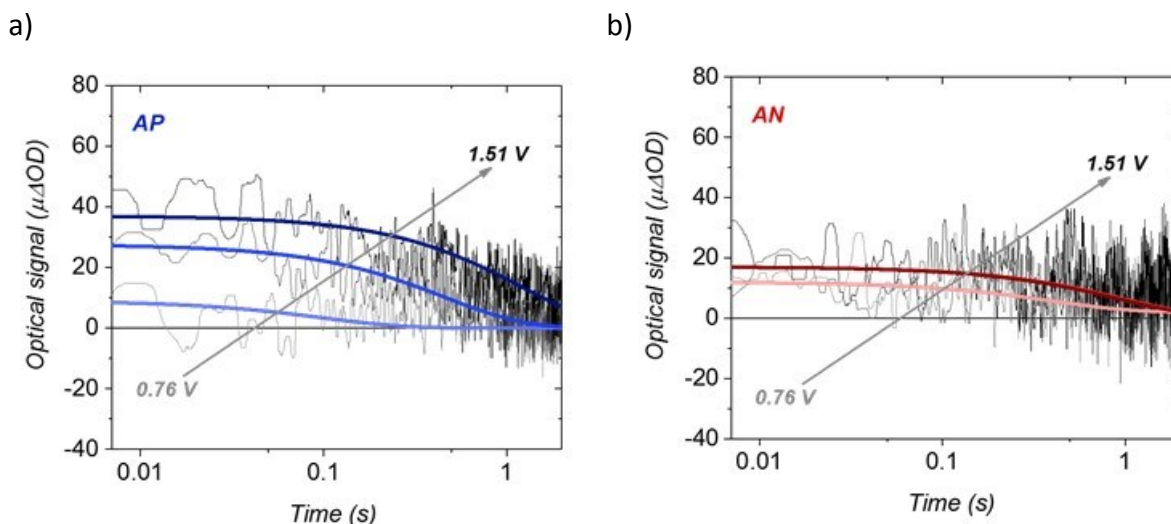


Figure 5-6. Transient absorption decays probed at 650 nm after a $130 \mu\text{J cm}^{-2}$ 355 nm laser pulse, of the planar $\alpha\text{-Fe}_2\text{O}_3$ photoanodes in 1 M NaOH electrolyte as a function of a positive applied potential, 0.76, 1.16 and 1.51 V vs RHE (increasing grey scale). a) AP and b) AN samples respectively. The solid lines (increasing colour scale) indicate the single exponential fit.

Figure 5-6.a and b, show the decay kinetics of the photogenerated hole absorption (probed at 650 nm) for both the AP and AN samples upon increasing applied potential. For both films no power law decays are observed at any applied potential. This is indicative of the absence of bimolecular recombination processes taking place within this $\mu\text{s} - \text{s}$ timescale.⁴⁸ In addition to that, in literature TA dynamics, decaying with single exponential kinetics have been assigned to the hole transfer kinetics to the electrolyte,^{15,48,49} As such, the observed TA signal in Figure 5-6.a and b were fitted to single exponential decays. From the fittings (solid lines in Figure 5-6.a and b), despite the similitudes between both samples, it is apparent that the TA signal for the AN film reaches a maximum amplitude at an earlier applied potential than that for the AP film. This correlates with the photocurrent arriving to plateau conditions $\sim 200 \text{ mV}$ earlier for the AN $\alpha\text{-Fe}_2\text{O}_3$ sample (see Figure 3-3). Another interesting observation is that the fitted single exponential time constants, upon increasing the applied potential, for the AP sample has a larger increase than that for the AN sample.

Figure 5-7 shows the TA kinetics of the ground state bleach decays as a function of applied potential in both, the AP and AN $\alpha\text{-Fe}_2\text{O}_3$ films, probed at 580 nm. This transient decay has been assigned to the loss of ground state absorbance caused by shallow traps near the conduction band.^{15,17} For both, AP and AN films, it is apparent that the transient signal decays within tens of μs . Additionally, the AP photoanode (Figure 5-7.a), exhibits a second and longer-lived decay phase at 580 nm. The amplitude of this transient bleach increases upon

increasing the applied potential suggesting that it corresponds to states available only under depletion conditions. Interestingly, this transient optical signal, which decays within $\sim 500 \mu\text{s}$, disappears upon annealing (compare with Figure 5-7.b).

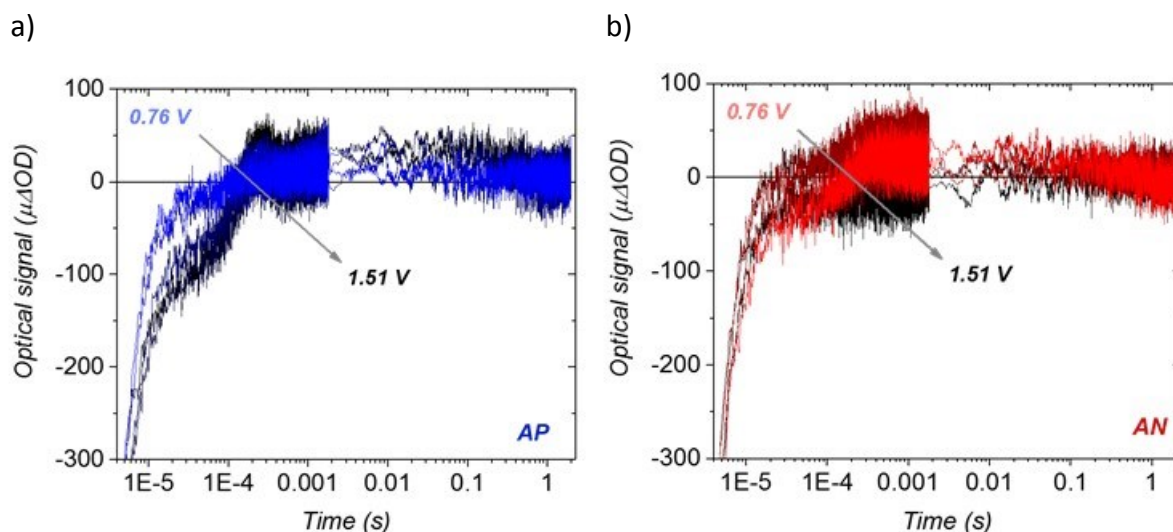


Figure 5-7. Transient absorption decays probed at 580 nm after a $130 \mu\text{J cm}^{-2}$ 355 nm laser pulse, of the planar $\alpha\text{-Fe}_2\text{O}_3$ photoanodes in 1 M NaOH electrolyte as a function of a positive applied potential, 0.76, 1.16 and 1.51 V vs RHE (increasing colour scale). a) AP (blue) and b) AN (red) samples respectively.

To further study the presence of these states that are significantly reduced upon annealing, the transient photocurrent (TPC) was measured concomitant with TAS as a function of applied potential. The TPC responses of both the AP and AN films are shown in Figure 5-8. It can be observed in this figure that the TPC (*i.e.*, electron extraction) peaks at $\sim 60 \mu\text{s}$ in both samples, most likely due to the similar film thicknesses ($\sim 20 \text{ nm}$). However, the AP photoanode (Figure 5-8.a) exhibits a cathodic spike at $\sim 300 - 400 \mu\text{s}$ that increases upon increasing the applied potential. These cathodic spikes are understood as the return of electrons from the external circuit to the film.²⁴ A similar process, detailed in the introduction, was described by Le formal *et. al.*,^{24,50} where similar cathodic spikes were assigned to back electron-hole recombination processes. However, opposite to the observations herein, back electron-hole recombination is reduced upon increasing the applied potential. This suggests that the observed potential dependant cathodic spikes in the AP film could be related to states that depopulate upon increasing the band bending and might act as electron traps.

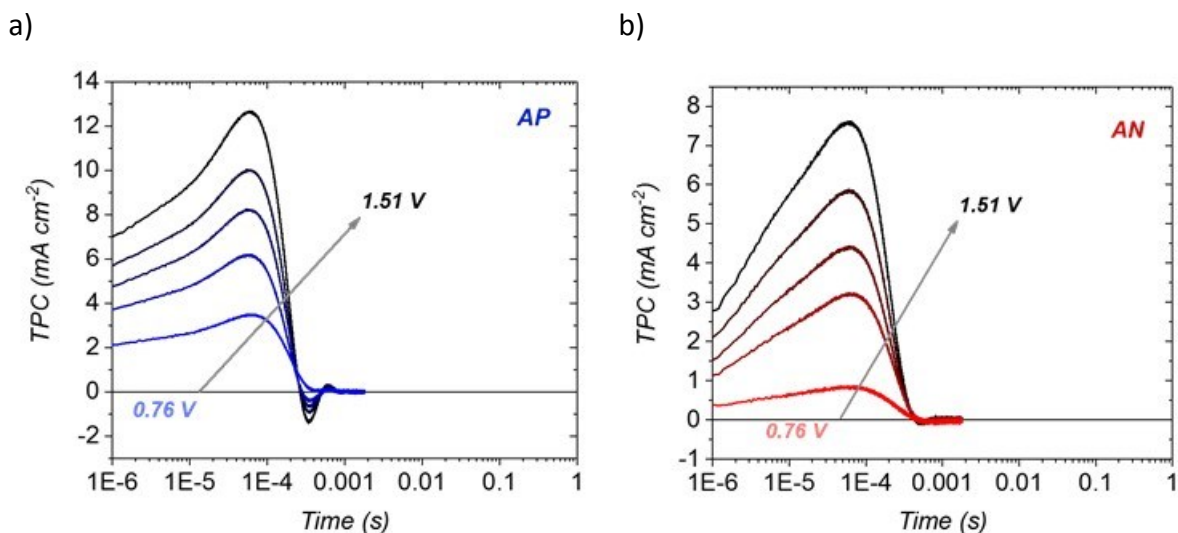


Figure 5-8. Transient photocurrent measurement after a $130 \mu\text{J cm}^{-2}$ 355 nm laser pulse, of the planar $\alpha\text{-Fe}_2\text{O}_3$ photoanodes in 1 M NaOH electrolyte as a function of a positive applied potential, from 0.76 to 1.51 V (colour scale) vs RHE for the a) AP (blue) and b) AN (red) samples respectively.

The observed cathodic spikes in the AP photoanode (Figure 5-8.a) occurs in a timescale analogous to the long-lived decay phase observed in TAS probing at 580 nm (Figure 5-7.a). Interestingly, both, TAS and TPC, discussed signals increase in magnitude upon increasing the applied potential and are significantly suppressed when the film is annealed. These states, not present in the AN sample, could be therefore, the responsible for the flattening of the TA spectral fingerprint of the AP film shown in Figure 5-5.b. The presence of such states under continuous (5 s On / 5 s Off) illumination conditions (*i.e.*, quasy steady-state) is further studied by photo-induced absorption spectroscopy.

Figure 5-9 shows the PIA absorption spectra of both AP and AN $\alpha\text{-Fe}_2\text{O}_3$ films under ~ 1 sun illumination conditions at different applied potentials. It is apparent from Figure 5-9.a that both spectra peak ~ 600 nm, similar to the absorption maxima found for the APCVD $\alpha\text{-Fe}_2\text{O}_3$ film shown in Chapter 3, suggesting similarities in the nature of the accumulated surface holes. However, interesting differences between the AP and An spectra are observed: (1) the AP film exhibits a wider spectrum than that for the AN film, coinciding with the TAS spectra shown in Figure 5-5 and (2) the overall absorption spectrum of the AP film is $\sim$ two fold larger than that for the AN film (see Figure 5-9.a, inset).

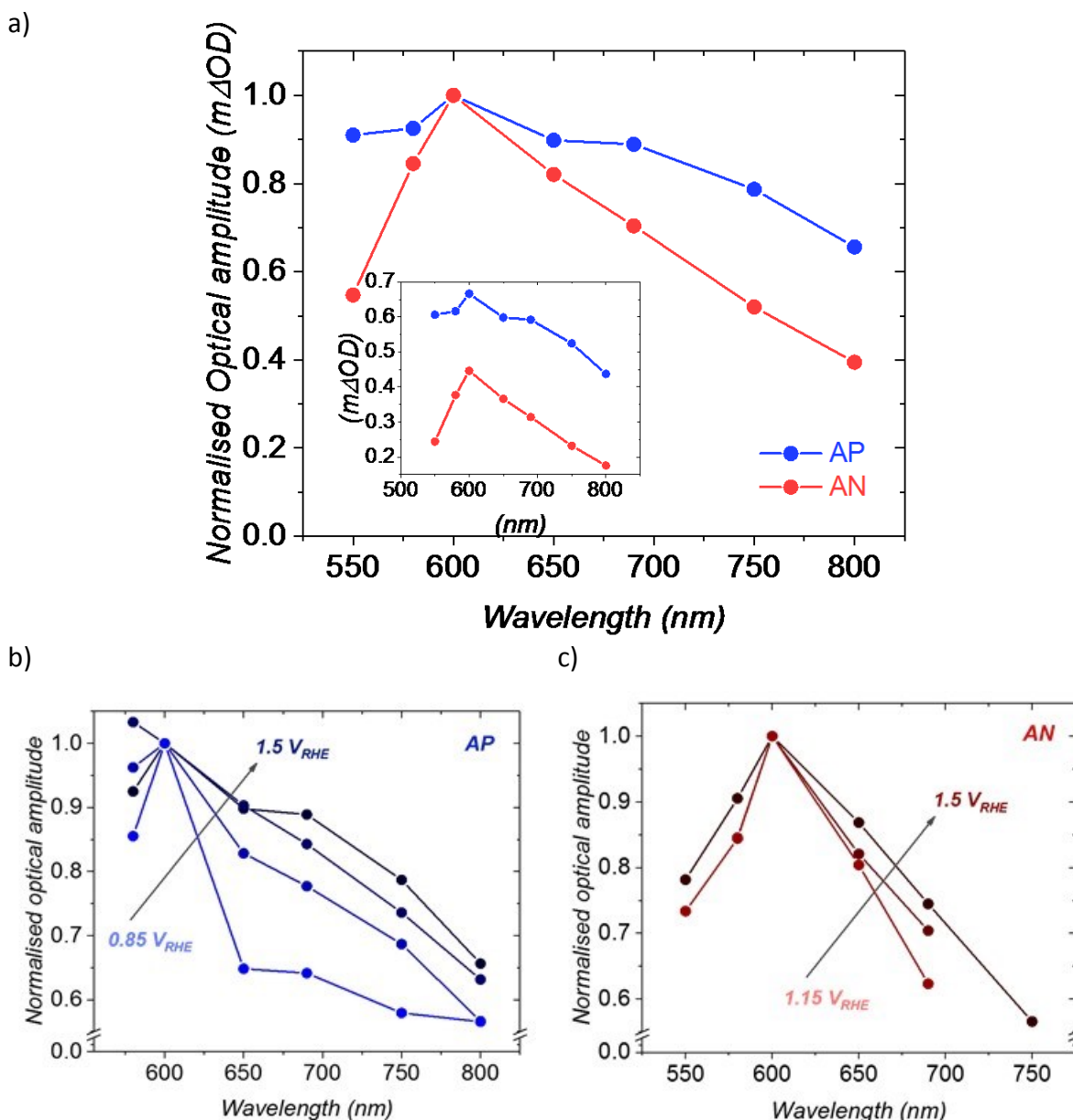


Figure 5-9. Normalised steady-state spectral response, measured ~ 5 s after a 16 mW cm^{-2} 365 nm LED continuous illumination pulse. a) $\alpha\text{-Fe}_2\text{O}_3$ photoanodes held at 1.50 V vs RHE of the planar, AP (blue) and AN (red), b) AP (blue) and c) AN (red) spectral response as a function of the applied potential from 0.8 to 1.5 (colour scale) V vs RHE, respectively in 1 M NaOH electrolyte.

The spectral fingerprints of the AP and AN $\alpha\text{-Fe}_2\text{O}_3$ photoanodes as a function of the applied potential is presented in Figure 5-9.b and c. It is evident, from comparing the figures, that (1) the absorption spectrum shape of the AP film depends on the applied potential whereas the AN is bias insensitive and (2) upon increasing the applied potential the AP film exhibits an increasing broad absorption band peaking $\sim 700 \text{ nm}$.

The observed difference in both spectra can, most obviously, be assigned to the annealing process, which can reduce defects associated with trap states as detailed in the introduction.

As such in AP hematite photoanodes, these states occur to deplete upon increasing the band bending causing a relatively long-lived decay phase observed in TAS (Figure 5-5.b) and a subsequent a positive absorption (Figure 5-9.b). Such states appear to be correlated with a cathodic electron flow (Figure 5-8.a) tentatively assigned to a ‘back electron trapping’ process. To further study the effect of the presence of these states under water oxidation catalytic conditions, light-induced spectroelectrochemistry (LI-SEC) was used to build rate law analyses under different conditions of applied potentials. These results are finally compared with the mechanistic analysis of water oxidation on APCVD α -Fe₂O₃ photoanodes in *Chapter 3*.

5.3.3. Rate law analysis

Before undertaking the rate law analysis as a function of the applied potential, the calibration of the hole signal is considered (measured at 650 nm), *i. e.* hole extinction coefficient calculation (see Figure 5-10), similarly to *Chapter 3*. Given the similarities between the photogenerated holes spectra of the AN, AP and the APCVD (shown in *Chapter 3*) hematite films, it is expected that the AP and AN samples exhibit comparable hole extinction coefficients. To confirm this, the hole extinction coefficient of the AP film was measured, following an experimental procedure reported by Le Formal *et. al.*³⁴ The AP photoanode was held at 0.85 V vs RHE, where no catalytic currents are observed and all the photogenerated holes recombine with the electrons from the conduction band. At this applied potential trap states are not expected to contribute to the hole optical signal as they are still filled.

Figure 5-10.a shows the kinetics of hole accumulation at the surface upon illumination and their decay once the light has been turned off. A concomitant TPC (Figure 5-10.b) measurement shows that all the charges extracted recombine with the accumulated holes. Therefore, the amount of charges extracted can be correlated with the steady-state optical signal (see Figure 5-10.c) giving rise to a relationship of $1 \text{ m}\Delta OD = 8.5 \text{ h}^+ \text{ nm}^{-2}$, similar to that for an APCVD film ($9.3 \text{ h}^+ \text{ nm}^{-2}$), equivalent to a hole extinction coefficient of $700 \text{ M}^{-1} \text{ cm}^{-1}$ for the AP sample compared to the $640 \text{ M}^{-1} \text{ cm}^{-1}$ reported for an APCVD film.³⁴

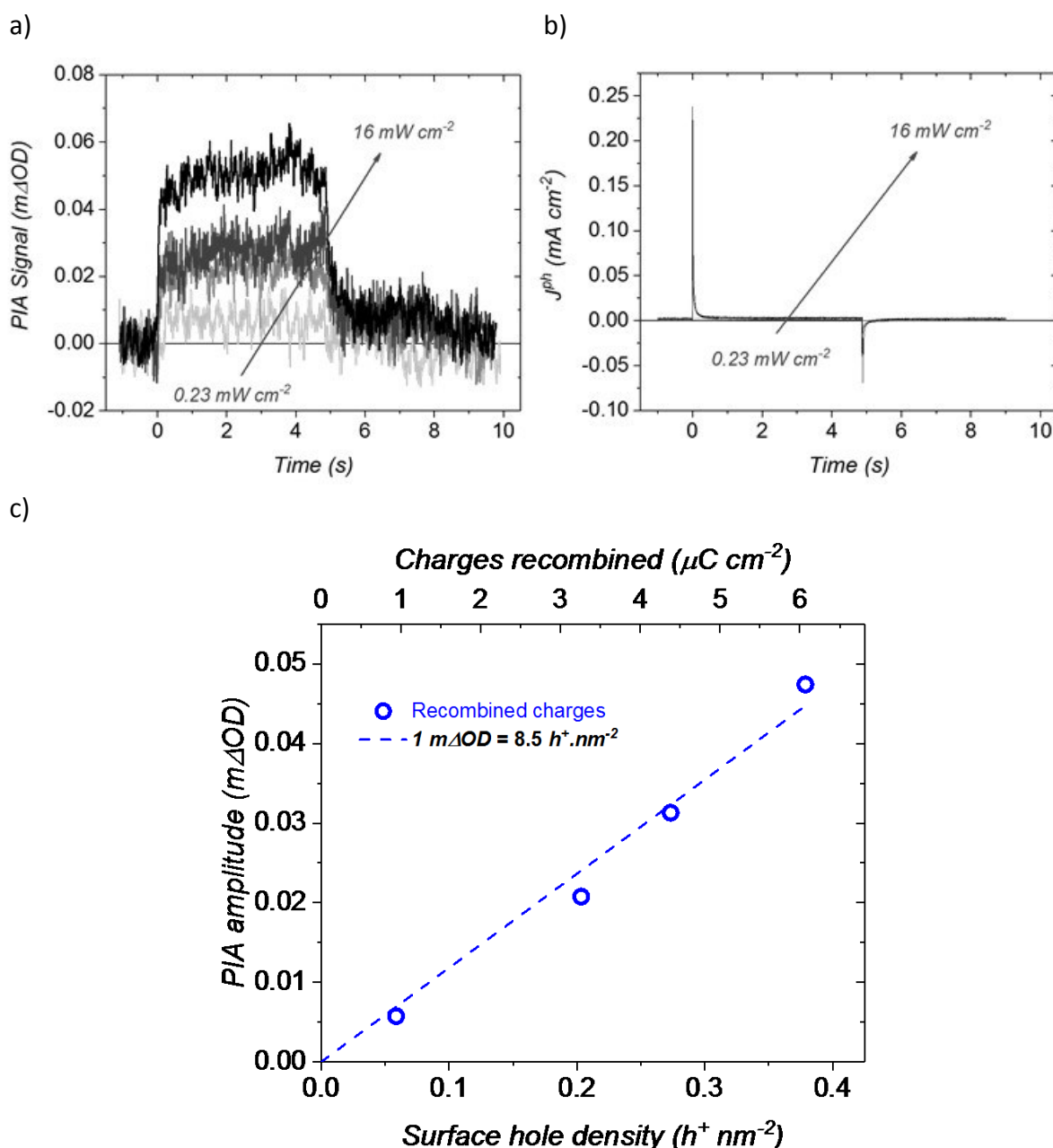


Figure 5-10. Photogenerated hole optical absorption calibration. a) PIA signal of the accumulated holes at the α -Fe₂O₃ surface monitored at 650 nm during the 5 s ON/5 s OFF pulsed 365 nm LED illumination at 0.85 V vs RHE, b) transient photocurrent density produced by the initial extraction and subsequent surface electron-hole recombination of the extracted charges and c) correlation between the recombined charges and the steady-state optical absorption measured at 650 nm and 0.85 V vs RHE as a function of light intensity, leading to a hole extinction coefficient of 700 M⁻¹cm⁻¹.

Light-induced absorption spectroelectrochemistry (LI-SEC) was used to study the mechanism and kinetics of the water oxidation reaction based on the mechanistic analysis in Chapter 3. Rate law analyses (see Figure 5-11) were undertaken at different applied potentials to explore the effect of the states tentatively assigned to trap states. The optical signals and TPC data is shown in the appendix.

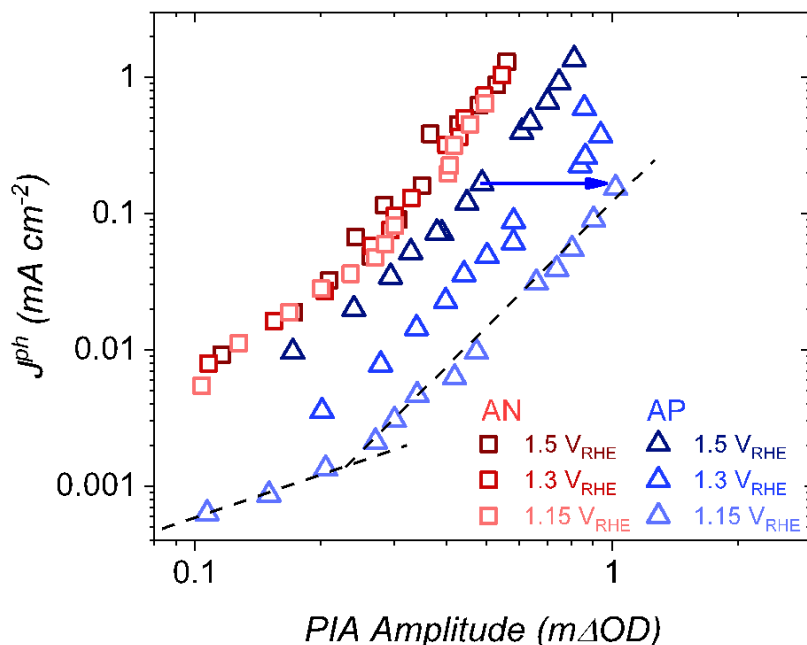


Figure 5-11. Photocurrent density (J^{ph}) vs. photoinduced absorption signal, probed at 650 nm, as a function of irradiation intensity at steady-state conditions for the water oxidation reaction on the AP (blue triangles) and AN (red squares) flat α -Fe₂O₃ photoanodes at different applied potentials. The dotted lines correspond the fitting for the 1st and 3rd reaction orders discussed in Chapter 3. The arrow indicates the increasing irradiation intensity needed to produce the same photocurrent upon decreasing the applied potential as more states are filled available to trap holes.

Figure 5-11 shows the log-log plot of the photocurrent density vs the 650 nm optical amplitude as a function of light intensity, at different applied potentials for both, the AP and AN, samples. It is apparent from this figure that all the rate laws exhibit a gradient of ~ 3 from an optical amplitude of ~ 0.2 m ΔOD . This is consistent with the 3rd order reaction mechanism that water oxidation undergoes in some of the most studied metal-oxide photoanodes discussed in Chapter 3, including an APCVD α -Fe₂O₃ film. The 1st order mechanism observed and discussed in Chapter 3, it is observed only for the lowest potential applied to the AP film.

It can also be observed in Figure 5-11 that the rate law data from the AN sample is independent of the applied potential, implying that the oxidation of water would occur with the same rate constant at the working range of potentials. This striking observation of surface holes reacting with virtually identical rate constants independent of the applied potential (*i.e.*, the ΔG for hole transfer does not change with the photovoltage), was also presented for the oxidation of methanol in Chapter 4.

On the contrary, the rate law analysis on the AP photoanode exhibits an applied potential dependence. It is apparent for this film that to reach the same photocurrent density, a higher

optical signal (*i. e.* higher surface hole density) is required upon reducing the applied potential (shown by the blue arrow in Figure 5-11). This observation is consequent with the increasing spectral absorption presented in Figure 5-9.b, upon increasing the positive applied potential, tentatively assigned to trap states. As such the presence of these states might cause the trapping of a fraction of the photogenerated electrons, increasing the amplitude of the optical signal (650 nm) assigned to photogenerated holes. At low applied potentials, such states might act as hole traps, reducing the surface hole density available for water oxidation. In consequence, to calculate the rate constant of water oxidation on the AP film the proportion of 'water oxidation optical signal' (*i. e.* density of holes that arrive to the surface and do reaction) needs to be extracted from the probed 650 nm optical amplitude. This will be addressed in the discussion section.

5.4. Discussion

Two planar and crystalline, undoped α -Fe₂O₃ photoanodes are studied in this *Chapter*, one as-prepared (AP) at 230 °C and the other is an equivalent film, but annealed at 600 °C (AN). The results presented herein have shown that the annealing process suppresses a 'back electron trapping' process evidenced by TPC measurements. The suppression of 'back electron trapping' is correlated with a significant reduction of trap states, observed by TAS and PIA measurements. Such traps, correlated with the cathodic spikes in the *J-V* curves, in the AP photoanode appear to be depleted upon increasing the applied potential. These traps seem to be responsible for a 'parasitic' photoinduced absorption when converting the PIA signal into surface hole density. Therefore, this increased density of traps at high applied potentials seems to be responsible for the unexpected dependence of the rate law data to the applied potential. As such, the discussion is organised as follows: (1) the evidence to assign the presented observations to trap states followed by (2) the rate law analysis.

5.4.1. Evidence of trap states competing with hole accumulation

The effect of the annealing process at 600 °C in the studied flat α -Fe₂O₃ photoanodes was evidenced in the *J-V* response (shown in Figure 3-3) in two ways, (1) the dark current and photocurrent onset potential shift of ~200 mV to more negative potentials and (2) the reduction in the cathodic spikes. Interestingly the plateau photocurrents produced by both films were almost identical. This might be consequence of the similar photovoltage (~0.9 V) exhibited by both the AP and AN films (with the photovoltage taken as the difference between

the onset potential for dark and photocatalysis).² Similar shifts in the dark current upon annealing have been observed previously in literature for hematite photoanodes. It has been hypothesised, that this effect could be caused by partial band edge unpinning due to the removal of surface states (states assigned also, arguably, to take part in the catalysis of water oxidation).^{3,5,25,42,46} It is important to note here that the observations presented in this *Chapter* consider the presence of states across the whole film, not only the surface, and their role in trapping and catalytic processes is the focus of this *Chapter*. An alternative explanation of the improvement in the J - V response of hematite photoanodes upon annealing has been proposed by Kronawitter *et. al.*⁴⁷ They used soft X-Rays absorption spectroscopy to propose that, at least in part, such improvement is caused by a better FTO/ α -Fe₂O₃ interface. Turning now to discuss the transient absorption data presented herein, the positive TA signals, probed at 650 nm, shown in Figure 5-6 were fitted based on literature assignments and were associated to the kinetics of hole transfer to the electrolyte.^{15,16,48,49,51}

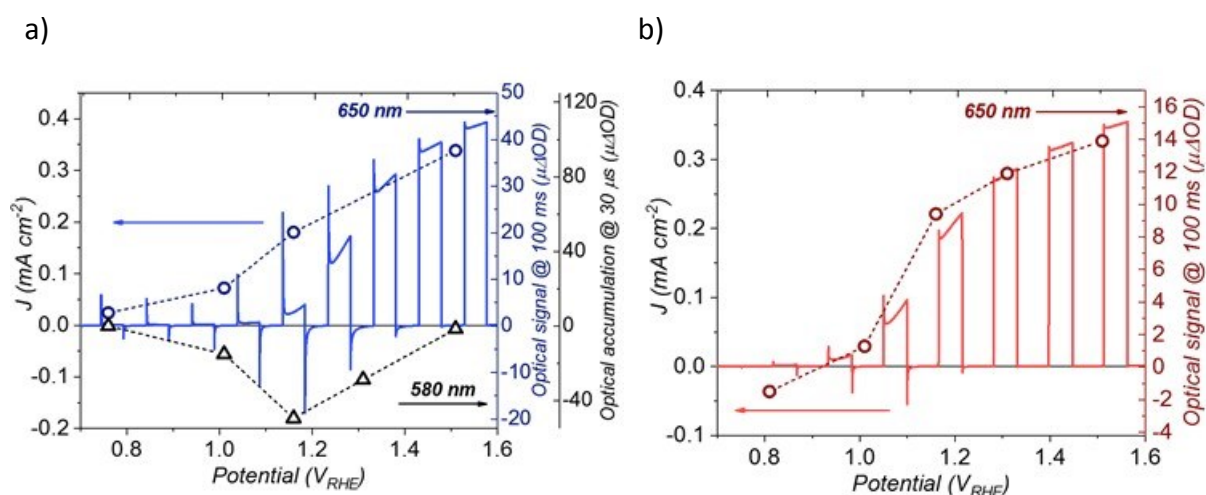


Figure 5-12. Correlation between the photocurrent-potential (J^{ph} - V) behaviour, in 1 M NaOH electrolyte, with the optical amplitude, measured at 100 μ s, of the photogenerated holes measured at 650 nm of both, a) AP (blue) and b) AN (red) α -Fe₂O₃ photoanodes. Additionally, for the AP (blue) photoanode it is shown the differential absorption ($\Delta \Delta OD$), measured at 30 μ s, corresponding to the trapped charges observed optically at 580 nm shown in Figure 5-7.a and electrically in Figure 5-8.

These long-lived photogenerated holes have been shown to be required to drive water oxidation.^{14,16,17,35} As such, the TA optical amplitude of the hole absorption, probed at 650 nm and measured at 100 ms, is shown in Figure 5-12. For the AN photoanode, the TA amplitude (empty red circles in Figure 5-12.b) tracks the J - V curve whereas the TA amplitude of the AP film (empty blue circles in Figure 5-12.a) appears to track the anodic spikes of the J - V . This

observation along with the larger TA amplitude to achieve similar photocurrent densities ($\sim 0.3 \text{ mA cm}^{-2}$) exhibited by the AP $\alpha\text{-Fe}_2\text{O}_3$ sample suggest that the 650 nm optical signal might be superimposed with the trap states broad absorption observed in Figure 5-5.b.

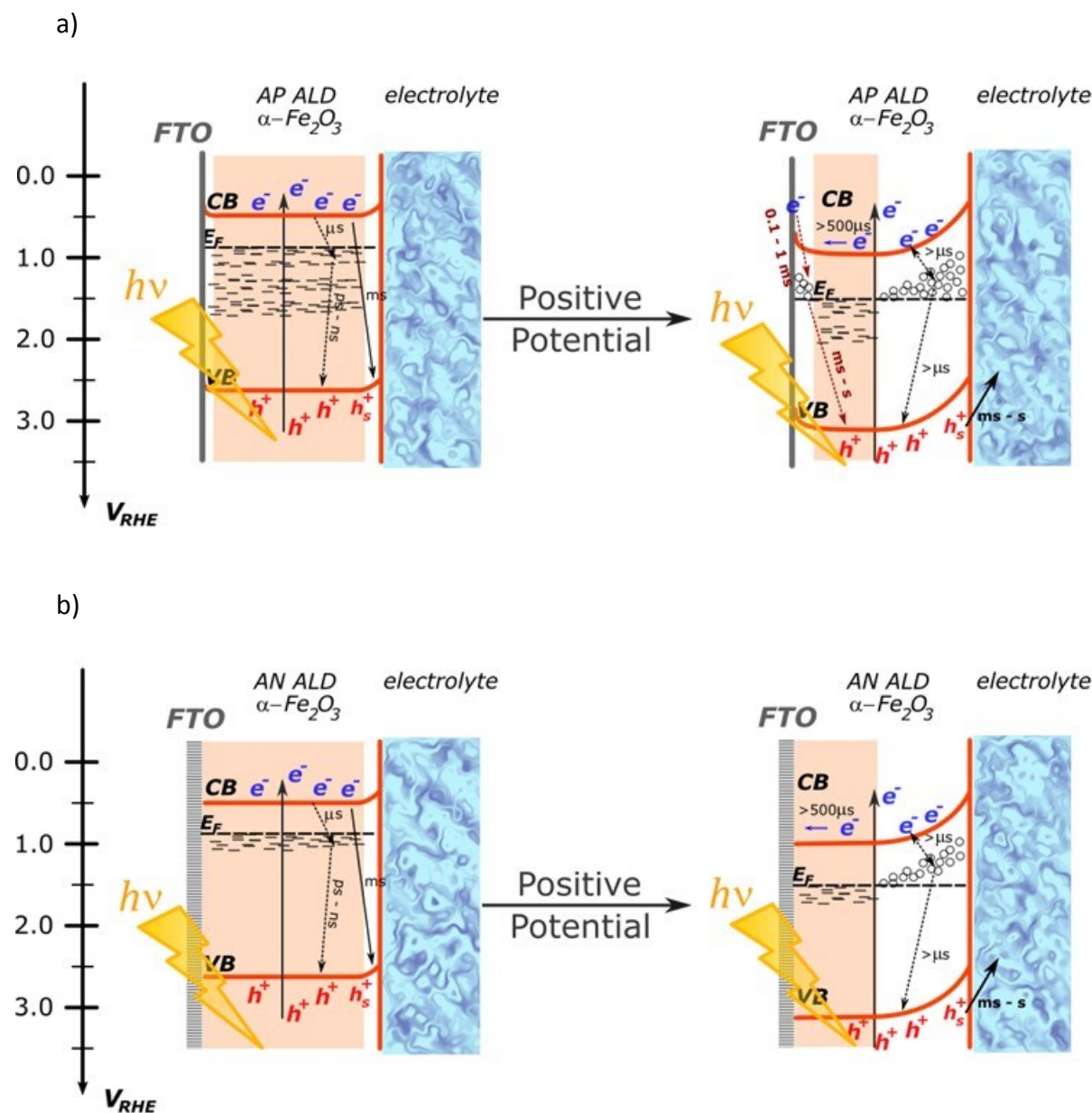


Figure 5-13. Schematic illustration of possible band structure and light induced processes upon increasing the applied potential (from left to right) in both, a) AP and b) AN ALD $\alpha\text{-Fe}_2\text{O}_3$ photoanodes respectively. The dashed arrows indicate trapping and recombination processes and the dashes and empty circles represent full and empty mid-band gap states, respectively.

The discussed trap states were observed, in the results section, as positive absorption features, at long timescales ($ms - s$), in the AP photoanode spectra in TAS (Figure 5-5.b) and PIA (Figure 5-9). However, at shorter timescales ($>ms$) these traps were detected optically

(Figure 5-7), and confirmed by TPC (Figure 5-8), by a decay phase 20 – 500 μs probed at 580 nm (*i.e.*, ground state bleach recovery). Interestingly, a differential amplitude ($\Delta \Delta OD$), calculated at 30 μs , of the referred decay phase probed at 580 nm in Figure 5-7, tracks the cathodic spikes in the J - V (see black triangles in Figure 5-12.a). As such, the negative spikes in the J - V can partly be assigned to trapping processes that might be in direct kinetic competition with water oxidation catalysis. It is important to note that at low applied potentials back electron-hole recombination processes, insensitive to the addition of methanol, is also expected in both the AP and AN photoanodes.

Based on the observations herein and literature on the dynamics of photogenerated charges in hematite photoanodes, a schematic illustration is presented in Figure 5-13 for the AP and AN hematite photoanodes. In this illustration, the AP film includes the presence of trap states also in the interface $\alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2$.

5.4.2. Rate law analyses and mechanistic implications

Upon illumination of flat undoped hematite photoanodes, at timescales relevant for water oxidation ($\text{ms} - \text{s}$) photogenerated holes appear to undergo trapping and back electron-hole recombination processes that compete kinetically with water oxidation. At least, the trapping processes are significantly suppressed by annealing the film. Under *in-operando* conditions at high applied potential, these states deplete in the AP film and hole trapping gives rise to a broad absorption in the visible (see Figure 5-9). Nevertheless, from the hole signal calibration (see Figure 5-10), it is apparent that the AP film exhibits a comparable hole extinction coefficient compared to an APCVD film (700 vs 640 $\text{M}^{-1}\text{cm}^{-1}$, respectively). This indicates that the chemical species (*i. e.* surface holes) responsible for water oxidation ($\text{Fe}^{\text{IV}}=\text{O}$ species discussed in *Chapter 3*) are the same in all hematite films regardless their synthetic route.

Figure 5-14 compares the optical absorption of the two films at a photocurrent value of 0.17 mA cm^{-2} (*i.e.*, at equivalent rates of reaction, see in Figure 5-14.a) under the same applied potential (1.5 V vs RHE). At these equivalent catalytic conditions, Figure 5-14.b shows that the AP film exhibits a higher optical absorption at 650 nm, for a given irradiation intensity. This higher absorption corresponding, as discussed before, to hole trapping. Therefore, to build a rate law for the AP film, it is necessary to calculate the contribution from the trapped holes (h_{T}^+) and the surface holes (h_{s}^+) to the steady-state optical signal probed at 650 nm.

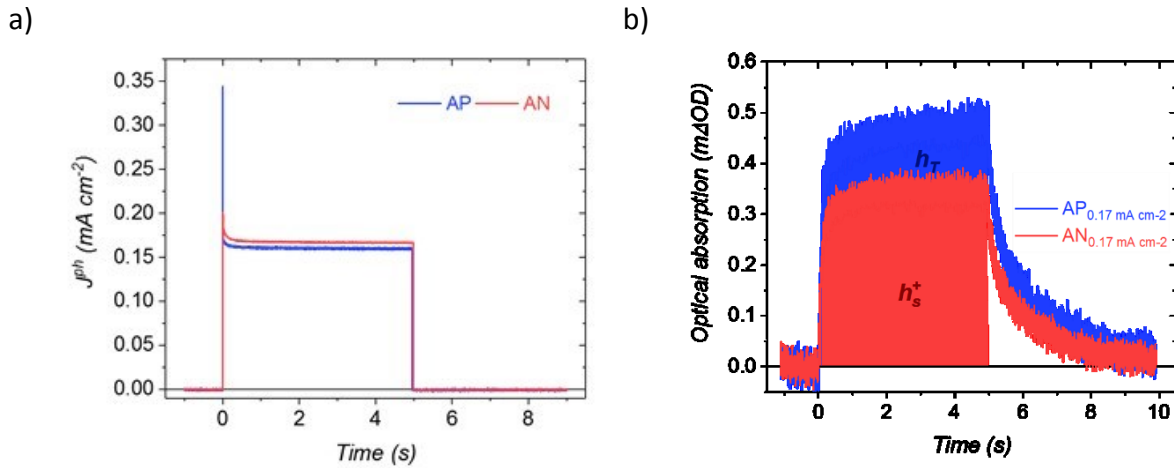


Figure 5-14. Comparison between the a) measured photocurrent density with the corresponding b) optical absorption probed at 650 nm of both, a) AP (blue) and b) AN (red) $\alpha\text{-Fe}_2\text{O}_3$ photoanodes held, for this example, at 1.5 V vs RHE in 1M NaOH.

A water oxidation rate law analyses for the AP photoanode can be built, after correcting for the trapped holes, based on two premises: (1) the nature of surface holes, $\text{Fe}^{\text{IV}}=\text{O}$ species that are responsible for oxygen evolution and gives rise to the 650 nm optical absorption, is the same for all the studied hematite films in this thesis and (2) the water oxidation rate constant does not change upon varying the potential, as shown for the methanol oxidation reaction in *Chapter 4*. Consequently, the rate of reaction (*i. e.* photocurrent density, Equation 5-1) would be the same for the equivalent hole accumulation in both, AP and AN films (see Figure 5-14.a).

$$(r_{WO})_{AP} = (r_{WO})_{AN} = k_{WO} \cdot (h_s^+)_{AN} = k_{WO} \cdot (h_s^+)_{AP} = J^{ph} \quad \text{Equation 5-1}$$

where k_{WO} is the observed rate constant, $(r_{WO})_{AP}$ and $(r_{WO})_{AN}$ are the water oxidation rates of reaction, $(h_s^+)_{AP}$ and $(h_s^+)_{AN}$ are the surface hole density values for the AP and AN films, respectively and J^{ph} is the photocurrent density. Considering the same water oxidation rate constant on both films, then the surface hole density involved in water oxidation must be the same on the AP and AN hematite films (Equation 5-2) at equivalent photocurrent densities.

$$(h_s^+)_{AN} = (h_s^+)_{AP} \quad \text{Equation 5-2}$$

Given that h_s^+ is proportional to the optical density, $(h_s^+)_{AN}$ for the AN film, is calculated directly from the optical absorption ($(A)_{AN} \propto (h_s^+)_{AN}$). On the other hand, for the AP film, the surface hole density $(h_s^+)_{AP}$ would be proportional to the optical absorption of the surface holes given by,

$$(h_s^+)_{AP} \propto (A)_{AP} - \varphi \cdot (A)_{AP} \quad \text{Equation 5-3}$$

where, $(A)_{AP}$ is the optical absorption for the AP film (see blue trace in Figure 5-14.b) and φ is the proportion of trapped holes at certain applied potential, which can be calculated combining Equation 5-2 and Equation 5-3.

$$(A)_{AN} = (A)_{AP} - \varphi \cdot (A)_{AP} \rightarrow \varphi = \frac{(A)_{AP} - (A)_{AN}}{(A)_{AP}} \quad \text{Equation 5-4}$$

From Equation 5-4, the average trapped holes proportion φ are calculated as 0.29 ± 0.02 , 0.53 ± 0.04 and 0.69 ± 0.05 when the applied potential is 1.5, 1.3 and 1.15 V vs RHE, respectively. Therefore, the proportion of optical absorption corresponding to the surface hole density reacting with water ($1 - \varphi$), at 1.5, 1.3 and 1.15 V vs RHE applied potentials, are 0.71, 0.47 and 0.31, respectively.

These calculated proportion of optical absorption, at different applied potentials, corresponding to surface holes reacting with water and eliminating optical contributions of trapped holes in the AP film was used therefore, to correct the optical densities (ΔOD) shown in Figure 5-11. Subsequently these corrected optical signals were converted in surface hole density using the measured hole extinction coefficient and plotted in the presented logarithmic rate law in Figure 5-15. This figure also compares the obtained rate laws for the AN photoanode at different applied potentials.

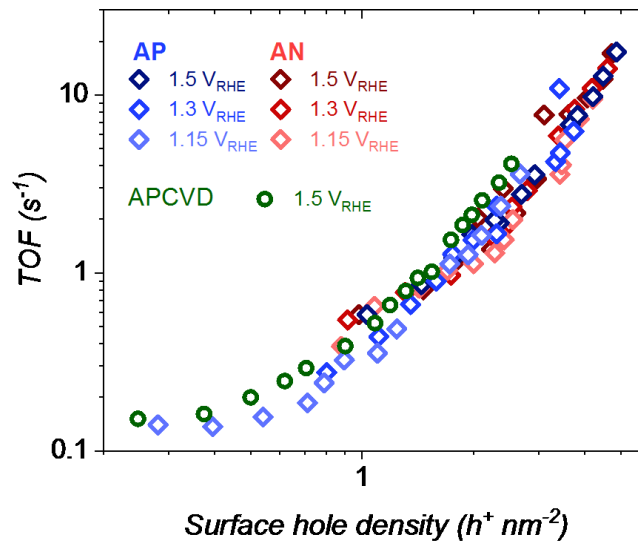


Figure 5-15. Comparative kinetic analysis, in ‘turn-over frequencies’ of water oxidation the AP (blue) and AN (red) α -Fe₂O₃ photoanodes at different applied potentials probed at 650 nm in 1M NaOH electrolyte. For comparison, equivalent data for an APCVD film (discussed in Chapter 3) is also shown. The rate law data is presented as ‘turn-over frequencies’ vs surface hole density.

Three remarkable observations are apparent from Figure 5-15: (1) the rate law data, independent of the applied potential, for the AP film overlaps with the AN sample. This confirms that the assumptions of same nature of surface holes in all films and independence of the rate constant with respect to the applied potential are correct, (2) the reaction pathways (1st and 3rd order) as well as the kinetics of the rate determining step are insensitive to a change in the Fermi level in the photoanode, as discussed for the methanol oxidation example in *Chapter 4*, and (3) the rate laws for both AP and AN α -Fe₂O₃ photoanodes overlap with the APCVD film data (from *Chapter 3*)

These observations can be rationalised from a molecular perspective, given that, as discussed in *Chapter 3*, the water oxidation reaction *in-operando* conditions, proceeds through the accumulation of photogenerated holes ($\text{Fe}^{\text{IV}}=\text{O}$) in a reaction cluster (see Figure 5-16). Therefore, it can be suggested that the reaction is driven by the same species in the three different α -Fe₂O₃ photoanodes studied in this thesis, the nanostructured, Si-doped APCVD film and the un-doped, planar as-prepared and annealed films. The rate constant of water oxidation on the very different hematite photoanodes studied herein is insensitive to nanostructure, doping or annealing. As such, the effect of annealing process as well as varying the applied potential affects recombination and trapping, not rate constant, therefore only determines the density of holes at the surface, which is the ultimate factor that governs the kinetics of the catalysis.

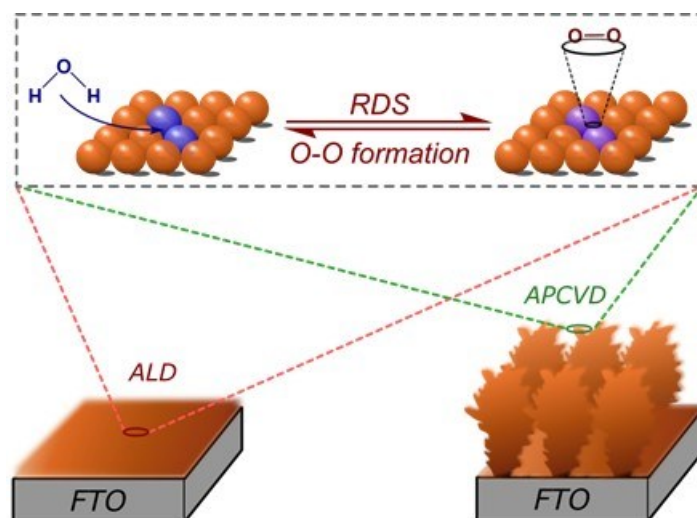


Figure 5-16. Schematic representation of the rate determining step in an ALD planar undoped compared to a Si-doped nanostructured α -Fe₂O₃ photoanodes. Upon hole accumulation, water oxidation reaction proceeds *via* the mechanism of reaction discussed in *Chapter 3* (herein only the rds, the O-O bond formation, of the reaction is represented).

5.5. Conclusions

Oxygen evolution is considered the kinetic bottleneck of solar driven water splitting in part due to the kinetic mismatch between light induced and catalytic events. To accomplish the purpose of designing more efficient photoanode materials, it is of paramount importance to understand the difference in charge carrier kinetics and mechanisms of action caused by the different synthetic routes of such materials. In this chapter I report the dynamics of photogenerated charge carriers on two un-doped, flat $\alpha\text{-Fe}_2\text{O}_3$ photoanodes annealed at different temperatures.

Transient absorption and transient photocurrent measurements allow to study the dynamics of holes recombination and transfer to the electrolyte as well as the kinetics of electron extraction. The annealing process on an $\alpha\text{-Fe}_2\text{O}_3$ photoanode caused the reduction of trap states improving the FTO/ TiO_2 / $\alpha\text{-Fe}_2\text{O}_3$ as well as the $\alpha\text{-Fe}_2\text{O}_3$ /electrolyte interfaces. Steady-state rate law analyses corroborated the presence of such states which do not participate in water oxidation as intermediates as some studies in literature had suggested previously.

The results presented herein allow to propose that what determines the kinetics of catalysis on $\alpha\text{-Fe}_2\text{O}_3$ photoanodes is only the surface hole density as well as the chemical nature of the surface holes ($\text{Fe}^{\text{IV}}=\text{O}$ in the case of hematite) regardless the synthetic route.

5.6. References

1. Cendula, P., Steier, L., Losio, P. A., Grätzel, M. & Schumacher, J. O. Analysis of Optical Losses in a Photoelectrochemical Cell: A Tool for Precise Absorptance Estimation. *Adv. Funct. Mater.* **28**, (2018).
2. Mayer, M. T. Photovoltage at semiconductor–electrolyte junctions. *Curr. Opin. Electrochem.* **2**, 104–110 (2017).
3. Ling, Y., Wang, G., Wheeler, D. A., Zhang, J. Z. & Li, Y. Sn-Doped Hematite Nanostructures for Photoelectrochemical Water Splitting. *Nano Lett.* **11**, 2119–2125 (2011).
4. Zhang, P., Wang, T. & Gong, J. Current Mechanistic Understanding of Surface Reactions over Water-Splitting Photocatalysts. *Chem* **4**, 223–245 (2018).
5. Jang, J.-W. *et al.* Enabling unassisted solar water splitting by iron oxide and silicon. *Nat. Commun.* **6**, (2015).
6. Tang, P. *et al.* Enhanced photoelectrochemical water splitting of hematite multilayer nanowire photoanodes by tuning the surface state via bottom-up interfacial engineering. *Energy Environ. Sci.* **10**, 2124–2136 (2017).
7. Sivula, K., Le Formal, F. & Grätzel, M. Solar Water Splitting: Progress Using Hematite (α -Fe₂O₃) Photoelectrodes. *ChemSusChem* **4**, 432–449 (2011).
8. Zandi, O., Klahr, B. M. & Hamann, T. W. Highly photoactive Ti-doped [small alpha]-Fe₂O₃ thin film electrodes: resurrection of the dead layer. *Energy Environ. Sci.* **6**, (2013).
9. Zandi, O., Schon, A. R., Hajibabaei, H. & Hamann, T. W. Enhanced Charge Separation and Collection in High-Performance Electrodeposited Hematite Films. *Chem. Mater.* **28**, 765–771 (2016).
10. Steier, L. *et al.* Low-Temperature Atomic Layer Deposition of Crystalline and Photoactive Ultrathin Hematite Films for Solar Water Splitting. *ACS Nano* **9**, 11775–11783 (2015).
11. Huang, Z. *et al.* In situ probe of photocarrier dynamics in water-splitting hematite (α -Fe₂O₃) electrodes. *Energy Environ. Sci.* **5**, 8923–8926 (2012).
12. Cherepy, N. J., Liston, D. B., Lovejoy, J. A., Deng, H. & Zhang, J. Z. Ultrafast Studies of Photoexcited Electron Dynamics in γ - and α -Fe₂O₃ Semiconductor Nanoparticles. *J. Phys. Chem. B* **102**, 770–776 (1998).
13. Pendlebury, S. R. *et al.* Ultrafast Charge Carrier Recombination and Trapping in Hematite Photoanodes under Applied Bias. *J. Am. Chem. Soc.* **136**, 9854–9857 (2014).
14. Kafizas, A., Godin, R. & Durrant, J. R. Charge Carrier Dynamics in Metal Oxide Photoelectrodes for Water Oxidation. in *Semiconductors for Photocatalysis* **97**, 3–46 (2017).
15. Barroso, M., Pendlebury, S. R., Cowan, A. J. & Durrant, J. R. Charge carrier trapping, recombination and transfer in hematite (α -Fe₂O₃) water splitting photoanodes. *Chem. Sci.* **4**, 2724–2734 (2013).
16. Pendlebury, S. R. *et al.* Correlating long-lived photogenerated hole populations with photocurrent densities in hematite water oxidation photoanodes. *Energy Environ. Sci.* **5**, 6304–6312 (2012).
17. Cowan, A. J. & Durrant, J. R. Long-lived charge separated states in nanostructured semiconductor photoelectrodes for the production of solar fuels. *Chem. Soc. Rev.* **42**, 2281–

- 2293 (2013).
18. Upul Wijayantha, K. G., Saremi-Yarahmadi, S. & Peter, L. M. Kinetics of oxygen evolution at α -Fe₂O₃ photoanodes: a study by photoelectrochemical impedance spectroscopy. *Phys. Chem. Chem. Phys.* **13**, 5264 (2011).
 19. Klahr, B., Gimenez, S., Fabregat-Santiago, F., Bisquert, J. & Hamann, T. W. Photoelectrochemical and Impedance Spectroscopic Investigation of Water Oxidation with "Co-Pi"-Coated Hematite Electrodes. *J. Am. Chem. Soc.* **134**, 16693–16700 (2012).
 20. Le Formal, F. *et al.* Passivating surface states on water splitting hematite photoanodes with alumina overlayers. *Chem. Sci.* **2**, 737–743 (2011).
 21. Peter, L. M., Wijayantha, K. G. U. & Tahir, A. A. Kinetics of light-driven oxygen evolution at [small alpha]-Fe₂O₃ electrodes. *Faraday Discuss.* **155**, 309–322 (2012).
 22. Peter, L. M. & Wijayantha, K. G. U. Photoelectrochemical Water Splitting at Semiconductor Electrodes: Fundamental Problems and New Perspectives. *ChemPhysChem* **15**, 1983–1995 (2014).
 23. Cummings, C. Y., Marken, F., Peter, L. M., Wijayantha, K. G. U. & Tahir, A. A. New Insights into Water Splitting at Mesoporous α -Fe₂O₃ Films: A Study by Modulated Transmittance and Impedance Spectroscopies. *J. Am. Chem. Soc.* **134**, 1225–1234 (2012).
 24. Le Formal, F. *et al.* Back Electron–Hole Recombination in Hematite Photoanodes for Water Splitting. *J. Am. Chem. Soc.* **136**, 2564–2574 (2014).
 25. Peter, L. M., Gurudayal, Wong, L. H. & Abdi, F. F. Understanding the role of nanostructuring in photoelectrode performance for light-driven water splitting. *J. Electroanal. Chem.* **819**, 447–458 (2018).
 26. Glasscock, J. A., Barnes, P. R. F., Plumb, I. C. & Savvides, N. Enhancement of Photoelectrochemical Hydrogen Production from Hematite Thin Films by the Introduction of Ti and Si. *J. Phys. Chem. C* **111**, 16477–16488 (2007).
 27. Ahmed, A. Y., Kandiel, T. A., Oekermann, T. & Bahnemann, D. Photocatalytic Activities of Different Well-defined Single Crystal TiO₂ Surfaces: Anatase versus Rutile. *J. Phys. Chem. Lett.* **2**, 2461–2465 (2011).
 28. Le Formal, F., Sivula, K. & Grätzel, M. The Transient Photocurrent and Photovoltage Behavior of a Hematite Photoanode under Working Conditions and the Influence of Surface Treatments. *J. Phys. Chem. C* **116**, 26707–26720 (2012).
 29. Dare-Edwards, M. P., Goodenough, J. B., Hamnett, A. & Trevellick, P. R. Electrochemistry and Photoelectrochemistry of Iron(III) Oxide. *J. Chem. Soc. Faraday Trans. I* **79**, 2027–2041 (1983).
 30. Klahr, B., Gimenez, S., Fabregat-Santiago, F., Hamann, T. & Bisquert, J. Water Oxidation at Hematite Photoelectrodes: The Role of Surface States. *J. Am. Chem. Soc.* **134**, 4294–4302 (2012).
 31. Zandi, O. & Hamann, T. W. The potential versus current state of water splitting with hematite. *Phys. Chem. Chem. Phys.* **17**, 22485–22503 (2015).
 32. Peter, L. M., Upul Wijayantha, K. G. & Tahir, A. A. Kinetics of light-driven oxygen evolution at α -Fe₂O₃ electrodes. *Faraday Discuss.* **155**, 309–322 (2012).
 33. Barroso, M. *et al.* Dynamics of photogenerated holes in surface modified α -Fe₂O₃ photoanodes for solar water splitting. *Proc. Natl. Acad. Sci.* **109**, 15640–15645 (2012).

34. Le Formal, F. *et al.* Rate Law Analysis of Water Oxidation on a Hematite Surface. *J. Am. Chem. Soc.* **137**, 6629–6637 (2015).
35. Francàs, L., Mesa, C. A., Pastor, E., Le Formal, F. & Durrant, J. R. *Chapter 5: Rate Law Analysis of Water Splitting Photoelectrodes. RSC Energy and Environment Series* (2018). doi:10.1039/9781782629863-00128
36. Ma, Y., Le Formal, F., Kafizas, A., Pendlebury, S. R. & Durrant, J. R. Efficient suppression of back electron/hole recombination in cobalt phosphate surface-modified undoped bismuth vanadate photoanodes. *J. Mater. Chem. A* **3**, (2015).
37. van de Krol, R. & Grätzel, M. *Photoelectrochemical Hydrogen Production*. (Springer, 2012). doi:10.1007/978-1-4614-1380-6
38. Takashima, T., Ishikawa, K. & Irie, H. Detection of Intermediate Species in Oxygen Evolution on Hematite Electrodes Using Spectroelectrochemical Measurements. *J. Phys. Chem. C* **120**, 24827–24834 (2016).
39. Tilley, S. D., Cornuz, M., Sivula, K. & Grätzel, M. Light-Induced Water Splitting with Hematite: Improved Nanostructure and Iridium Oxide Catalysis. *Angew. Chemie Int. Ed.* **49**, 6405–6408 (2010).
40. Young, K. M. H., Klahr, B. M., Zandi, O. & Hamann, T. W. Photocatalytic water oxidation with hematite electrodes. *Catal. Sci. Technol.* **3**, 1660–1671 (2013).
41. Zandi, O. & Hamann, T. W. Determination of photoelectrochemical water oxidation intermediates on haematite electrode surfaces using operando infrared spectroscopy. *Nat. Chem.* **8**, (2016).
42. Zandi, O. & Hamann, T. W. Enhanced Water Splitting Efficiency Through Selective Surface State Removal. *J. Phys. Chem. Lett.* **5**, 1522–1526 (2014).
43. Le Formal, F. *et al.* Passivating surface states on water splitting hematite photoanodes with alumina overlayers. *Chem. Sci.* **2**, (2011).
44. Steier, L. *et al.* Understanding the Role of Underlayers and Overlayers in Thin Film Hematite Photoanodes. *Adv. Funct. Mater.* **24**, 7681–7688 (2014).
45. Klahr, B. M., Martinson, A. B. F. & Hamann, T. W. Photoelectrochemical Investigation of Ultrathin Film Iron Oxide Solar Cells Prepared by Atomic Layer Deposition. *Langmuir* **27**, 461–468 (2011).
46. Sivula, K. *et al.* Photoelectrochemical Water Splitting with Mesoporous Hematite Prepared by a Solution-Based Colloidal Approach. *J. Am. Chem. Soc.* **132**, 7436–7444 (2010).
47. Kronawitter, C. X. *et al.* On the Interfacial Electronic Structure Origin of Efficiency Enhancement in Hematite Photoanodes. *J. Phys. Chem. C* **116**, 22780–22785 (2012).
48. Ma, Y., Pendlebury, S. R., Reynal, A., Le Formal, F. & Durrant, J. R. Dynamics of photogenerated holes in undoped BiVO₄ photoanodes for solar water oxidation. *Chem. Sci.* **5**, 2964–2973 (2014).
49. Kafizas, A. *et al.* Where Do Photogenerated Holes Go in Anatase:Rutile TiO₂ ? A Transient Absorption Spectroscopy Study of Charge Transfer and Lifetime. *J. Phys. Chem. A* **120**, 715–723 (2016).
50. Ma, Y., Le Formal, F., Kafizas, A., Pendlebury, S. R. & Durrant, J. R. Efficient suppression of back electron/hole recombination in cobalt phosphate surface- modified undoped bismuth

- vanadate photoanodes. *J. Mater. Chem. A* **3**, 20649–20657 (2015).
51. Cowan, A. J., Leng, W., Barnes, P. R. F., Klug, D. R. & Durrant, J. R. Charge carrier separation in nanostructured TiO₂ photoelectrodes for water splitting. *Phys. Chem. Chem. Phys.* **15**, 8772 (2013).

Chapter 6. Concluding remarks and future work

6.1. Concluding remarks

The main aim of this thesis has been to understand the key factors governing the solar fuels catalytic process on metal-oxide electrodes using spectroelectrochemical techniques, such as transient absorption spectroscopy, transient photocurrent and light-induced spectroelectrochemistry. For this purpose, the limiting process in photoelectrochemical water splitting, i.e., the catalysis of water oxidation reaction was investigated, focusing on APCVD hematite photoanodes. An alternative oxidation reaction is explored to overcome the kinetic limitations of water oxidation. Additionally, some of the key factors for efficient photoanodes can be controlled by its synthesis method and post-synthesis treatments. As such, ALD hematite photoanodes with different post-synthesis treatments were also studied and compared to APCVD films.

Chapter 3 focused on the catalysis of water oxidation on four different metal-oxides photoanodes, focusing on hematite for a mechanistic study. A plausible water oxidation mechanism on hematite photoanodes is proposed, whose rate determining step depends upon the accumulation of three surface holes at 1 sun illumination conditions. This accumulation of holes in a cluster of reaction was found to be associated with the redox power of the reaction cluster. This is remarkably similar to the function of different biological systems such as the oxygen evolution centre in the photosystem II. *Chapter 3* concluded also that the rate determining step found for $\alpha\text{-Fe}_2\text{O}_3$ photoanodes shares striking similitudes with photoanodes such as TiO_2 , BiVO_4 and WO_3 .

Chapter 4 examined the oxidation of organic substrates using methanol as substrate model. The surface hole accumulation was found to reduce the complexity of the reaction, allowing the photoanode to function more efficiently. Additionally, the faster kinetics of methanol oxidation and excellent selectivity towards formaldehyde allow to propose the possibility of a hydrogen production concomitant with the selective synthesis of high added-value chemicals.

In *Chapter 5*, the effect of post-synthesis treatment was evaluated with two different ALD $\alpha\text{-Fe}_2\text{O}_3$ photoanodes. A high temperature treatment, i.e., an annealing process caused a reduction in the density of trap states of these photoanodes, that reduce the efficiency

towards water oxidation. However, by comparing the kinetics and mechanism of water oxidation on ALD to APCVD photoanodes it can be concluded that, the key factor that determines the rate constant of water oxidation catalysis on α -Fe₂O₃ photoanodes is only the surface hole density as well as the chemical nature of the surface holes regardless the synthetic route.

6.2. Future work

Despite the main objectives of this thesis were achieved, different questions arose from this work.

From *Chapter 3*, the 1st order of reaction was thought to proceed through the formation of H₂O₂ that subsequently decomposes to O₂. However, further evidence is required. As such, the detection of this chemical species during water oxidation at low irradiation intensities is required.

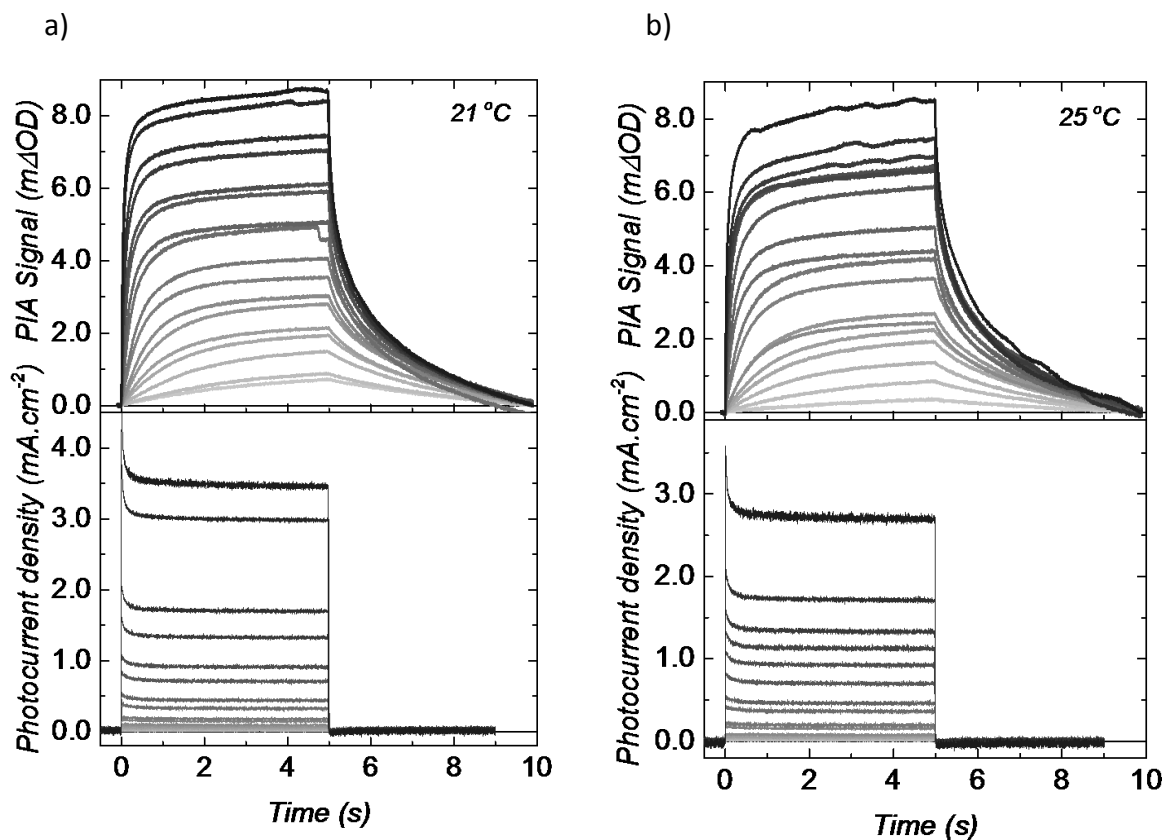
From *Chapter 4*, it was observed that after 1 hour of reaction, the Faradaic efficiency of methanol oxidation to produce formaldehyde appeared to decrease. A rate law analysis could be used to correlate that lower Faradaic efficiency with other possible oxidation reactions.

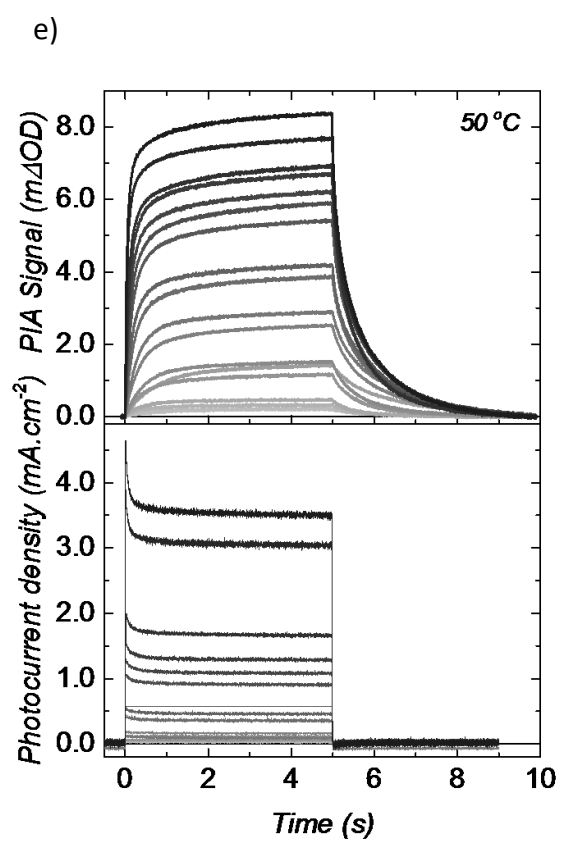
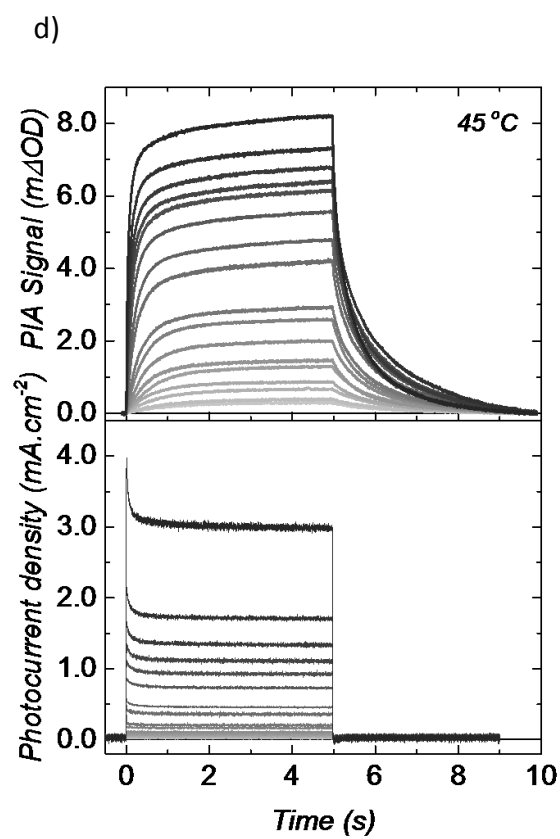
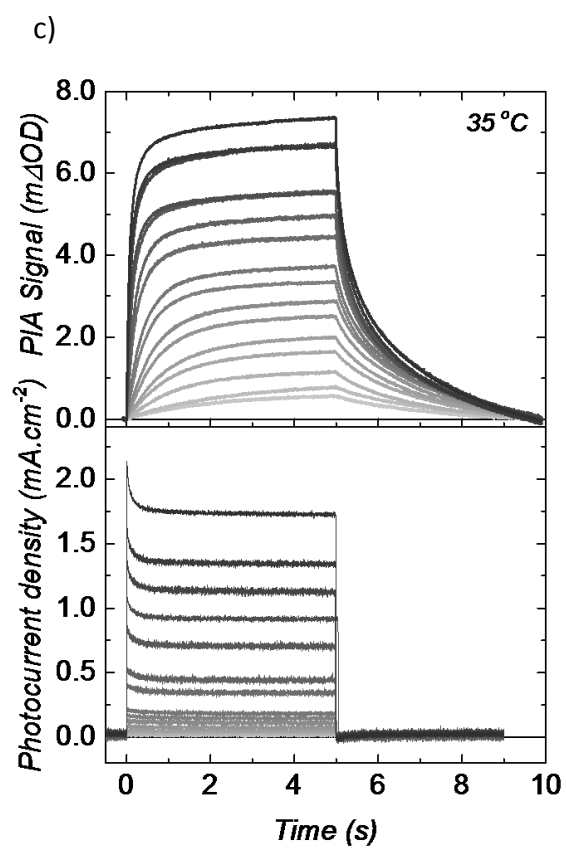
From this *Chapter*, methanol can be changed for another organic substrate. For example, glycerol oxidation is an interesting reaction to study. This is due to glycerol is a by-product from the biodiesel industry, which is growing rapidly. Interestingly, degradation of glycerol can produce dihydroxyacetone, which costs ~250 fold the glycerol cost.

From *Chapter 5*, the rate law analysis at low applied potentials of the as-prepared ALD hematite photoanode exhibited the 1st order reaction found also for the APCVD film. Oxygen measurements as well as H₂O₂ at these conditions could give insights into the function of the as-prepared ALD photoanode towards water oxidation.

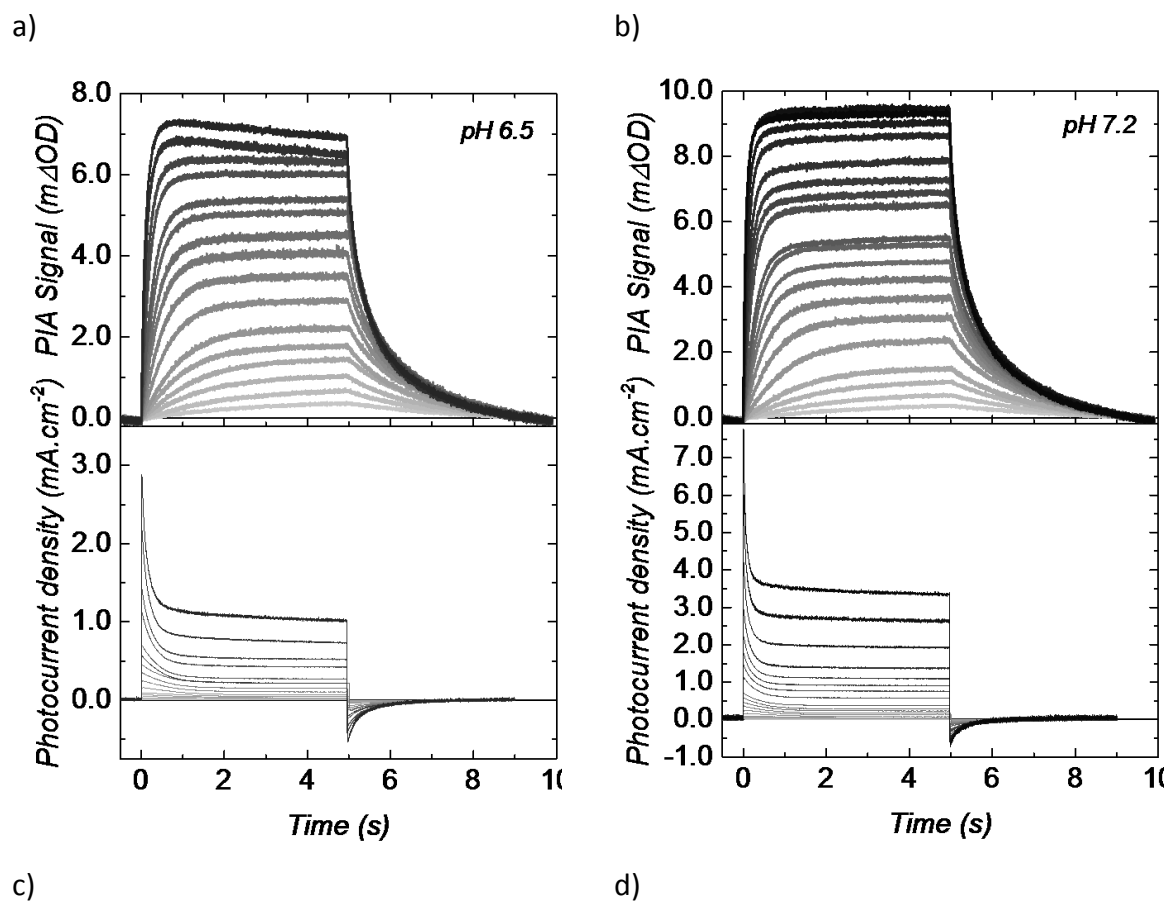
Appendix

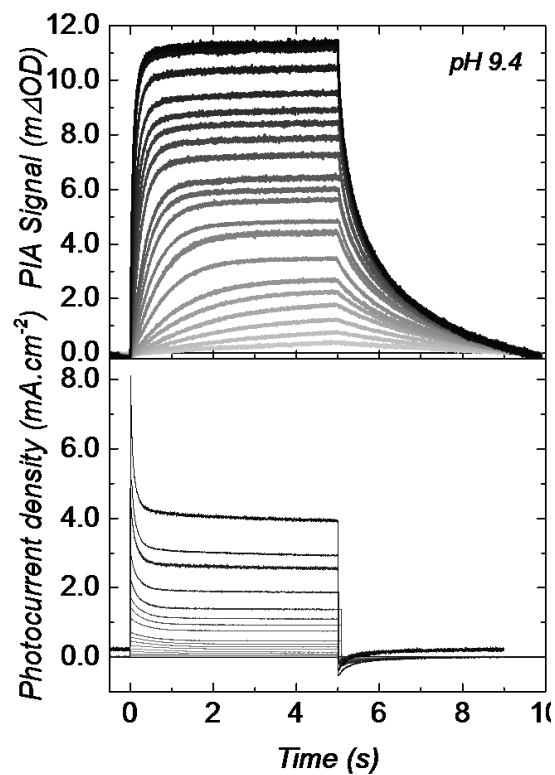
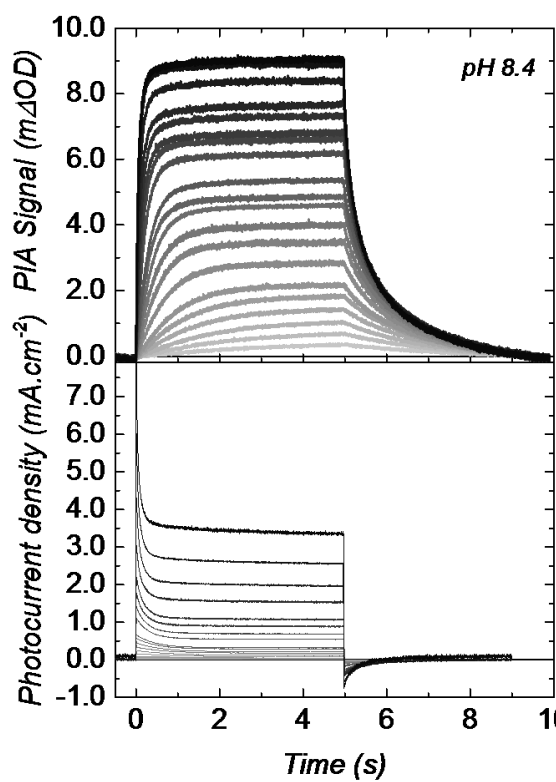
1. **Figure A-1.** Raw LI-SEC data for the oxidation of water on $\alpha\text{-Fe}_2\text{O}_3$ as a function of 5 s on/5 s off pulsed 365 nm illumination (~ 1 to $\sim 35\text{ mW cm}^{-2}$) under 1.5 V vs RHE applied potential, *top*: PIA signal of surface valence band hole density (p_s) probed at 650 nm and, *bottom*: simultaneously assay of TPC at a) 21 °C, b) 25 °C, c) 35 °C, d) 45 °C and e) 50 °C



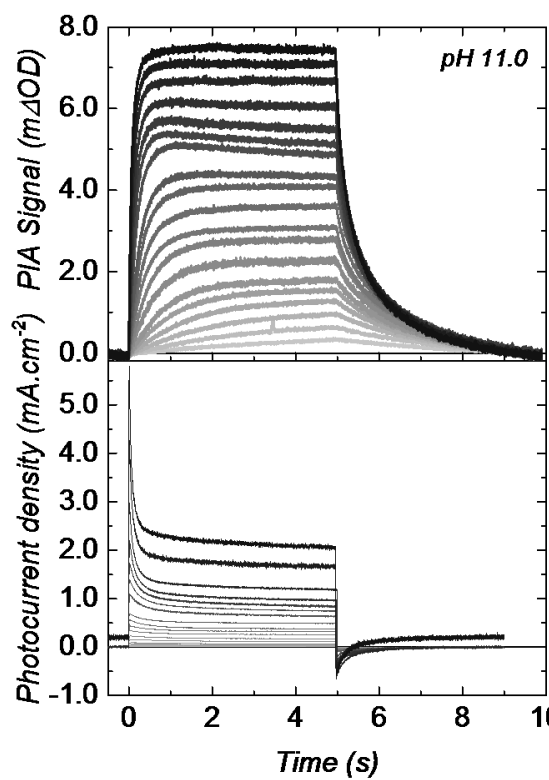


2. **Figure A-2.** Raw LI-SEC data for the oxidation of water on $\alpha\text{-Fe}_2\text{O}_3$ as a function of 5 s on/5 s off pulsed 365 nm illumination (~ 1 to $\sim 35\text{ mW cm}^{-2}$) under 1.5 V vs RHE applied potential, *top*: PIA signal of surface valence band hole density (p_s) probed at 650 nm and, *bottom*: simultaneously assay of TPC at a) pH 6.5, b) pH 7.2, c) pH 8.4, d) pH 9.4, e) pH 11.0, f) pH 12.4, g) pH 13.0 and h) pH 13.7.

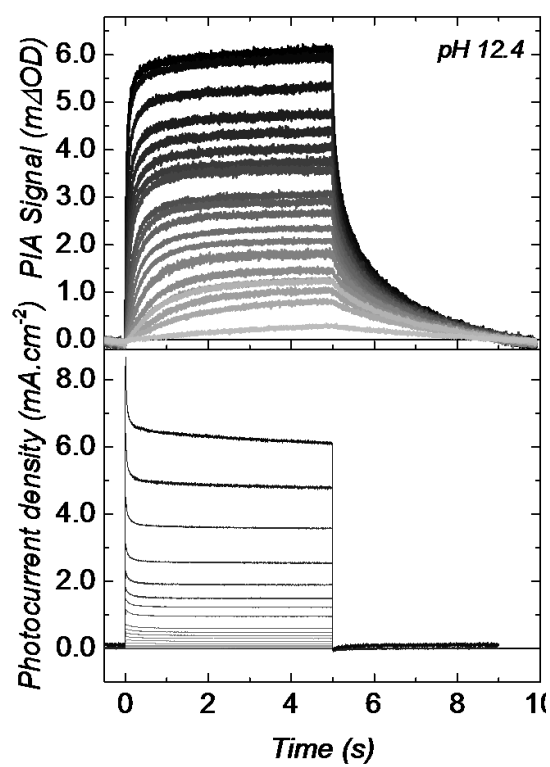




e)

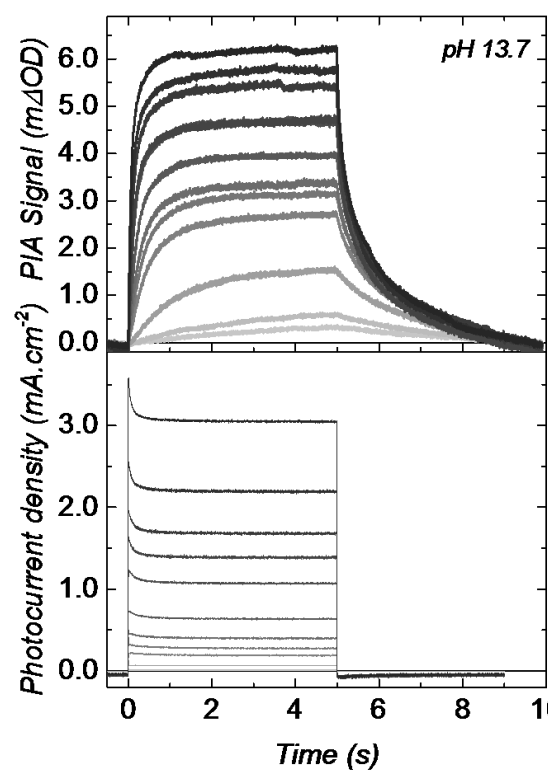
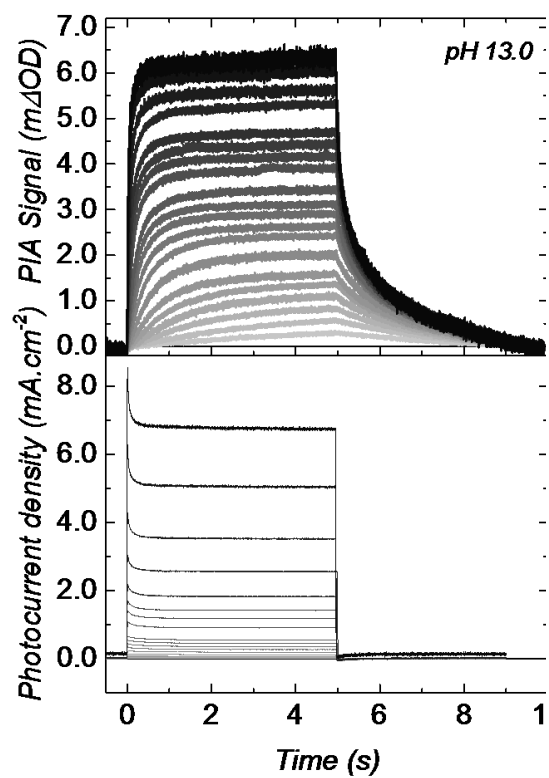


f)



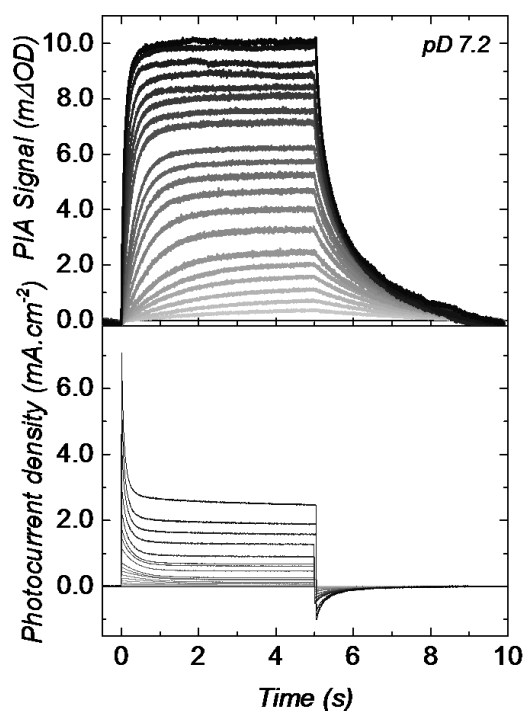
g)

h)

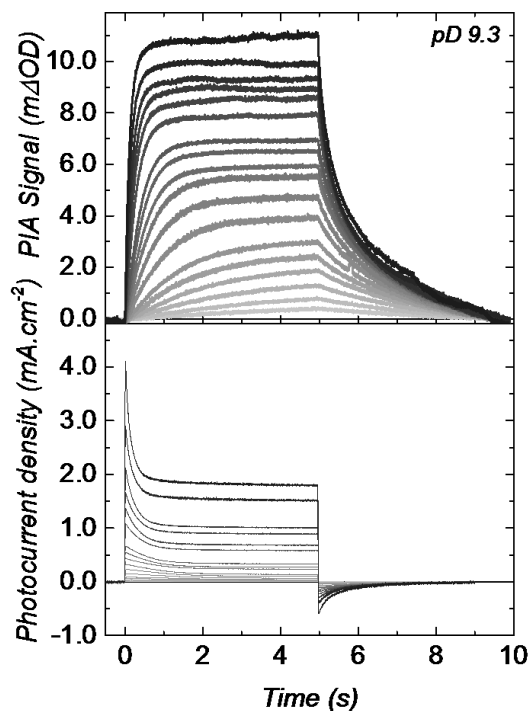


3. **Figure A-3.** Raw LI-SEC data for the oxidation of water on $\alpha\text{-Fe}_2\text{O}_3$ as a function of 5 s on/5 s off pulsed 365 nm illumination (~ 1 to $\sim 35\text{ mW cm}^{-2}$) under 1.5 V vs RHE applied potential, *top*: PIA signal of surface valence band hole density (p_s) probed at 650 nm and, *bottom*: simultaneously assay of TPC at a) pD 7.2, b) pD 9.3, c) pD 11.0, d) pD 12.3, e) pD 13.0 and f) pD 13.7.

a)

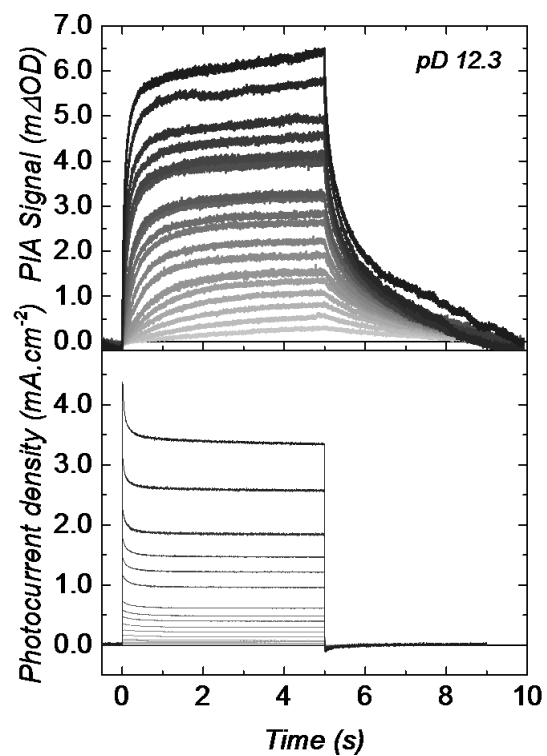
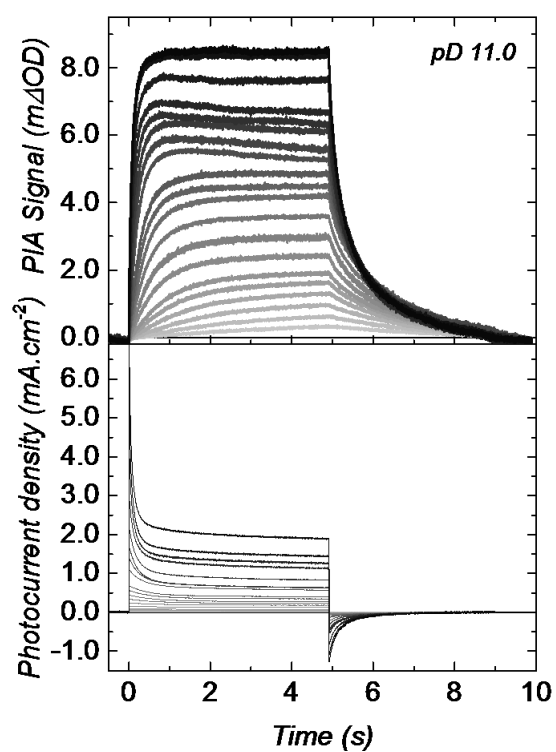


b)



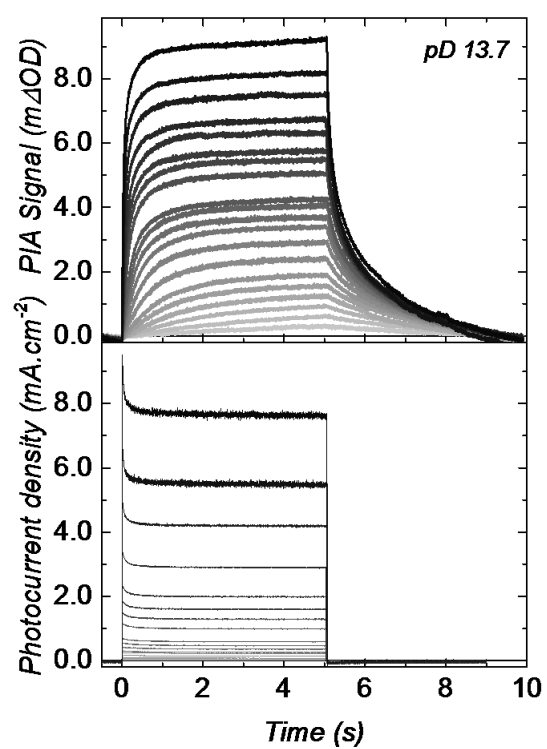
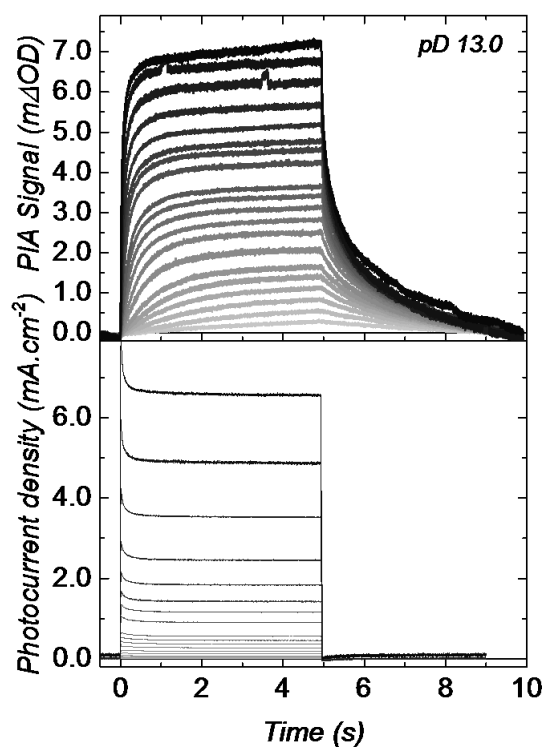
c)

d)

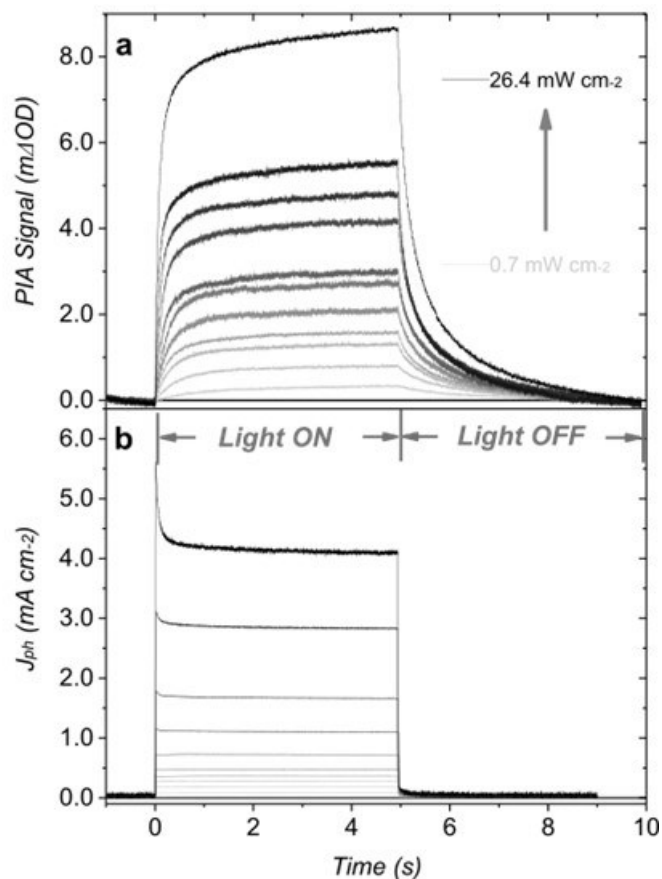


e)

f)



4. **Figure A-4.** Raw LI-SEC data for the oxidation of 95% CD₃OD in 0.1 M NaOD in D₂O on α -Fe₂O₃ as a function of 5 s on/5 s off pulsed 356 nm illumination (~ 1 to ~ 26 mW cm⁻²) under 0.55 V vs Ag/AgCl for kinetic isotope effect study, a) PIA signal of surface valence band hole density (p_s) probed at 650 nm and b) simultaneous assay of TPC.



5. **Figure A-5.** Raw LI-SEC data for the oxidation of 4% CH₃OH in 0.1 M NaOH on TiO₂ as a function of 5 s on/5 s off pulsed 356 nm illumination (~ 2 to ~ 64 mW cm⁻²) under -0.80 V vs Ag/AgCl, a) PIA signal of surface valence band hole density (p_s) probed at 500 nm and b) simultaneous assay of TPC.s

