

Transient Spectroscopic Studies of Photocatalysts for CO₂ and Proton Reduction

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*To my parents and my
brother*

Except when specific reference are made, the material presented in this thesis, is the result of my own work. The dissertation does not exceed 100 000 words in length.

Ernest Pastor
October 2015

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Abstract

The abstract for this thesis is written in English, Catalan and Spanish

In English

In this thesis, optical and electrochemical techniques are used to study the factors controlling catalytic function in solar-to-fuel conversion systems.

Chapter 3, the first results chapter, considers a system for CO₂ reduction based on a Re photocatalyst anchored to TiO₂. This chapter reports evidence that the immobilisation of the photocatalyst via covalent bonds improves the stability of one of the key reaction intermediates resulting in higher catalytic yields. This chapter also provides insight into the nature and timescale of the steps in the mechanism of CO₂ reduction.

Chapter 4 considers a proton reduction system based on a Ru absorber, a Ni electrocatalyst and a sacrificial electron donor. This chapter discusses the mechanism behind the strong pH dependence in this system. The results show that whereas the electron transfer between the dye anions and the electrocatalyst is pH independent, the generation of dye anions and the catalytic function of the electrocatalysts have opposite pH-dependencies.

Chapter 5 considers a photocathode for proton reduction based on a Cu₂O/Al:ZnO buried p-n junction with protection and catalyst layers. The results presented show that the buried junction controls charge separation and the photocurrent onset. Furthermore, the catalyst layer is found to slow down charge recombination and help achieve high reduction yields. This chapter also discusses the mechanism of proton reduction and how the nature of the rate-limiting step has an impact in the recombination kinetics.

Chapter 6 discusses the use of transient absorption spectroscopy to study high refractive index materials with high quality interfaces. This chapter investigates light interference effects in TiO₂, Cu₂O and a CH₃NH₃PbI₃ perovskite device. The results show that interference effects in these materials can dominate their transient spectra, hindering its interpretation. However, it is found that this spectroscopy can also be used to extract information about the changes of the refractive index.

In Catalan

Aquesta tesi investiga els factors que controlen l'activitat catalítica de sistemes per a la conversió d'Energia solar en combustibles mitjançant tècniques òptiques i electroquímiques. La tesi es centra especialment en l'ús de espectroscòpia resolta amb el temps (TAS) per a investigar la cinètica de les reaccions de reducció de protons i CO_2 iniciades amb llum.

El primer capítol de resultats és el *Capítol 3*. En aquest capítol s'estudia un sistema de reducció de CO_2 basat en un fotocatalitzador de Re suportat a TiO_2 . Aquí també es demostra que la immobilització del fotocatalitzador mitjançant enllaços covalents resulta en un augment de la estabilitat d'un intermediari de reacció clau. Aquesta estabilització es tradueix en una millora de l'eficiència catalítica del sistema. En aquest capítol també s'estudia la naturalesa i cinètica dels diferents passos en el mecanisme de reducció de CO_2 a CO.

En el *Capítol 4* s'estudia un sistema de reducció de protons basat en un fotosensibilitzador de Ru, un electrocatalitzador de Ni i un reductor de sacrifici. També es discuteix quin és el mecanisme darrere de la dependència d'aquest sistema amb el pH. Els resultats del capítol demostren que mentre la transferència electrònica entre els anions del fotosensibilitzador i l'electrocatalitzador és independent del pH, la generació d'anions del fotosensibilitzador i l'activitat catalítica de electrocatalitzador tenen dependències de pH oposades.

En el *Capítol 5* s'estudia un fotocàtode per a la reducció de protons basat en una unió *p-n* entre Cu_2O i Al:ZnO amb capes protectores i catalítiques. Els resultats demostren com la separació de càrregues i, per tant, l'inici de la fotocorrent estan determinats per la unió *p-n*. A més a més, la capa catalítica actua reduint la recombinació de càrregues separades i, consegüentment, contribueix significativament a aconseguir alts rendiments quàntics. En aquest capítol també es discuteix el mecanisme de reducció de protons i com la naturalesa del pas limitant té un gran impacte en la cinètica de recombinació.

En el *Capítol 6* s'investiga l'ús de TAS per a estudiar materials amb alts índex de refracció i superfícies de gran qualitat. També s'estudien les interferències òptiques

que ocorren al TiO_2 , al Cu_2O i a una cel.la de perovskita $\text{CH}_3\text{NH}_3\text{PbI}_3$. Els resultats demostren com l'interferència òptica en aquests materials pot dominar l'espectre temporal dificultant la seua interpretació. Tot i això aquesta interferència també es pot utilitzar per a obtindre informació sobre els canvis en l'índex de refracció que tenen lloc a aquests materials després de l'excitació amb llum.

In Spanish

En esta tesis se investigan los factores que controlan la actividad catalítica de sistemas para la conversión de energía solar en combustibles, mediante técnicas, ópticas y electroquímicas. La tesis se centra especialmente en el uso de espectroscopia resuelta en el tiempo (TAS) para investigar la cinética de las reacciones de reducción de protones y CO₂ iniciadas con luz.

El primer capítulo de resultados es el *Capítulo 3*. En este capítulo se estudia un sistema de reducción de CO₂ basado en un fotocatalizador de Re anclado a TiO₂. En este capítulo se demuestra que la inmovilización del fotocatalizador mediante enlaces covalentes, resulta en un aumento de la estabilidad de un intermediario clave de reacción. Esta estabilización se traslada en una mejora de la eficiencia catalítica. En este capítulo también se estudia la naturaleza y cinética de los diferentes pasos en el mecanismo de reducción de CO₂ a CO.

En el *Capítulo 4* se estudia un sistema de reducción de protones basado en un fotosensibilizador de Re, un electrocatalizador de Ni y un reductor de sacrificio. En el capítulo se discute cual es el mecanismo detrás de la dependencia de este sistema con el pH. Los resultados del capítulo demuestran que mientras la transferencia electrónica entre los aniones del fotosensibilizador y el electrocatalizador es independiente del pH, la generación de aniones del fotosensibilizador y la función catalítica del electrocatalizador tienen dependencias de pH opuestas.

En el *Capítulo 5* se estudia un fotocátodo para la reducción de protones basado en una unión *p-n* entre Cu₂O y Al:ZnO con capas protectoras y catalíticas. Los resultados demuestran como la separación de cargas, y por tanto, el inicio de la fotocorriente están determinados por la unión *p-n*. Además, la capa catalítica actúa reduciendo la recombinación de cargas separadas y consecuentemente contribuye significativamente a conseguir altos rendimientos cuánticos. En este capítulo también se discute el mecanismo de reducción de protones y como la naturaleza del paso limitante tiene un gran impacto en la cinética de recombinación.

En el *Capítulo 6* se investiga el uso de TAS para estudiar materiales con altos índices de refracción y superficies de gran calidad. En este capítulo se estudian interferencias

ópticas que tienen lugar en el TiO_2 , el Cu_2O y en una célula de perovskita $\text{CH}_3\text{NH}_3\text{PbI}_3$. Los resultados demuestran como la interferencia óptica en estos materiales puede dominar el espectro temporal dificultando su interpretación. A pesar de eso, esta interferencia puede utilizarse también para obtener información sobre los cambios en el índice de refracción que tienen lugar en estos materiales después de la excitación con luz.

List of publications

1. “Solar H₂ generation with molecular catalysts self-assembled on dye-sensitised semiconductors.” Willkomm. J; Orchard. L.K; Reynal. A; **Pastor**. E; Durrant. J; Reisner. E; *Chem. Soc. Rev*, **2016**, 45,9
2. “Rate Law Analysis of Water Oxidation on a Hematite Surface.” Le Formal. F., **Pastor** E., Tilley S.D., Mesa C., Pendlebury S., Grätzel M.,Durrant ;J. Am. Chem. Soc, **2015**, 137,6692
3. “Unravelling the pH-dependence of a molecular photocatalytic system for hydrogen production.” Reynal A., **Pastor** E., Gross A.M., Selim S., Reisner E., Durrant J.; *Chem. Sci.* **2015**, 6, 4855
4. “Improving CO₂ to CO reduction catalysis through immobilisation of molecular Re catalyst on TiO₂”. Windle C.D., **Pastor** E., Reyanl A., Withwood A.C., Vaynzof Y., Durrant J.R., Perutz R.N., Reisner E. *Chem. Eur J.* **2015**, 21, 3746
5. “Interfacial charge separation in Cu₂O/RuO_x as a visible light drive CO₂ reduction catalyst.” **Pastor** E., Pesci F.M., Reynal A., Handoko A.D, Guo M., An X., Cowan A.J., Klug D.R., Durrant J.R., Tang J. *Phys. Chem. Chem. Phys.* **2014** ,16 , 5922.
6. “Efficient Light-driven oxygen generation not limited by the catalytic properties of the catalyst” Forcada F.L., Matheu R., **Pastor** E., Reynal A., Berardi S., Sala X., Llobet A., Durrant J., *In preparation*

7. “Two pathways identified in the water oxidation on anatase TiO₂-how the hole concentration dictates a change in the reaction mechanism.” Kafizas A., Ma Y., **Pastor** E., Pendlebury S; Mesa C., Le Formal F., Noor N., Ling M., Sotelo-Vazquez C., Carmalt J.C., Parkin P.I., Durrant J., *In preparation*
8. “Thin-film interferences in femtosecond transient absorption spectroscopy of semiconductors for solar energy conversion”. **Pastor** E., Dimitrov S., Stavrinou P., Lou J., Mayer T.M., Reynal A., Tilley D., Grätzel M., Durrant J., *In preparation.*
9. “Unravelling the effect of morphology and in the charge recombination kinetics of anatase and Rutile TiO₂”. *In preparation.*
10. “The role of the catalyst in a multi-junction photocathode based on earth abundant Cu₂O”. **Pastor** E., Le Formal F., Mayer T.M., Tilley D., Grätzel M., Durrant J., *In preparation*

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Chapter One

Introduction

A case for research into solar energy is made in this chapter. The concept of artificial photosynthesis and its challenges are explained. The key theoretical concepts and a review of the recent advances in the photochemical reduction of CO₂ and protons are introduced.

1.1. A case for research into energy sources

The world faces daunting problems of environmental and political nature. The large increases in global population,[1] and our strong reliance on natural resources to obtain food and energy are putting enormous strains on the planet. In addition, the difficulty in obtaining these resources is a constant source of conflicts and inequality across the world. With limited resources, whether this is due to scarcity or to exploitation limitations, the status quo is unlikely to improve.[2, 3] Energy and energy provision are at the heart of the problem, but they can also be drivers of a solution. Energy is the capacity to perform work and as such it is a means to prosperity and economic development. It is only through energy consumption that rapid economic development and improvements in life standard are achieved.[2]

The need to obtain resources, in order to maintain the quality of life, is to a great extent, behind the unfair distribution of wealth and a catalyst for conflicts.[4] The solution to these problems is apparent: access to energy must be available to all in a competitive way. The current provision of energy significantly relies on the use of fossil fuels and nuclear power. The latter presents increasing safety and technological challenges and will not be discussed here.[5] The former, on the other hand, presents exploitation problems because, albeit the constant findings of gas and oil, the extraction of crude materials is expensive and a source of problems.[4] Furthermore, the energy structure in developed countries and the economy built around it is optimised for the use of these two sources. It is, therefore, unlikely that wealthy countries will jeopardise their energy supply by favouring the access of less developed countries to this energy market, with the consequent impact on demand and cost that this would entail. Renewable energies, as a whole, seem the most suited solution.[5]

The development of an energy infrastructure to exploit natural resources such as wind and sun in areas where currently no infrastructure exists is challenging.[6] In many, if

not all, cases this enterprise is not economically viable for poor regions. Consequently, those countries that currently have an energy sector must lead the change. Allowing less developed countries to produce energy and exploit renewable natural resources, in order to improve their economy and their life standard, might prove very rewarding for all. For start it will reduce the levels of inequality and poverty. In addition to this, it might also help control the population growth in the less developed countries and therefore help mitigate the impact that human existence has on the environment, both through the use of energy sources and land to grow food. Developed countries can also directly benefit from this. Firstly from the technological and industrial point of view it would encourage research and technological improvements. These could help reduce production costs so that the upgrade of their energy infrastructures to more a sustainable system becomes attractive and viable. Economically it would allow the development of new industrial and economic sectors. More importantly the existence of this sectors would be directly linked to the success of the less developed regions in developing and exploiting their energy sector. In other words, in developing their economies and their life standards. It is this mutual dependency that is likely to create a framework of cooperation and ultimately reduce conflicts. Beyond the economical benefits this author strongly believes that it is a moral responsibility of the developed countries, which constantly exploit natural resources to maintain their life standards, to aid the less developed regions to develop a long-lasting energy and economic sector. In this context the use of renewable energy sources are key to a sustainable and fairer world.

1.2. A case for solar energy

If we want develop an energy system capable of meeting the energy needs worldwide this system must rely on an abundant energy source. Furthermore, in order to minimise supply conflicts this source must be, to a large extent, available to all. Looking into nature for inspiration, the only source that supplies unlimited energy worldwide to sustain life is the Sun through the photosynthetic process. Indeed, the average solar energy incident at the Earth's surface is $\sim 120\,000$ TW.[2, 5] This largely exceeds our most demanding energy estimates (~ 43 TW in 2100).[5] Figure 1-1 provides a summary of the suitability of solar energy for our purpose. Solar energy can be harvested in four forms; namely as biomass, in solar concentrators,

solar thermal and in photovoltaic devices. The first, although useful in some regions, is not practical for large-scale application as it uses land valuable for food growth.[2] The other two rely on the conversion of solar energy into heat or electricity. The latter is very attractive as we are able to use and transport electric currents efficiently. Nonetheless electricity supply from solar energy must overcome the inherent intermittency of solar radiation. For this, batteries and methods of storing energy need to be used.[7] It is in these realms where solar-to-fuel conversion strategies can be useful.[8] Inspired in the photosynthetic process, the artificial storage of solar energy in the form of chemical energy would allow us to store and transport large amounts of energy efficiently.[9] Furthermore the use of sunlight to recycle industrial waste products such as CO₂, by converting it into other energy carriers, opens the possibility of maintaining key industrial processes that currently rely heavily on the supply of fossil fuels. In this author's opinion, solar energy and photocatalysis are the most reliable ways to create a sustainable global energy economy that reduces inequality within regions and minimises our impact in the planet's ecosystems.

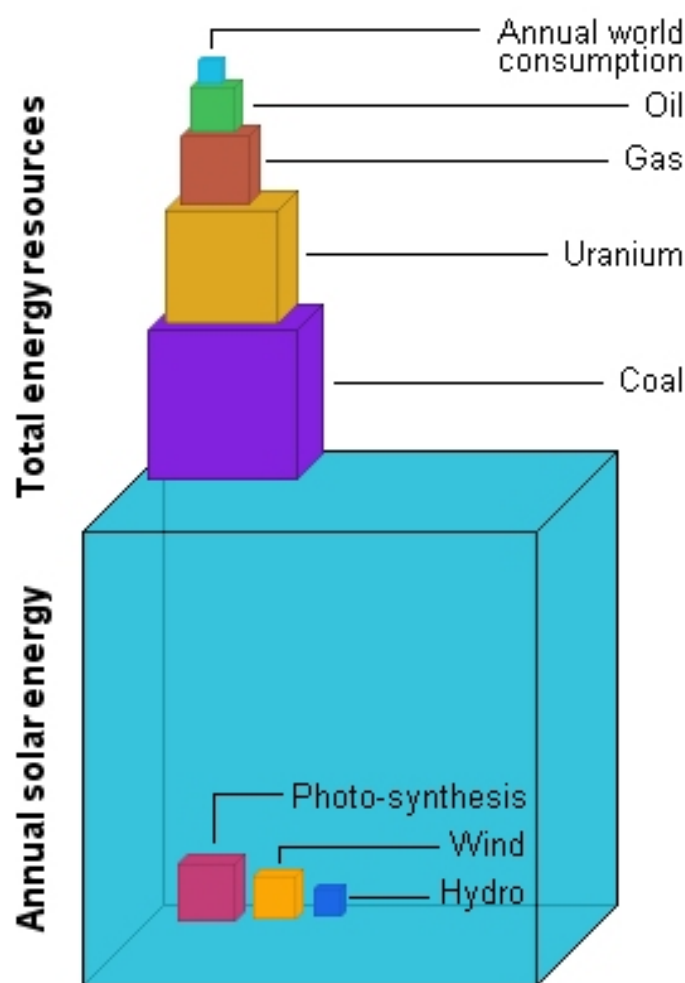


Figure 1-1 Diagram from the World Energy Council. The boxes in the top represent the approximate energy consumption and the estimated remaining energy sources. The bottom box represents the incident solar radiation. Inside this cube the energy obtained from photosynthesis and the energy that could be potentially extracted from wind and hydro energy are also represented.

1.3. Artificial photosynthesis

The storing of energy in the form of chemical bonds is currently achieved, at a global scale, in the photosynthetic process. Plants use solar energy to drive the synthesis of glucose from water and CO_2 . The same process can be artificially envisaged as a means to store energy for human consumption. For this purpose, the production of glucose is not practical; instead the generation of H_2 from water ($\text{H}_2\text{O}/\text{H}^+$) and/or liquid fuels such as methanol from CO_2 is a far more attractive alternative.[7]

Figure 1-2 shows the Frost diagram for Hydrogen, Carbon and Oxygen at pH = 7. The plot represents the Gibbs free energy against the oxidation number. In the diagram the most stable oxidation states appear in the bottom of the graph whereas the least stable appear in the top part. The slope of the line between two adjacent species represents the reduction potential for inter-conversion and, any specie (or intermediate) above this line is unstable with respect to disproportionation. The vertical offset of an intermediate, is associated to the overpotential for the conversion reaction; in other words, the additional energy, with respect to the reaction equilibrium potential, required to achieve the reaction with useful rates. Higher vertical offsets in the Frost diagrams are therefore indicative of processes with large activation energies.

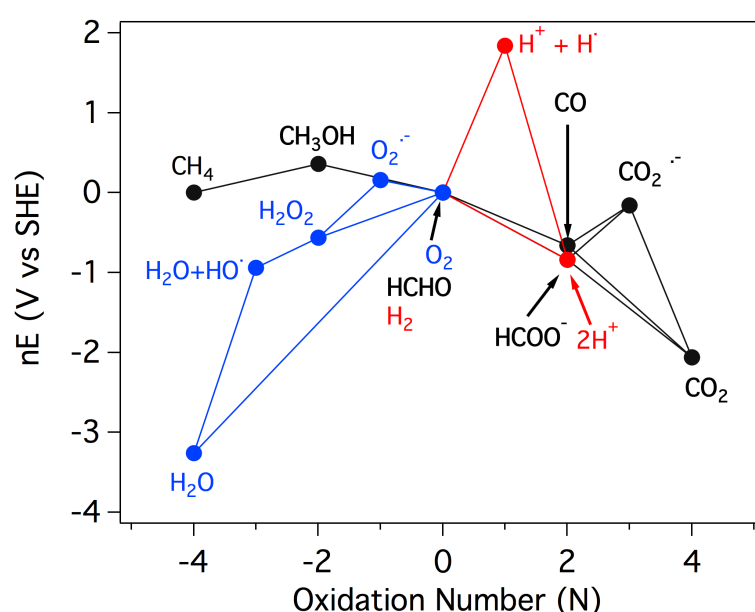
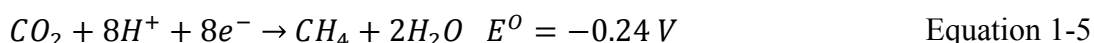
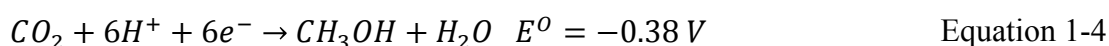
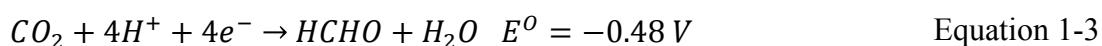
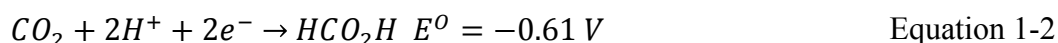
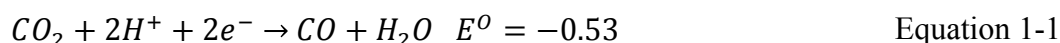


Figure 1-2 Frost diagram of Carbon, Hydrogen and Oxygen at pH 7. The potential values were taken from references: [10-12] The plot is a representation of the standard Gibbs Free energy against the oxidation number (N).

Both H_2O ($H_2O/2H^+$) and CO_2 are indispensable to sustain life on earth and are therefore intrinsically stable; consequently in the Frost diagram they are represented at the bottom of the graph. This indicates that the transformation of these energy-poor species into energy-rich fuels and energy carriers (H_2 , CH_4 , CO) is not a thermodynamically favourable process. Indeed, direct production of CO , $HCOOH$ or H_2 through two, one-electron steps may require the formation of $H^\cdot$ and $CO_2^{\cdot-}$. These are very energetic and unstable radicals and their high vertical coordinate in the Frost

diagram reveals that large energy requirements are associated with their generation, potentially resulting in large overpotential requirements for fuel synthesis.

In order to avoid these unstable intermediates catalysts are required. Catalysts can help stabilise high-energy intermediates, thereby lowering the energy barrier for the conversion process. For example, the generation of CO_2^- is not favoured due to the structural rearrangement needed to transform the linear CO_2 to bend CO_2^- . [13] The activation energy associated with this structural change can be reduced through the coordination of the CO_2 molecule to a metal surface. In the Frost diagram this is represented by lowering its coordinate of the intermediate towards the line linking the reactants and products. [14] Alternately, the catalyst can also provide a new route for the reaction. In the case of the reduction of CO_2 , a suitable catalyst might allow multiple electron transfers to be coupled with simultaneous proton transfers. This process is energetically more favoured than the one electron reduction as shown in the equations below (vs NHE at pH = 7) for the reduction of CO_2 . [13, 15] .



Efficient catalysts are, therefore, paramount to achieve the conversion of solar energy into chemical energy. But, in order to do so, the catalytic process must be coupled to a light absorption event. This is schematically represented in Figure 1-3 for a generic process. The solar-to-fuel conversion process is initiated by the photo-excitation of a light absorber. The photogenerated excited state must subsequently evolve into a charge separated state that drives the desired reactions via catalysis. It is noteworthy that the forward, fuel-generating processes (black arrows) are in direct competition with deactivation processes (red arrows). Therefore, in order to achieve efficient energy conversion, photocatalytic systems must be designed to favour the catalytic reaction whilst avoiding any deactivation path. [16, 17]

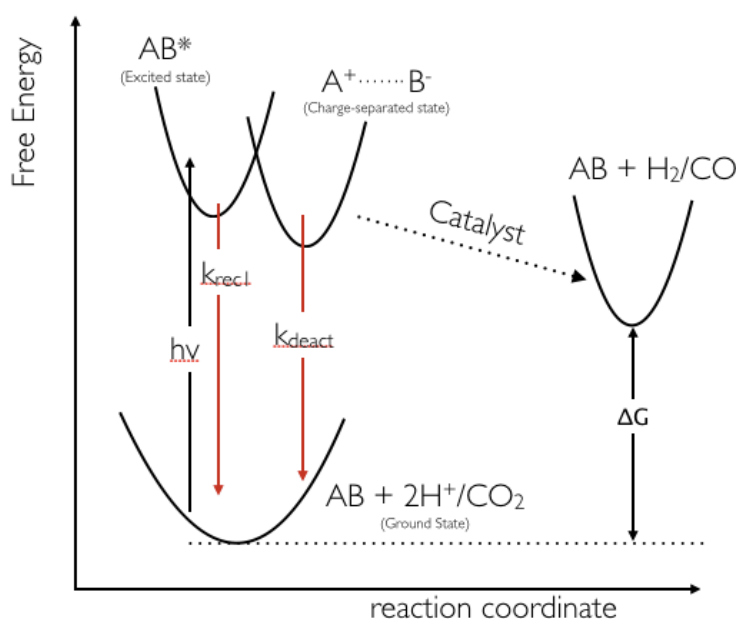


Figure 1-3 Schematic diagram of a light induced reaction. Upon excitation an excited state is generated, this evolves into a charge-separated state which drives the desired reaction with the aid of catalysts.

1.3.1. Catalytic approaches for solar-to-fuel conversion

Two types of catalysts are used in the conversion of solar energy into fuels: molecular catalysts and solid-state catalysts. The vast majority of molecular catalysts are based on transition metal complexes, whereas solid-state catalysts are usually semiconducting metal oxides and more recently organic based such as carbon nitrides.[18] Metallic catalysts are also often used alongside semiconductors in order to enhance their catalytic activity.[19]

Molecular catalysts can be advantageous compared to solid-state electrodes because: (i) they can sustain multiple oxidation states and proton-coupled electron transfers [13] and (ii) their selectivity can be easily tuned by ligand modifications; the ligands can also be chosen in order to have an active role in the catalysis, for example, by allowing an even distribution of accumulated reduction equivalents across the molecule and hampering deactivation reactions.[20, 21] Solid-state catalysts, on the

other hand, are typically rigid structures and their properties are difficult to modify. However, they are generally robust and the possibility to use them as fixed electrodes is technologically advantageous. Recently, the combination of molecular and solid-state catalysts to form a hybrid system is attracting increasing attention.[22] This combination allows, in principle, to harness the advantages of both type of catalysts.

In order to convert solar energy into chemical energy, a light absorber is required in the catalytic system (see for example Figure 1-4). Solid-state semiconductor materials are capable of absorbing photons with energy greater than their band gap, thereby initiating the photocatalytic process. The photoexcitation leads to the generation of photocharges, which can subsequently react with substrates such as CO₂ or protons (Figure 1-3). For molecular systems two routes are possible to drive light-initiated catalysis by:

- (i) coupling the catalyst with a light absorber (dye). This can be achieved with both individual components separately in solution or by chemically linking the molecules forming dyads.[23] The latter approach has the benefit of increased intramolecular electron transfer rates albeit being synthetically challenging.[23]
- (ii) using a molecular photocalysts, which simultaneously harvest light and catalyses the reaction of interest.[24]

In any complete photocatalytic system both oxidation and reduction reactions must take place. In a molecular homogeneous system this can be achieved by either directly linking the catalysts with a chemical bond or by using a redox mediator. [24] In heterogeneous systems this can be done by using redox mediators or connecting the electrodes via an external wire. Three overall strategies to achieve the conversion of solar energy into chemical fuels are described below. For clarity, only the cathode has been considered to absorb light. However, more complex combinations, including those where the anode is the light-absorbing unit, are also conceivable.

Molecular homogeneous catalysis: Figure 1-4 shows three possibilities to operate a molecular catalyst in homogeneous phase. In the first one the reduction catalyst (Cat(-)) is both a catalyst and a light absorber (a photocalyst).[24] Upon excitation the

redox mediator reductively quenches the excited state of the photocatalyst. The catalyst then drives the reduction of the electrolyte (for example, the reduction of CO_2 to CH_3OH). Simultaneously, the redox mediator is regenerated by oxidation of the oxidation catalyst ($\text{Cat}(+)$), which subsequently oxidises the electrolyte (for example, the oxidation of H_2O to O_2). In the second option, the redox mediator is replaced by a linker (a chemical bond) between catalysts and thus, forming a supramolecular structure. The excited state of the reduction photocatalyst ($\text{Cat}^*(-)$) is reductively quenched by the oxidation catalyst. Subsequently, each catalytic side drives the reduction or oxidation of the electrolyte. In the third approach a molecular dye is used as a light-absorbing unit. Upon light excitation of the dye, its excited state is reductively quenched by the redox mediator. The reduced dye (dye anion) then transfers an electron to the reduction catalyst that subsequently reduces the electrolyte. The redox mediator is simultaneously regenerated by the oxidation catalyst. An example of a homogeneous molecular catalyst based on the combination of a Ni electrocatalyst and a Ru dye is discussed in *Chapter 3*.

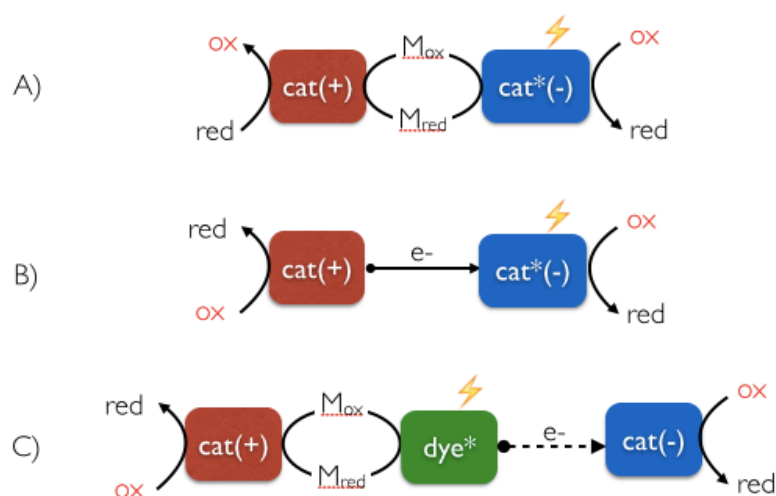


Figure 1-4 Schematic representation of three approaches for the solar-to-fuel conversion employing molecular catalysts in a homogeneous solution. In A) a reduction photocatalyst ($\text{cat}^*(-)$) is used alongside a redox mediator. In B) the reduction photocatalyst is linked to an oxidation electrocatalyst. In C) a molecular dye is used as a light absorption unit with the aid of a redox mediator.

Solid-State heterogeneous catalysis: Figure 1-5 shows a solid-state, semiconductor based photocatalytic system. Light excitation of the photocathode followed by charge

separation results in the accumulation of reduction equivalents (electrons) in the cathode. These can subsequently reduce the electrolyte, taking advantage of the inherent catalytic properties of the semiconductor material. Simultaneously, the cathode is regenerated by electrons flowing from the anode where the oxidation of the electrolyte takes place. In this case, the anode is a transparent semiconductor coated with metallic nanoparticles that catalyse the oxidation reaction. Catalyst overlayers are often used to enhance the catalytic performance of solid-state electrodes.[25] It is also possible to design a system in which both electrodes are semiconducting materials that absorb light. This is often known as a tandem cell.[26] An example of solid-State heterogeneous catalytic system based on a Cu_2O light absorber and a RuO_x catalyst overlayer is discussed in *Chapter 5*.

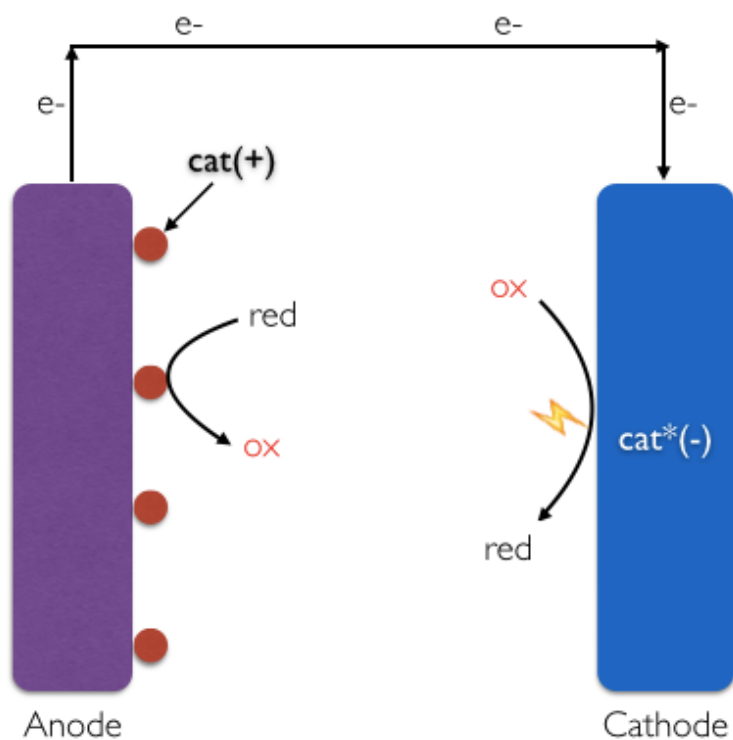


Figure 1-5 Schematic representation of a solid-state photocatalytic system. The cathode absorbs light and initiates the reduction of the electrolyte. In the anode side the oxidation of the electrolyte occurs in a metallic catalyst. The electrodes are connected via an external wire rather than a redox mediator.

Hybrid catalysis: Figure 1-6 shows a hybrid photocatalytic system combining solid-state electrodes and molecular catalysts. The catalysts are immobilised to the surface of a semiconductor that, in this design, acts only as an insert, high-surface area scaffolding structure.[27-29] The system operates like any of the homogeneous molecular systems described above using a redox mediator. This hybrid approach, often termed heterogenisation of molecular catalysts, has recently gained increasing attention. Hybrid systems offer the possibility of combining the flexible catalytic properties of molecular catalysts with the robustness and technological convenience of solid electrodes. They also increase the range of solvents in which to drive the catalytic reaction, as the molecules do not need to be dissolved. For water splitting this is important, as heterogenisation allows the use of non-water soluble catalysts. From the point of view of CO₂ reduction, the solvent choice is even more critical for other reasons. In pure water a strong competition with the proton reduction reaction might occur and, the speciation of CO₂ at different pH will affect the outcome of the reduction reaction.[30] Furthermore, the solubility of CO₂ in water is 6 to 7 times smaller than in non-aqueous solvents.[10, 29] However, some organic solvents might compromise the integrity of the catalyst and/or participate in the catalytic cycle. Heterogenisation of CO₂ reduction catalysts may avoid this key technological constraint.

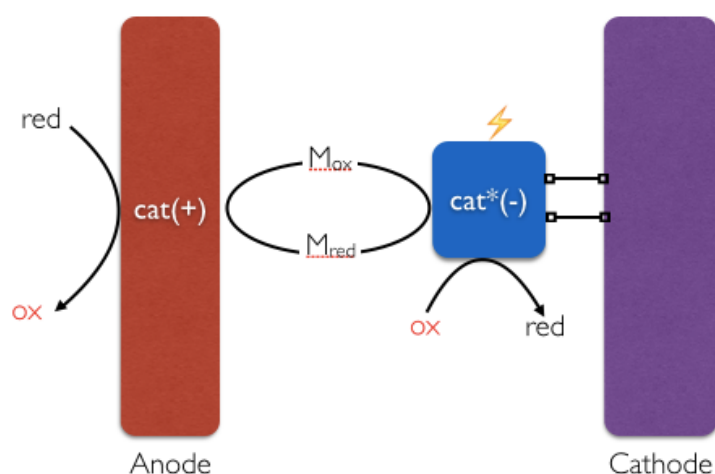


Figure 1-6 Schematic representation of a hybrid photocatalytic system. The reduction photocatalyst is covalently anchored to an inert electrode. A redox mediator is used to connect the anode and the cathode.

The systems described above are representative of the complete solar-to-fuel conversion systems discussed in the literature.[24] However, the properties of the oxidation and reduction catalysts are often better studied as individual electrodes rather than as part of a complete device. For that reason, most of the literature available often focuses only on one of the reaction (the oxidation or the reduction). In order to do so for molecular catalysis, the redox mediator is often replaced by sacrificial donors. This approach allows us to focus exclusively in the catalytic properties of one of the catalysts and hence study the factors limiting and controlling its function.

This thesis focuses on the study of photocathodes and their performance in catalytic reduction of protons and CO₂. Despite the importance of these reactions as the fuel-generating reactions, significantly fewer efforts have been dedicated to understand the factors limiting the performance of photocathodes and reduction photocatalysts, compared to photoanodes and oxidation photocatalysts. Large efforts, for example, have been dedicated to understand the electrocatalytic and photocatalytic oxidation of water using semiconductors, such as Fe₂O₃ or TiO₂, and molecular catalysts often based in Ru.[19, 31, 32] Despite the substantial synthetic efforts to develop efficient reduction catalysts, there is not yet an equivalent understanding of their physical properties.

1.4. Catalytic approaches for reduction reactions

In order to study the properties of reduction catalysts for light-initiated reactions three approaches are often used: (i) reduction photocatalysts with sacrificial electron donors, (ii) a combination of a dye and a molecular reduction electrocatalyst with a sacrificial electron donor and (iii) a photocathode in a Photo-Electrochemical Cell (see section 1.3). These three system designs are studied in this thesis.

Typically, sacrificial electron donors are based on organic compounds, such as Triethanolamine (TEOA), triethylamine (TEA), ascorbic acid (AA). Inorganic donors such as sulphide (S²⁻) and sulphite (SO₃²⁻) are also often used as electron donors.[33]

1.4.1. Requirements for Reduction catalysis

In order to achieve efficient reduction catalysis the catalyst employed must meet at least three requirements, beyond those expected of any catalyst:

- (i) **Stability:** they must be sufficiently robust to sustain the multiple reduction conditions and the release of products; they must also kinetically favour the desired reaction as opposed to deactivation paths.
- (ii) **Selective:** they must be selective for the desired reaction. In a complete device, for example, a proton reduction catalyst must selectively reduce protons rather than the O_2 generated on the counter electrode. Selectivity is particularly critical for the reduction of CO_2 . In water, this needs to compete with the reduction of protons. Furthermore, as shown in equations 1 to 5, even if the reduction of CO_2 is achieved the desired selectivity towards a specific carbon based product can be challenging. Most of the studies available for CO_2 reduction, both in electrochemical and photochemical systems, report a mix of products such as CO and formic acid.[29] So far, enzymes have shown the highest selectivity amongst CO_2 reduction catalysts.[12] Several studies have attempted to overcome this problem in non-biological systems through the rational design and synthesis of catalysts with the desired catalytic properties.[13] Hence, devising ways of controlling the exposed facets in solid-state catalysts and the redox properties of molecular catalysts is pivotal.[34]
- (iii) **Energetics:** The catalyst must have a redox potential more reductive than that of the redox reaction of interest.[19] This must be true for the multiple electron transfers that the catalyst has to sustain.

1.4.2. Photoelectrochemical cells for reduction reactions

The interface of a semiconductor and an electrolyte in a Photoelectrochemical cells (PEC) offers a technologically convenient way of achieving the conversion of solar energy into fuels. PECs have been used, for example, to generate H_2 , CO or MeOH

from water and CO₂. [29, 35] PEC have gained increasing interest in the recent years following the large advances in nanostructured materials which have allowed greater control over surfaces and interfaces. [26] For reduction purposes, PECs rely on the interface between p-type semiconductors with an electrolyte.

Semiconductors are characterised by a conduction band, a valence band, and a Fermi level or electrochemical potential (Figure 1-7A). When a semiconductor is brought in contact with a redox active electrolyte with an electrochemical potential, $-qE^0$, where E^0 is the Nerst potential of a redox pair, charges will flow across the interface until an equilibrium of the Fermi levels is attained. As a consequence, a p-type semiconductor in equilibrium with the electrolyte will normally have, an excess of negative charge in the electrode side and an excess of positive charges in the solution side (Figure 1-7B). This charge transfer results in a region, on both sides of the junction, where the distribution of charges differs from the bulk known as space-charge layer. In the semiconductor side, the depletion of majority carriers (holes) in the equilibration process results in a downward bending of the conduction and valence band across the depleted region. The electric field present in this region favours the transfer of electrons into the positively charged electrolyte. The energy difference between the valence band energy in the bulk (E_{VB}^b) and the valence band energy in the interface (E_{VB}) is known as the built in potential and determines the strength of the electric field. [19, 36, 37]

Under illumination with photons of energy greater than the band gap, electrons and hole pairs are generated perturbing the equilibrium condition. The new distribution of holes and electrons is described at any given time under non-equilibrium by the quasi-Fermi level of holes ($E_{F,p}$) and electrons ($E_{F,n}$) respectively. (Figure 1-7C). The splitting between the quasi-Fermi levels corresponds to the free energy generated by the semiconductor. Under conditions where no current flows, this difference is termed open-circuit potential or photovoltage and it determines the capacity of the semiconductor to drive light-initiated reactions. In order to achieve the reduction of protons (or CO₂), the quasi-Fermi level of electrons must be more reductive than that of the redox reaction of interest. In the same way, in order to achieve the oxidation of water, the quasi-Fermi level of holes must be more oxidative than the reduction potential of water. Hence, to drive the complete water splitting reaction, the free

energy needs to be at least equal to the energy required to split water (1.23 V).[19] In practice due to the slow reaction kinetics and the existence of deactivation (recombination) routes, an additional driving force is required to drive the reactions, this is known as overpotential. Few semiconductors can drive the unassisted splitting of water, as often the photovoltage or the quasi-Fermi level energy is not sufficient to drive the reaction. However, an advantage of PECs is that an external potential can be supplied to the cell to compensate the voltage not provided by the semiconductor/electrolyte junction. This extra energy can be provided by a solar cell. [26]

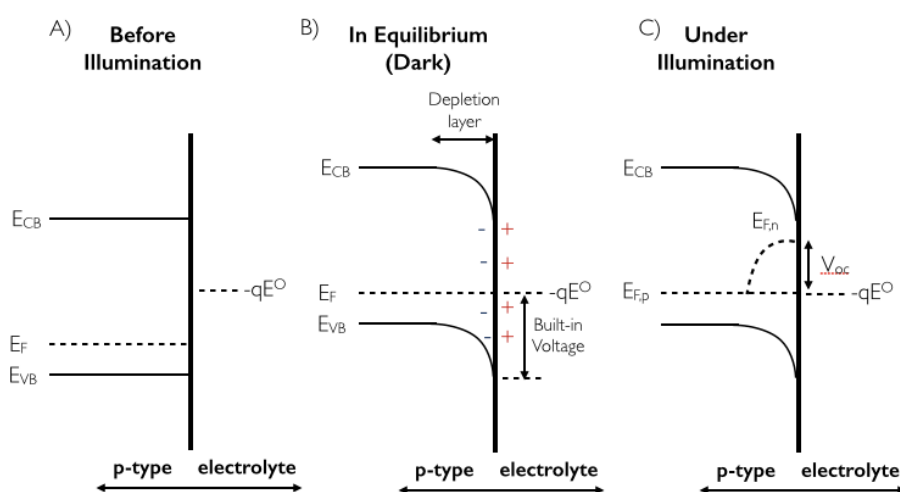


Figure 1-7 Energy band diagram of a p-type semiconductor in contact with an electrolyte with electrochemical potential $-qE^0$. In equilibrium an excess of negative charges accumulates in the semiconductor side resulting in the development of a built in potential and the bending of the bands. Under illumination the Fermi level is split into two quasi-Fermi levels, one for electrons and one for holes. The energy difference between the quasi-Fermi levels is the free energy provided by the semiconductor. Under conditions where no current flows this is known as open circuit voltage.

1.5. Assessing the efficiency of photocatalytic systems

The determination of the efficiency of solar-to-fuel conversion systems and of a figure of merit for photocatalysis is complicated and controversial. This is aggravated by numerous reaction conditions in which catalysts can be employed and the lack of

standardisation in the field of solar-to-fuel conversion. Nonetheless, generally the following parameters are used: (i) the Quantum Yield (QY), defined as the number of electrons stored in chemical bonds per incident photon; (ii) the Turnover Number (TON), defined as the cumulative number of moles of products produced per mole of catalyst and (iii) the Turnover Frequency (TOF) defined as the TON per unit of time (iv) the Faradaic efficiency which describes the catalytic selectivity of the system as the fractional number of redox equivalents converted into the desired product.[29]

In photoelectrochemical cells two parameters are of importance; (i) the photocurrent onset and (ii) the maximum current achieved. In order to understand these, it is convenient to imagine a system in which the limiting reaction takes place in the cathode. In this ideal system, the complementary oxidation in the anode is assumed take place without restriction. As described above, in order to drive the reduction of water, the quasi-Fermi level of electrons needs to be more reductive than the electrochemical potential of the H^+/H_2 pair and any additional required overpotential. If this condition is met, the electric field in the space charge layer will drive electrons towards the electrolyte. If the electrode is polarised by an external voltage source so that no band bending and, consequently no electric field develops, no net electron flow will take place. The applied voltage at which this occurs is that which compensates the built-in potential of the space charge layer and, is commonly known as the flat-band potential (V_{fb} , Figure 1-8). In an ideal PEC, where no overpotential under illumination exists, a reductive photocurrent will be monitored at applied potentials more reductive than the flat band. However, in systems where an overpotential exists under illumination, an energy needs to be supplied to initiate the reduction of protons. The applied potential at which a significant photogurrent is observed is known as the photocurrent onset. The difference between the photocurrent onset and the flat band potential is therefore a measure of the overpotential for the reaction. [18] In order to compare different photocathodes, it is useful to define the overpotential with respect to a certain current. In PEC for solar-to-fuel conversion, the overpotential is often defined as the difference between the flat band and the potential at which $\mu 1 \text{ mA cm}^{-2}$ is attained (this varies depending on the reaction under study).[38] The photocurrent onset, the overpotential and the flat band condition are depicted in Figure 1-8.

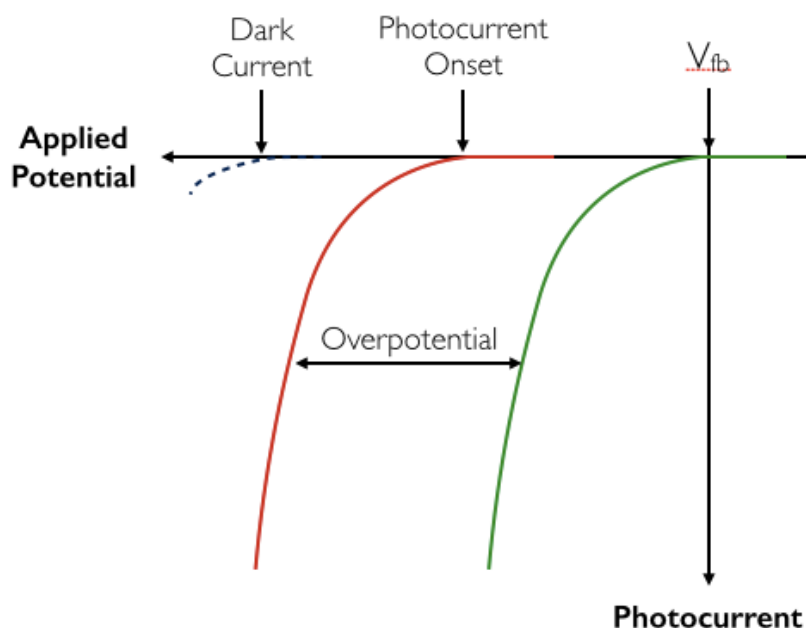


Figure 1-8 Photocurrent density versus applied potential of an ideal photocathode (green line) and a photocathode where overpotential exists (red line). Also shown the current obtained in the dark (dashed)

1.6. Examples of photocatalytic systems for CO₂ and Proton reduction

The reduction of protons, and specially the reduction of CO₂, are complex reactions, as it has been previously discussed. In order to achieve these reactions, flexible and versatile catalysts are needed.

1.6.1. Proton reduction

Up to date the benchmark electrocatalysts for H₂ evolution are based on noble metals such as Pt or enzymes like hydrogenases.[14, 35, 39-43] Such systems, despite being highly efficient, have serious disadvantages hampering large-scale applications such as their fragility (specially that of enzymes) or low abundance in the Earth's crust (eg. that of Pt).[44] To address this issue, synthetic efforts have focused on the design of H₂ evolution molecular catalysts based on earth-abundant elements such as Fe,[45-48] Co,[49-52] Ni,[42, 53-57] Mo,[58-60].[61]. Amongst them, Fe,[45, 47, 62] and Ni,[56, 57, 63, 64] in particular, have been extensively explored for photoelectrochemical applications.

Efficient proton reduction has also been achieved in PEC based on p-GaInP₂ and GaAs,[65] or p-InP,[66] and more recently on p-type Si.[67] However, the use of PECs has several engineering problems associated with it, such as the separation of products or the corrosion of the electrodes with time. One of the most important issues though, is the need to use abundant materials in order to be suitable for large-scale applications.[68] This makes PECs based on InP or GaAs less attractive despite their promising efficiencies. Recently, Cu₂O has emerged as a promising semiconductor solar-to-fuel conversion.[35] This metal oxide absorbs visible light and has suitable energetics for the reduction of protons and water but, like many other materials with similar properties, it is intrinsically unstable. Nonetheless, advances in synthetic methods have permitted some overcoming of these limitations,[69] leading to the development of Cu₂O photocathodes with impressive performances and stabilities under operation conditions.[70]

Recently, increasing research efforts are focusing in the so-called hybrid systems combining molecular catalysts and solid-state electrodes. Molecular proton reduction electrocatalysts, specially those based on Ni and Co, have been immobilised on the surface of photoelectrodes such as GaP,[71] as well as dye-sensitised TiO₂[42] and NiO.[72, 73] These systems are emerging as alternatives to homogeneous systems although they are still relatively unexplored.[22]

1.6.2. CO₂ reduction

Like the reduction of H₂ the photoelectrochemical reduction of CO₂ can also be achieved using semiconductors, such as p-type Si, CdTe, InP, GaAs, GaP, Cu₂O n-type TiO₂. [29, 34, 74] However, all these systems suffer from poor selectivity producing mixtures of C-based products from CO₂, as well as H₂ from proton reduction. High selectivity and efficiencies have been achieved combining enzymes (carbon monoxide dehydrogenases) and molecular dyes, however these systems are too fragile and their operation conditions are too restrictive for any large-scale application.[75] Due to these limitations, most of the efforts have focused on the use of catalysts based on transition metal complexes. These catalysts are often used in two ways: by combining the catalyst with a light absorber (dye) or by using molecules that

are light absorbers and catalysts simultaneously (photocatalysts). Amongst the first type, catalysts based on earth-abundant Ni and Co have been investigated. Macrocyclic Ni(cyclam) and Co(cyclam), for example, have been shown to selectively reduce CO₂ to CO.[76, 77] However, these catalysts generally perform better as electrocatalysts than as part of a photocatalytic system. [78]. Poor intermolecular electron transfer kinetics between the dye and the catalyst units has often been suggested to hamper the catalytic reaction and to be detrimental for the stability of the system.[79] One strategy to overcome these problems is the direct binding of the catalyst and the sensitiser via covalent bonds to build a dyad. In this context, most of the studies have focused on supramolecular dyads of Ni and Re.[13] Although the activity of these systems is often enhanced compared to the bimolecular approach, the design of the molecules is synthetically challenging, making them less attractive.

On the other hand, amongst molecules that act simultaneously as the light absorber and catalyst (i.e. molecular photocatalysts), most of the work has focussed on metallomacrocycles, metalloporphyrines and Re complexes.[15, 21, 80] Porphyrines have excellent light absorption properties, however their catalytic performance is low. Re complexes, on the other hand, are both good light absorbers and catalysts.[23] Rhenium bipyridine tricarbonyl complexes, in particular, have been extensively studied due to their high selectivity for the production of CO from CO₂. However, these photocatalysts suffer from poor photostabilities. Efforts to improve this, as well as the overall efficiency have focused on the development of supramolecular dyads and the heterogenisation of inert surfaces.[81] Despite large synthetic efforts dedicated to the development of CO₂ reduction catalysts, efficiencies still remain low and long-term stability is elusive.

1.7. Kinetics of solar-to-fuel conversion

In summary, the storage of solar energy in the form of chemical bonds is extremely challenging. The catalysts employed must be selective for a specific reaction, they must be stable in order to sustain multiple electron transfers and finally they must be efficient. A key factor behind these requirements is the kinetics of the catalytic process. Overall, the kinetic competition between the forward, fuel forming reactions,

and the recombination reactions controls the performance of the overall catalytic system. On one side, slow catalytic reactions hamper the desired reaction by favouring undesired side processes such as the reaction with other substrates and/or deactivation pathways. On the other hand, fast dominating recombination reactions often lead to low quantum yields and low solar-to-fuel conversion efficiencies. Therefore, understanding and controlling, kinetic competition between catalytic reactions and recombination or deactivation processes is fundamental to the performance of solar-to-fuel conversion systems. [16]

In molecular systems, the generation of a specific intermediate often controls the catalytic yield. In systems combining a molecular dye and a catalyst, this process can be limited by the electron transfer kinetics from the photoexcited dye to the catalyst.[13, 17] Fast recombination of the dye's excited state will lead to low transfer yields. This reaction can be limited by the encounter of both molecules in the bulk of the solution or by the energetics of the reaction. These problems are further aggravated by the need to accumulate 2 or more reduction equivalents. For example, the 2-electron reduction of a cobaloxime H_2 evolution catalyst by a Ruthenium dye, has been found to be limited by the electrochemical potential of the catalyst. In this system, the second electron reduction is disfavoured energetically compared to the first electron reduction. This hampers the accumulation of enough intermediates to drive the reduction of protons efficiently.[82]

In systems based on semiconductor/electrolyte junctions, the capacity of the system to drive the desired reaction is controlled by the photovoltage of the system; namely the splitting between the quasi-Fermi levels. The latter depends on the concentration of carriers and therefore is controlled by the kinetics of the system. Figure 1-9 shows the multiple reactions that can occur in a semiconductor PEC at open circuit. Upon light excitation, the electric field drives the electrons towards the interface where they can be transferred to the electrolyte, while holes are driven away from the interface. In direct competition with this process, electrons and holes can recombine (i) via trap states at the surface; (ii) in the bulk of the material or (iii) directly from the space charge layer. Holes can also escape the interfacial potential barrier and be transferred to the electrolyte. If the recombination reactions are not sufficiently suppressed the

photovoltage generated by the semiconductor will be reduced, consequently decreasing the driving force for the desired reaction. [32]

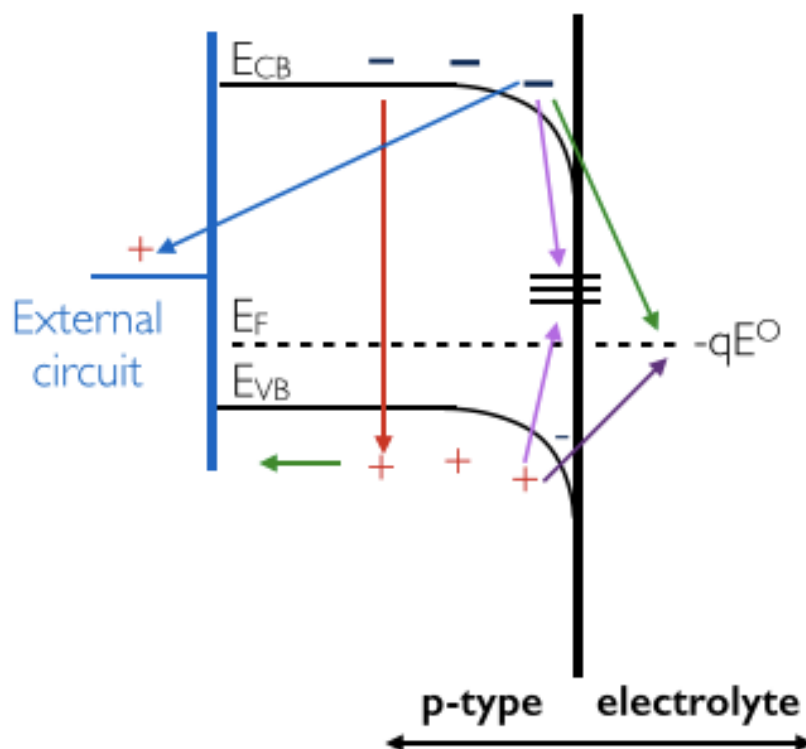


Figure 1-9 Competing reaction occurring in a p-type semiconductor after photoexcitation. The transfer of electrons to the electrolyte and extraction of holes through the external circuit (green arrow) competes with the recombination of charges via trap states (purple arrow), bulk recombination (red arrow), the transfer of holes to the electrolyte (dark purple arrow) and the recombination of extracted holes with electrons in the space charge layer (blue line)

Often it is possible to reduce the impact of recombination reactions by synthetically modifying the system or tuning the operation conditions. Recombination via surface states can be significantly suppressed by passivation of these states with a thin insulating layer; this layer must be sufficiently thick to protect the material but thin enough to allow tunnelling of charges to the electrolyte.[69] For example thin Al_2O_3 coating layers have been shown to reduce surface recombination on Fe_2O_3 electrodes.[83] Bulk recombination and back electron hole recombination can be suppressed by increasing the width of the space charge layer and thus, increasing the energy barrier for recombination.[84] This has previously been achieved in electrodes

for solar-to-fuel conversion by (i) applying an external bias,[84] by (ii) using additive molecules that help tune the energy bands [69] and by (iii) anchoring co-catalyst to the semiconductor.[85] In chapter 5 a solid-state photocathode for proton reduction is studied and the different routes to reduce the impact of recombination reactions are explored.

It follows from the discussion above that understanding the mechanism through which recombination reactions take place, as well as the mechanism of the catalytic reaction are fundamental to the development of efficient solar to fuel devices. For this purpose Transient Absorption Spectroscopy is attracting increasing attention. TAS allows the monitoring of photocatalytic, short-lived reaction intermediates which cannot be studied by steady state absorption spectroscopies. Using TAS it is possible to study the kinetics of intermediates from the femtosecond to seconds timescale and hence, this technique is most relevant for the study of solar-to-fuel conversion systems in which recombination reactions and catalytic reactions can take place at very different timescales.[22]

1.8. In this thesis

This thesis aims to investigate the reactions kinetics of intermediates in order to understand their deactivation routes as well as their role in the catalytic process. Transient Absorption Spectroscopy in combination to other electrochemical techniques is used for this purpose. The systems studied are:

- (i) A Re molecular photocatalyst for CO₂ reduction.
- (ii) A homogeneous system from proton reduction based on a Ru dye and a Ni electrocatalyst.
- (iii) A multi-junction solid-state proton reduction system based on p-Cu₂O with protection and catalytic layers.

The goal of this thesis is to understand what are the key factors behind the competition between recombination (deactivation) reactions and the catalytic reaction. Specifically it aims to:

- 1) **Understand the effect of surface immobilisation of molecular photocatalysts on the kinetics of reaction intermediates.** Despite the increasing interest in hybrid systems for solar-to-fuel conversion, little information is available in the literature about the mechanism by which the use of semiconductor scaffoldings can improve the stability and performance of solar-to-fuel conversion systems.
- 2) **Understand the effect of pH in the kinetics of electron transfer in a homogeneous photocatalytic systems.** Many systems have been reported in the literature showing strong pH- dependent activity however, little is know about the origins of this dependency. Understanding how pH can affect the kinetics and performance of systems can help tailor the design of dyes and electrocatalysts.
- 3) **Identify of the optical signals associated with electrons of a state-of-the art photocathode for proton reduction based on abundant Cu₂O.** The kinetics and accumulation of electrons under operation conditions is of great interest as they are responsible for the reactivity with protons. This information is not available in the literature as Cu₂O electrodes suffer from poor stability in the absence of protective layers.
- 4) **Elucidate the role of the buried p-n junction in the Cu₂O photocathode.** This junction has been suggested to be responsible for the outstanding performance of this system however little is know about it. Understanding its role in the catalytic process can help guide the design of other multi-junction photocathodes.
- 5) **Elucidate the role of the multi-junction structure and the catalyst in the charge carrier dynamics of the Cu₂O photocathode.** It is important to understand whether the nature of the catalyst and the overlayers have an impact on the separation and recombination of charges and to what extent these affect the proton reduction catalysis. This is important in order to tailor the fabrication of multi-junction electrodes to specific needs.
- 6) **Elucidate the ultrafast carrier recombination kinetics in Cu₂O. In order to do this, the impact of optical interference effects in TAS needs to be studied.** Understanding the kinetics of recombination of charge carriers in Cu₂O is key to improve the performance of Cu₂O based electrodes. For this purpose, TAS can be used. However, TAS measurements of are susceptible to

optical interference effect. In order to define the extent of information regarding charge carrier kinetics we can extract from a TAS experiment, first it is necessary to address the influence of any optical interference effects. Understanding of these phenomena, the limitations they impose and the new information they can provide is key to understand transient absorption data and ultimately the kinetics of charge carriers.

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Chapter Two

Experimental Methods

The main experimental techniques employed in this thesis: TAS (Transient Absorption Spectroscopy), PIA (Photo-Induced Absorption Spectroscopy), as well as, other standard characterisation methods are described in this chapter.

2.1. Materials and sample preparation

In this thesis two molecular catalysts have been employed (i) $[\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}]$ as a CO_2 reduction catalyst and (ii) $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{PhCH}_2\text{P}(\text{O})(\text{OH})_2}_2)]$ as a proton reduction catalyst. Details about these catalysts can be found in *Chapters 3* and *4* respectively. In addition to this, in the thesis, solid-state materials based on Cu_2O , TiO_2 and a $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite have been employed. Details on these samples can be found in *Chapters 5* and *6* respectively. The sample preparation conditions and providers are described in each chapter.

2.2. Transient Absorption Spectroscopy (TAS)

The main experimental technique employed in this thesis is Transient Absorption Spectroscopy. The first part of this chapter discusses the interaction of light and matter and gives a description of this technique.

2.2.1. Interaction of light and matter

When a sample is illuminated with a light beam, the intensity of this incident beam is often attenuated after crossing the sample. The processes contributing to the attenuation are:

- (i) *Absorption*, when the frequency of the incident beam resonates with a transition from a ground to excited state of the sample. Part of this absorbed intensity is lost as heat or emitted at lower frequencies
- (ii) *Reflection* from internal and external sources
- (iii) *Scattering* in multiple directions due to inelastic and elastic processes.

Experimentally, it is found that the intensity of a light beam traversing a material of thickness dx is:

$$dI = -\alpha I dx \quad \text{Equation 2-1}$$

Where I is the light intensity and α accounts for the amount of reduction caused by the nature of the material. If there is negligible scattering, α is called *absorption coefficient*. The integration of the above equation is known as the Lamber-Beer law and relates the incoming light intensity I_o (excluding reflection loses) to the thickness and properties of the material:

$$I = I_o e^{-\alpha x} \quad \text{Equation 2-2}$$

The absorption coefficient is related to the transition between two energy states of population N_1 and N_2 by:

$$\alpha = \sigma(\nu)(N_1 - N_2) \quad \text{Equation 2-3}$$

Where $\sigma(\nu)$ is the frequency dependant transition cross section, which accounts for the probability of the transition. For low intensity irradiations $N_2 \ll N_1$, consequently the absorption coefficient is proportional to the population density of the lowest energy state.

$$\alpha = \sigma(\nu)N_1 \quad \text{Equation 2-4}$$

Experimentally, it is possible to directly measure the transmission of a sample $T = I_t/I_o$ where I_t is the transmitted light; the reflectivity $R = I_r/I_o$ where I_r is the reflected light and the absorbance $A=1-T$. The absorbance of the samples can also be measured from the transmission as $A = OD = -\log (T)$.

2.2.2. Principles of TAS

Transient Absorption Spectroscopy is a powerful technique to study the interaction of light mad matter. It was first developed by Porter in 1950 to study the reactivity of free radicals, the concentration of which was too small to be investigated by direct methods, such as absorption spectroscopy. In a TAS experiment the photochemical system is excited with a short light pulse ('pump') and the resulting changes in optical density are monitored following the transmission of a second beam of light ('probe'), which is delayed by a fixed time relative to the pump. The technique relies of the fact

that the excited state and the transient states generated after excitation have an absorption of their own which can be monitored at specific wavelengths. In a direct absorption spectroscopy experiment, the sample is continuously excited and consequently the long-lived intermediates dominate the population masking any short-lived intermediate. However, under short-pulsed excitation it is possible to monitor both fast and long-lived intermediates.

The original technique developed by Porter, termed flash-photolysis, employed a continuous light beam as probing light. In this set up the time resolution of the system is only limited by the response time of the detection electronics and hence it is limited to a few nanoseconds. In order to monitor faster reactions and achieve femtosecond resolution, a pump-probed method was developed in which both the excitation and the probe sources were pulsed. In this set-up the time resolution is determined only by the width of the pump and the probe pulse.

In this thesis both a flash-photolysis and a pump-probe set up have been employed. The first was used to monitor the kinetics of photospecies in the microsecond to second timescale, whereas the later was used to access the femtosecond to nanosecond timescale.

2.2.3. Calculating the change in optical density (ΔOD)

After photoexcitation the initial absorbance or optical density of a sample (OD_o) will change finite a amount ($\Delta OD(t, \lambda)$) due to the photoreaction, hence the total absorbance of the system is:

$$OD(t, \lambda) = OD_o(\lambda) + \Delta OD(t, \lambda) \quad \text{Equation 2-5}$$

The intensity of the transmitted light after excitation is related to the intensity before the pulse (I_{in}) and the absorbance of the sample by

$$I(t, \lambda) = I_{in}(\lambda)10^{-OD(t, \lambda)} \quad \text{Equation 2-6}$$

Rearranging the two equations we have that:

$$I(t, \lambda) = I_{in}(\lambda)10^{-OD_o(\lambda) - \Delta OD(t, \lambda)} \quad \text{Equation 2-7}$$

$$I(t, \lambda) = I_{in}10^{-OD(\lambda)}10^{-\Delta OD(t, \lambda)} \quad \text{Equation 2-8}$$

Thus:

$$\Delta OD(t, \lambda) = -\log \left(\frac{I_o}{I(t, \lambda)} \right) \quad \text{Equation 2-9}$$

Where $I_o = I_{in}10^{-OD(\lambda)}$

$$\Delta OD(t, \lambda) = -\log \left(1 + \frac{\Delta I(t, \lambda)}{I_o(\lambda)} \right) \quad \text{Equation 2-10}$$

Equation 2-10 points out that there is no need to monitor the absolute value of the transmitted light but only the relative change. This is convenient since the detection signal, namely the voltage drop across the photodiode $\Delta V(t)$, is proportional to the light intensity:

$$\frac{\Delta I(t, \lambda)}{I_o(\lambda)} = \frac{\Delta V(t)}{V_o} \quad \text{Equation 2-11}$$

where, V_o is the voltage drop before the excitation.

Hence:

$$\Delta OD(t, \lambda) = -\log \left(1 + \frac{\Delta V(t)}{V_o(\lambda)} \right) \quad \text{Equation 2-12}$$

2.2.4. Contributions to the TAS signal

The excitation of a sample from their ground state to an excited state will cause a change in the optical density. In a TAS experiment this change will appear as:

- (i) A negative signal, corresponding to a decrease in absorbance ($\Delta OD < 0$) due to the loss (depopulation) of the ground state following excitation. Stimulated emission will also appear as a negative change in optical density.
- (ii) A positive signal, corresponding to an increase in absorbance ($\Delta OD > 0$) due to the appearance of a new absorption band following excitation (excited state absorbance)

2.3. The TAS set –up

2.3.1. Flash-photolysis

The microsecond-to second measurements were conducted using a home-built system (Figure 2-1). The samples were irradiated with an laser pulse (< 10 ns) from an Nd:YAG laser (Big Sky laser Technologies ULTRA CRF system) which provided the third harmonic excitation (355 nm). To achieve wavelength tunability a commercially available tuneable OPO (Opoletter) pumped with a Nd:YAG laser was employed. A liquid light guide (0.5 cm diameter) was used to direct the excitation to the sample. The probe source was a 100W Bentham IL tungsten lamp. The probe wavelength was selected using a monochromator (OBB-2001, Photon Technology International) placed in front of the sample. The change in transmission after excitations was recorded using a Si photodiode (Hamatsu S3071), the signal output of which was electronically amplified (Constronics amplifier) and recoded in an oscilloscope (Tektronics TDS 2012c) and a DAQ card (National Instruments USB-6211). The

decays reported in this work are normally the average of 100 to 1000 laser pulses, unless otherwise stated. The data was processed using software based on Labview.

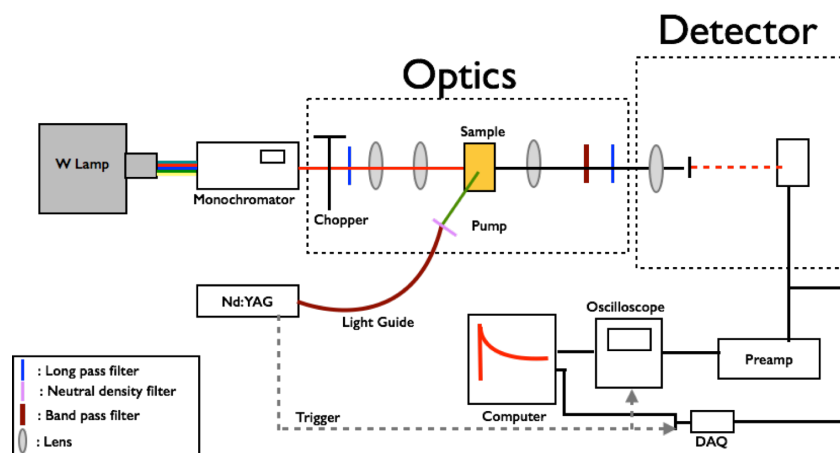


Figure 2-1 Schematic representation of the Flash-Photolysis system employed in this thesis to monitor transient changes in optical signal in the microsecond to second timescales

2.3.2. Pump-Probe

The femtosecond to nanosecond measurements were conducted using a commercially available system (Figure 2-2). The system composes a regenerative amplified Ti:sapphire laser (Solstice Spectra-Physics) and a Helios spectrometer (Ultrafast systems). The former generates 92 fs width, 1 kHz 800 nm pulses which are used to (1) pump Transient Optical Parametric Amplifier (TOPAS, spectra-physics) in order to generate the pump pulse (blue path) and (2) generate visible or Near-IR probe light using a Ti:Sapphire crystal (red path). The final pump wavelength is selected via a frequency mixer (NirUVis, Light Conversion). The probe is delayed with respect to the pump using a motorised translational stage. A 500 Hz (2 ms) synchronized chopper is used to block alternative pulses. The change in absorbance is calculated from adjacent blocked/unblocked pulsed. The transmitted probe beam is focused into a fibre-optic-coupled multichannel spectrometer (CMOS for visible and InGaAs for near IR). The time zero (t_0) is defined as the half-amplitude of a step rise.

The time resolution of the pump-probe experiment is only optically limited as the measured parameter is the energy of the transmitted probe pulse. The average instrument response function is 200 fs.

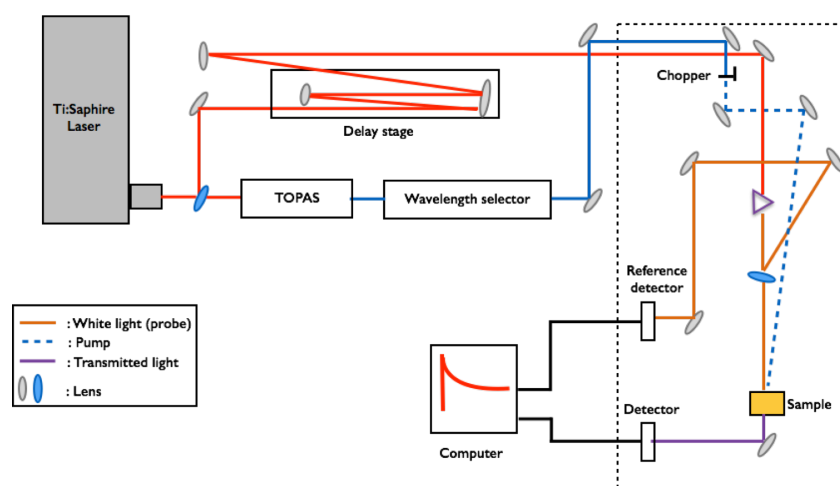


Figure 2-2 Schematic representation of the Pump-Probe system employed in this thesis to monitor transient changes in optical signal in the femtosecond to nanosecond timescales

2.3.3. Photo-Induced Absorption Spectroscopy (PIA)

The Flash-Photolysis set-up was modified to monitor the change in optical density (ΔOD) during and after continuous illumination of a sample. The aim of this modification was to be able to monitor small changes in absorbance due to the accumulation of phospecies under constant irradiation like sunlight illumination. For that purpose, the pump source of the flash-photolysis experiment was replaced by a 365 nm LED. The long light pulses were generated using a frequency generator (TG300, Thurlby Thandar Instruments) set up to generate a 5V square wave of (typically) 0.09Hz which triggered a MOFSET (STF8NM50N, STMicroelectronics), the LED power supply (QL564P, TTI), the oscilloscope and the DAQ card used to measure the optical signal. A diagram of the set-up is shown in Figure 2-3.

In this work, PIA was employed to study a photocathode material in PEC cell, in order to measure the accumulation of electrons at the semiconductor electrolyte interface. For such study it was important to simultaneously monitor the photocurrent generated by the illumination source. This was achieved by measuring the voltage change across a resistor (98 Ohm or 9.8 kOhm) using the oscilloscope.

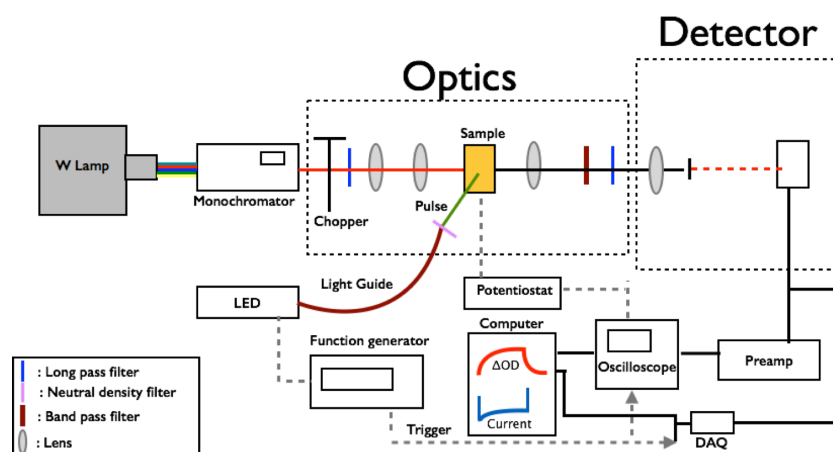


Figure 2-3 Schematic representation of the PIA system employed in this thesis to monitor transient changes in optical signal and current under continuous illumination.

A typical PIA signal is shown in Figure 2-4. At t_0 continuous illumination starts. This results in an increase in the amplitude of the signal until a steady state is reached. This increase corresponds to the accumulation of species (e.g. excited states, electrons, holes) under illumination. A steady state condition is reached at time t_m , when the rate at which the excited state is generated matches that at which it is consumed. Such consumption might be due to recombination or due to reaction with the electrolyte. The amplitude at t_m is a probe of the population of photogenerated species under steady state conditions and consequently it might be wavelength dependent. By recording the amplitude at t_m at different wavelength it is possible to obtain the steady state spectra of the excited state and therefore elucidate its composition.

At t_f the light is turned off. In this instant the generation reaction is interrupted and the subsequent signal decay corresponds exclusively to the consumption of the excited state by either recombination or reaction with the electrolyte.

If the process studied is photoelectrochemical in nature it is possible to measure the photocurrent and the optical signal simultaneously. Figure 2-4B shows the photocurrent change measured alongside the PIA signal of Figure 2-4A. In this case upon illumination (t_0) a cathodic current is monitored indicating that a reduction is taking place in the photocathode. Immediately after illumination (t_i) a spike of current might occur resulting in a photocurrent decrease. This can be understood as in terms

of an overlap between the dominant cathodic current and a small anodic current due to an oxidation process. This can be indicative of an initial recombination process (for example between electrons in the material and extracted holes). After this process a steady state is reached once the rate of generation matches that of consumption due to recombination or reaction. When the light is turned off (t_f) a change in the current direction might occur resulting in an anodic current. An anodic current corresponds to the predominance of an oxidation process. Consequently the decay at t_d can be indicative of the recombination of accumulated species with extracted charges. The integration of the photocurrent transient provides evidence of the number of charges involved in the electrochemical process. Further information on the interpretation of transient photocurrent measurements can be found in references [1] and [2].

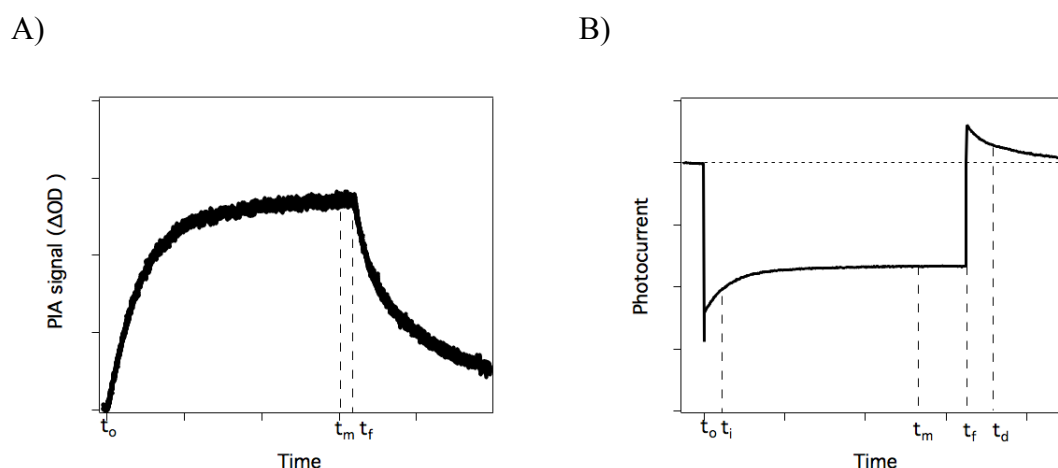


Figure 2-4 A) Typical PIA signal obtained after illumination of a sample with a continuous light pulse of duration t_f . The signal reaches a steady state at t_m . B) Typical Photocurrent change, for a photocathode, measured simultaneously with the PIA signal.

2.4. Time-Correlated Single Photon Counting (TCSPC)

TCSPC is a time-resolved fluorescence technique, often used to monitor the fluorescence of a sample after photoexcitation in the nanosecond timescale. As with the changes in optical density the fluorescence is proportional to the population of the

excited state, hence the measurement of its kinetics provides useful information about photochemical reactions. In this work TSPC were performed using Horiba Jobin Yvon TXB Fluorocube system. A 404 nm laser was employed as excitation source with a repetition rate of 100 kHz (10 μ s). The photoluminescence decays of films were done air whereas solutions were N₂-Purged prior the measurement. . The instrument response at Full Half Maximum was 200-250 ps.

2.5. Steady State Absorption and Photoluminescence Spectroscopy

Transmission and specular reflectance of the samples were measured with a UV-VIS spectrometer (Perkim-Elmer Lamda-25) and an integrating sphere (Shimadzu). Photoluminescence spectra were measured with a Horiba Jobin Yvon (Fluorolog-3) at room temperature. See individual chapters for excitation details. The PL data presented in this work has been corrected for the number of photons absorbed unless otherwise stated.

For reference, an excellent account of spectroscopic methods can be found the book: “*Optical Spectroscopy: Methods and Instrumentations*” by Tkachenkp (Elsevier).

2.6. Photoelectrochemical set-up

In order to study the catalytic properties under applied potential of only one of the electrodes of a PEC, a 3-electrode set up was employed (Figure 2-5). In this configuration an external potential is applied only between the electrode of interest (the working electrode) and a reference electrode. The potential of the second electrode (the counter electrodes) is allowed to vary without restriction to compensate the electrical charge. By doing so the any overpotential or losses in the counter electrode can be omitted.

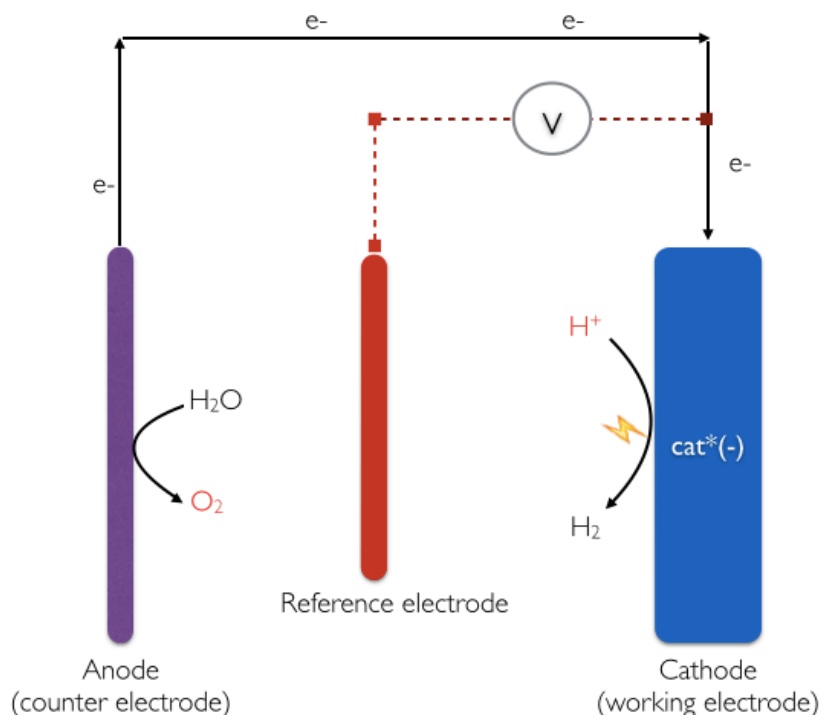


Figure 2-5 Schematic representation of a 3-electrode electrochemical set-up

In the experiments described in *Chapter 5*, the working electrode was the cathode (Cu_2O) and the counter electrode was a Pt mesh. A silver/silver chloride reference electrode with saturated KCl solution ($E^\circ(\text{Ag}/\text{AgCl}) = +0.197 \text{ V}$ vs NHE) was employed as a reference.

The potentials applied (E') were converted to the Reversible hydrogen Electrode according to the Nerst equation:

$$E(\text{RHE}) = E^\circ(\text{Ag}/\text{AgCl}) + E' + 0.059 \cdot \text{pH} \quad \text{Equation 2-13}$$

2.7. References

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2. Peter, L.M., K.G.U. Wijayantha, and A.A. Tahir, *Kinetics of light-driven oxygen evolution at [small alpha]- Fe_2O_3 electrodes*. Faraday Discussions, 2012. **155**(0): p. 309-322.

Chapter Three

Kinetic study of a hybrid CO₂ reduction photocatalyst

In this chapter, the immobilization of molecular photocatalyst for CO₂ reduction on the surface of electrodes is shown to improve the stability of reaction intermediates. This stabilisation directly translates into higher photocatalytic yields. For this purpose, a model [Re(bpy)(CO)₃L] type CO₂ reduction photocatalyst is studied (L= axial ligand). The kinetics of one of the key reaction intermediates are studied and the results, when the photocatalyst is in solution and when it is covalently anchored to the surface of TiO₂ are compared. The results from this study also provide insight into the nature of the electron transfer reactions in this system and provide an approximate timescale for the different steps of the accepted CO₂ to CO reduction mechanism.

Part of the results presented in this chapter is included in the publication:

“Improving the photocatalytic reduction of CO₂ to CO through immobilisation of a Molecular Re catalyst on TiO₂.” Chemistry A European Journal, 2015, 21, p.3746

3.1. Introduction

The reduction of CO₂ to energy-rich fuels such as CH₄ or CO is extremely challenging both when attempted electrochemically and photochemically. Two of the key problems are the poor selectivity and the stability of the catalysts. Semiconductors, such as p-type Si, CdTe, InP, GaP, Cu₂O have been used to reduce CO₂, albeit with poor selectivity.[1-3] High selectivity can be achieved combining enzymes and molecular dyes, however these systems are too fragile for large-scale application.[4] To overcome the limitations of semiconductors and biological systems, molecular catalysts are attracting strong interest. CO₂ to CO reduction has been achieved using macrocyclic Ni(cyclam) and Co(cyclam) in electrocatalytic and photocatalytic systems.[5-7] These complexes, despite their suitable catalytic properties, are not light active and they need to be coupled to a molecular dye or a semiconductor to initiate light-driven catalysis. Amongst the CO₂ reduction catalyst that can act both as catalyst and light absorber, Rhenium bipyridine tricarbonyl complexes have been intensively explored due to their promising performance to date,[8] and are the subject of this study.

3.1.1. Characteristics of [Re(bpy)(CO)₃L] photocatalyst for CO₂ to CO conversion

[Re(bpy)(CO)₃L] type photocatalysts, where L = Cl⁻, Br⁻ have been widely studied as photocatalysts for CO₂ reduction since the first report by Lehn and co-workers in 1983.[9] Upon light irradiation, a transition occurs from the Re(I)-d⁵ metal centre to the antibonding π^* orbital of the bipyridine ligand. The resulting excited state is a powerful reductant, more so than the ground state and is therefore capable of undergoing redox reactions.[10, 11] Specifically, in the presence of sacrificial donors such as triethanolamine (TEOA) the excited state is readily quenched giving rise to reduced species which, can further react with substrates.[12] For the conversion of CO₂ to CO, the highest TOF using Re(I) type photocatalyst so far achieved is $\sim 15 \text{ h}^{-1}$ in organic solvents and with illumination at wavelength greater than 400 nm.[13] Modification of this catalyst's coordination sphere by replacing the axial ligand with a thiocyanate group yielded a TON of $\sim 13 \text{ h}^{-1}$ under similar conditions.[14] Despite these modest performances (for comparison carbon monoxide dehydrogenases,

CODH, operate at TOF of up to 40000 s^{-1})[4] Re(I) photocatalysts remain the most efficient and selective CO₂ reduction catalysts. A major limitation for these catalysts is their poor photostability in solution, a problem that is aggravated in the presence of sacrificial donors.

Photostability issues are not unique for Re complexes. Many other transition metal complexes such as [Ru(bpy)₃]⁺ suffer from the same problem. Interestingly, Ru complexes have been widely used as photoabsorbers in dye sensitised solar cells (DSSC) where they exhibit remarkable photostabilities.[15] As opposed to bulk solutions, in DSSC the molecules are covalently anchored to the surface of a semiconductor, which restricts their movement and changes their reactivity.[16] Surprisingly, the heterogenisation of [Re(bpy)(CO)₃L] catalysts for CO₂ photoreduction has not been extensively studied and it is only now that as this route is being explored.[17-21] Recently Reisner and co-workers, reported that the heterogenisation of a Re(I) photocatalyst (hereof referred as : **Re^{Pic}**) for CO₂ reduction on TiO₂ results in larger photocatalytic yields (Figure 3-1) .[22] Upon immobilisation of the catalyst, they found a 26-fold increase in the reduction of CO₂ to CO compared to the homogeneous solution, as well as an increase in the stability of the system. Their heterogeneous system provided the advantages of working on solid electrodes whilst retaining the selective catalytic properties of the homogenous system. The elucidation of the reasons behind these improvements, as well as the mechanism of CO₂ reduction in this system is key to understanding how heterogenisation of molecular catalysts can help the solar-to-fuel conversion, and is the focus of this chapter.

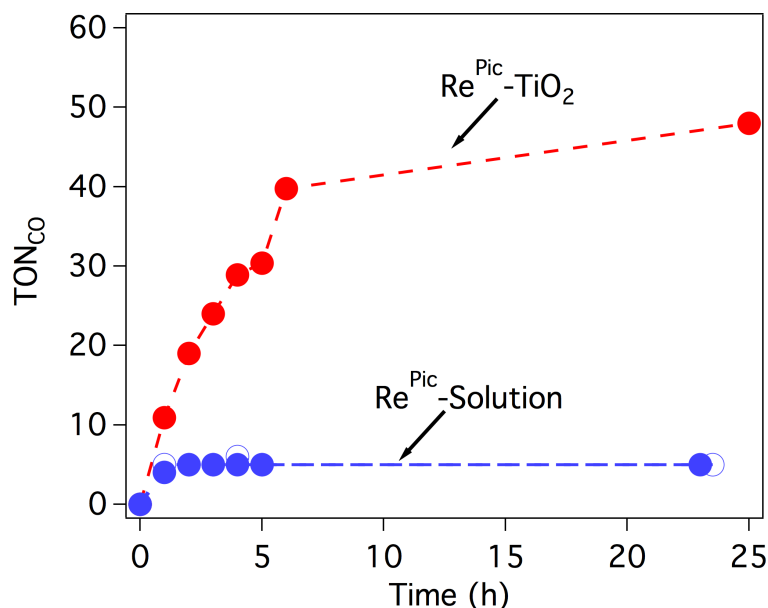


Figure 3-1 Photocatalytic performance of the Re photocatalyst anchored to TiO₂ (red circles) and in solution with and without TiO₂ particles in suspension (filled and empty circles respectively). Reproduced from reference [22]

3.1.2. CO₂ reduction mechanism in [Re(bpy)(CO)₃L] type complexes

Mechanistic elucidation is key for the improvement of catalysts. Figure 3-2 shows the accepted mechanism for the reduction of CO₂ to CO using [Re(bpy)(CO)₃L] catalysts based on the latest experimental evidence.[23]

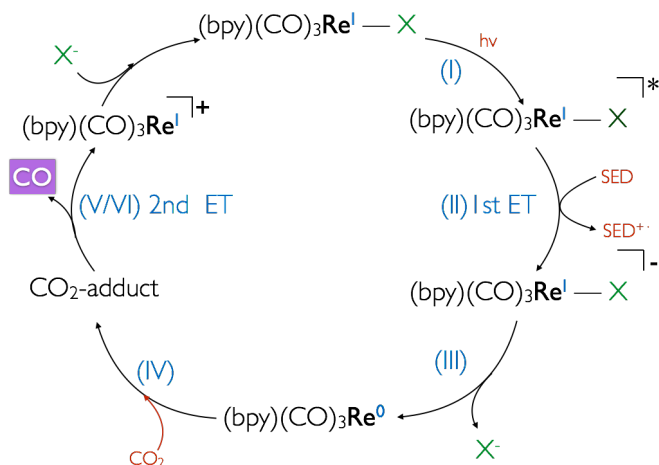


Figure 3-2. Proposed mechanism for the photoreduction of CO₂ by a Re photocatalyst based on the literature. [23]

Steps:

- (1) Excitation of the photocatalyst generating an excited state.
- (2) Reductive quenching of the excited state by a sacrificial electron donor forming a radical species with the electron localised in the bipyridin ligand.
- (3) Elimination of the axial ligand and replacement by a solvent molecule.
- (4) Electrophilic attack by a CO₂ molecule
- (5) Second electron transfer from a second singly reduced catalyst or a sacrificial radical molecule. The second electron is located in the metal centre rendering a configuration Re⁰(bpy⁻)
- (6) Evolution of CO and formation of the solvent coordinated complex

The key intermediates in step 3 and 4 have been recently identified by means of Cold-Spray Ionization Spectroscopy[23] and the electronic structure of the two-electron reduced complex (Re⁰(bpy⁻), step 5) has been identified by X-ray absorption spectroscopy and stop-flow spectroscopy. These findings provide evidence of the non-innocent role of the bipyridine ligand in this system and its importance for the selective electro- and photoreduction of CO₂. [24, 25] Further discussion of the mechanism of CO₂ reduction, in relation to the Re complex studied in this chapter, is given in the discussion sections.

3.2. In this chapter

Improving the photostability and efficiency of systems for CO₂ reduction is key for the future development of this technology. A promising route, to achieve this is the immobilisation of photocatalysts on the surface of electrodes. Heterogenisation of a highly active Re photocatalysis has been shown to lead to higher photocatalytic yields and better photostabilities than homogeneous photocatalysis under the same conditions. Both these improvements are likely related; they may stem from an improvement in the lifetime and kinetics of the reaction intermediates that, in the heterogeneous system, favour catalysis as opposed to recombination or degradation. In order to unravel the mechanism behind these improvements, in this chapter, Transient Absorption Spectroscopy is used to study the deactivation pathways and

reactivity of the optically active Re-based photocatalyst and to compare the kinetics of reaction intermediates in solution and on the surface of TiO₂.

3.3. Experimental methods

The system studied in this work consists of a Re photocatalyst based on the original [Re^I(CO)₃Cl] reported by Lehn in 1983.[9] This catalyst was modified to include phosphonate groups in the bipyridine ligand and a picoline group as the axial ligand (L). Figure 3-3 shows the structure of the photocatalysts that, in this is here referred as **Re^{Pic}**. The complex was prepared by Dr. Chrstopher Windle (University of Cambridge).[22] Further details can be found in the appendix to this thesis.

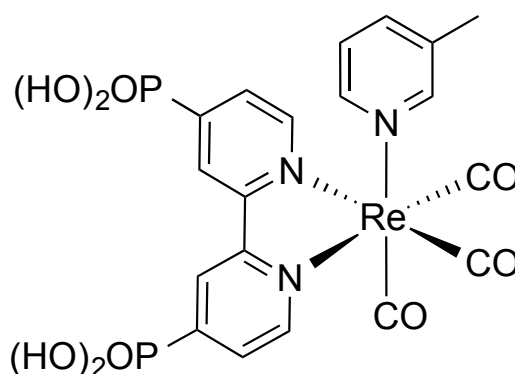


Figure 3-3 Structure of the [Re(2,2'-bipyridine-4,4'-biphosphonic acid)(CO)₃(3-picoline)] (**Re^{Pic}**) catalyst employed in this study.

For catalytic and spectroscopic experiments the complex was anchored to anatase TiO₂. Homogeneous samples were prepared dissolving the photocatalyst (0.1 mM) in a water/DMF mixture (1:2). TEOA was used as a sacrificial electron donor and was added, when required to give a concentration of 1 M. Anatase TiO₂ films were employed for the spectroscopy study as their small particle size minimized scattering effects and enhanced optical transparency leading to higher signal/noise ratios. Anatase TiO₂ films (8 μm thick, 1x1.5 cm² in area), were prepared using the Dr Blade technique. In order to functionalize the TiO₂ films, they were immersed in 0.3 mM solutions of the photocatalyst during 48 h in the dark to avoid photodegradation. The samples were dried under vacuum to for 1 h to remove traces of water and kept in the dark in between experiments.

The transient studies shown here were collected using the TA apparatus described in *Chapter 2*. For this particular experiment, the excitation wavelength was chosen to be 414 nm, at a pulse rate of 0.5 Hz and an intensity of 300 $\mu\text{J}/\text{cm}^2$. The samples were purged with N_2 before each experiment. The TCSPC and photoluminescence experiments were collected using the device described in Chapter using an excitation of 404 nm.

3.4. Results

3.4.1. Assignment of the CO_2 reduction intermediate kinetics

Figure 3-4 shows the steady state absorption and photoluminescence of the Re^{Pic} photocatalyst. The illumination of $[\text{Re}(\text{bpy})(\text{CO})_3\text{L}]$ type complexes with visible light results in the formation of an excited state with triplet character with a characteristic broad emission centred at ~ 600 nm.

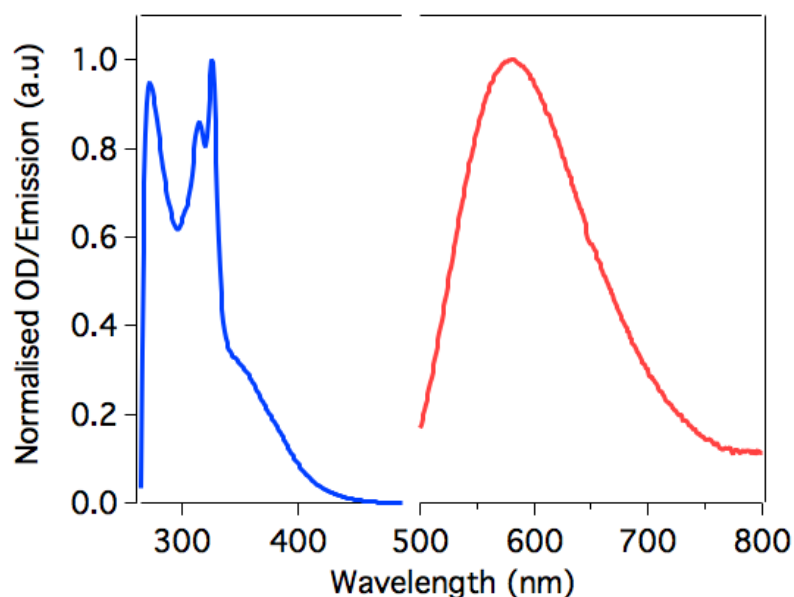


Figure 3-4 Steady state absorbance (blue) and photoluminescence following 404 nm excitation of Re^{Pic}

The emission of this triplet state can be used to study the interaction the photoexcited catalyst with the sacrificial electron donor. Figure 3-5 shows the emission decay at

600 nm for Re^{Pic} and Re^{Pic} immobilised onto TiO_2 ($\text{Re}^{\text{Pic}}\text{-TiO}_2$) under N_2 . In both systems the luminescence decays with a $t_{50\%} > 20$ ns. The addition of the sacrificial electron donor (TEOA) results in a quenching of approximately 90% the emission within $t_{50\%}=10$ ns assigned to the electron transfer from TEOA to $(\text{Re}^{\text{Pic}})^*$. Notably, the inset in Figure 3-5 shows that, the emission of Re^{Pic} anchored onto TiO_2 is qualitatively similar to that of Re^{Pic} anchored onto Al_2O_3 , a semiconductor with a much higher conduction band than TiO_2 .

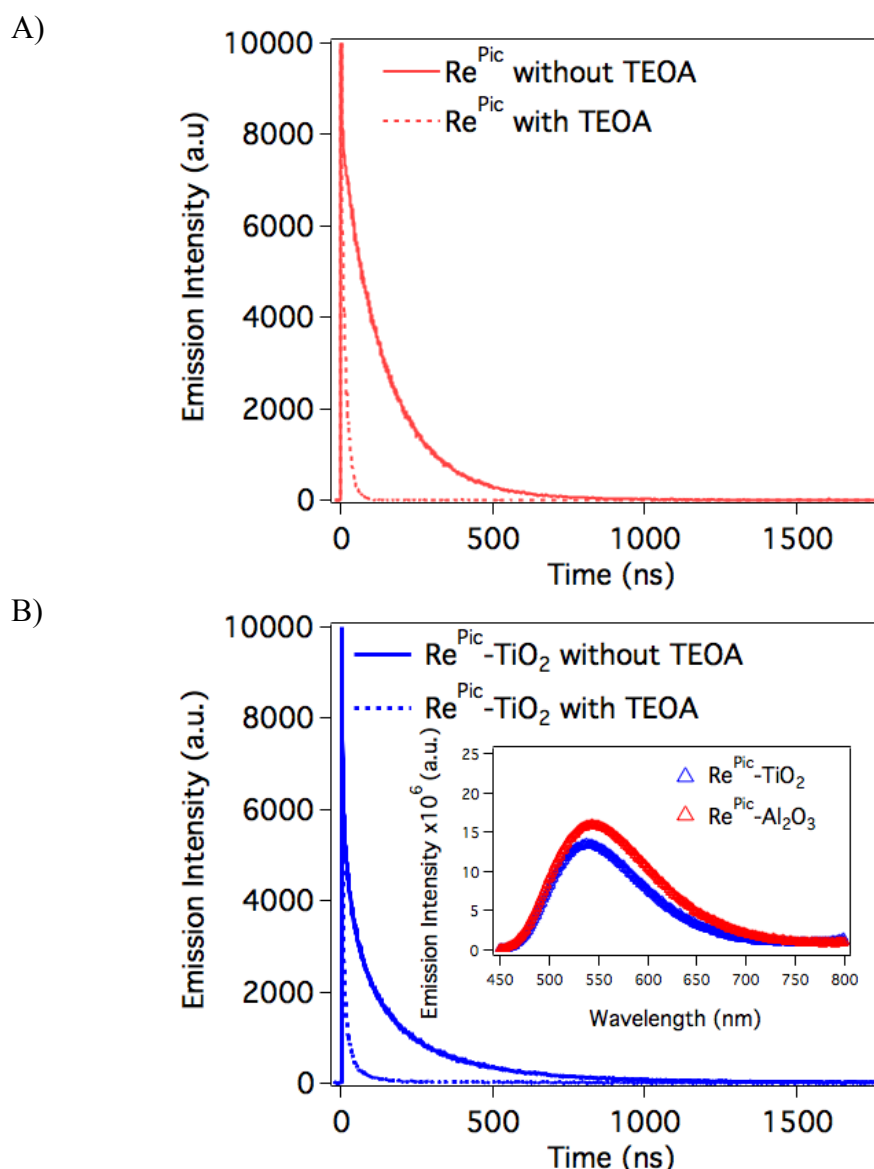


Figure 3-5 Photoluminescence decays measured at 600 nm following 404 nm excitation of A) 0.1 mM Re^{Pic} and B) $\text{Re}^{\text{Pic}}\text{-TiO}_2$ in the absence (solid lines) and presence (dashed lines) of a sacrificial electron donor TEOA (1 M). The inset shows the steady state emission spectra in air of Re^{Pic} anchored to TiO_2 and Al_2O_3 following 404 nm excitation.

Pulsed optical excitation of Re^{Pic} and $\text{Re}^{\text{Pic}}\text{-TiO}_2$ in the presence of TEOA results in two absorption features; a peak centered at 500 nm and a broad signal in the near-IR part of the spectra (800-900 nm), as shown in Figure 3-6. The near-IR band has a smaller absorption relative to the 500 nm signal. This difference in absorption amplitude is more pronounced for the $\text{Re}^{\text{Pic}}\text{-TiO}_2$ system.

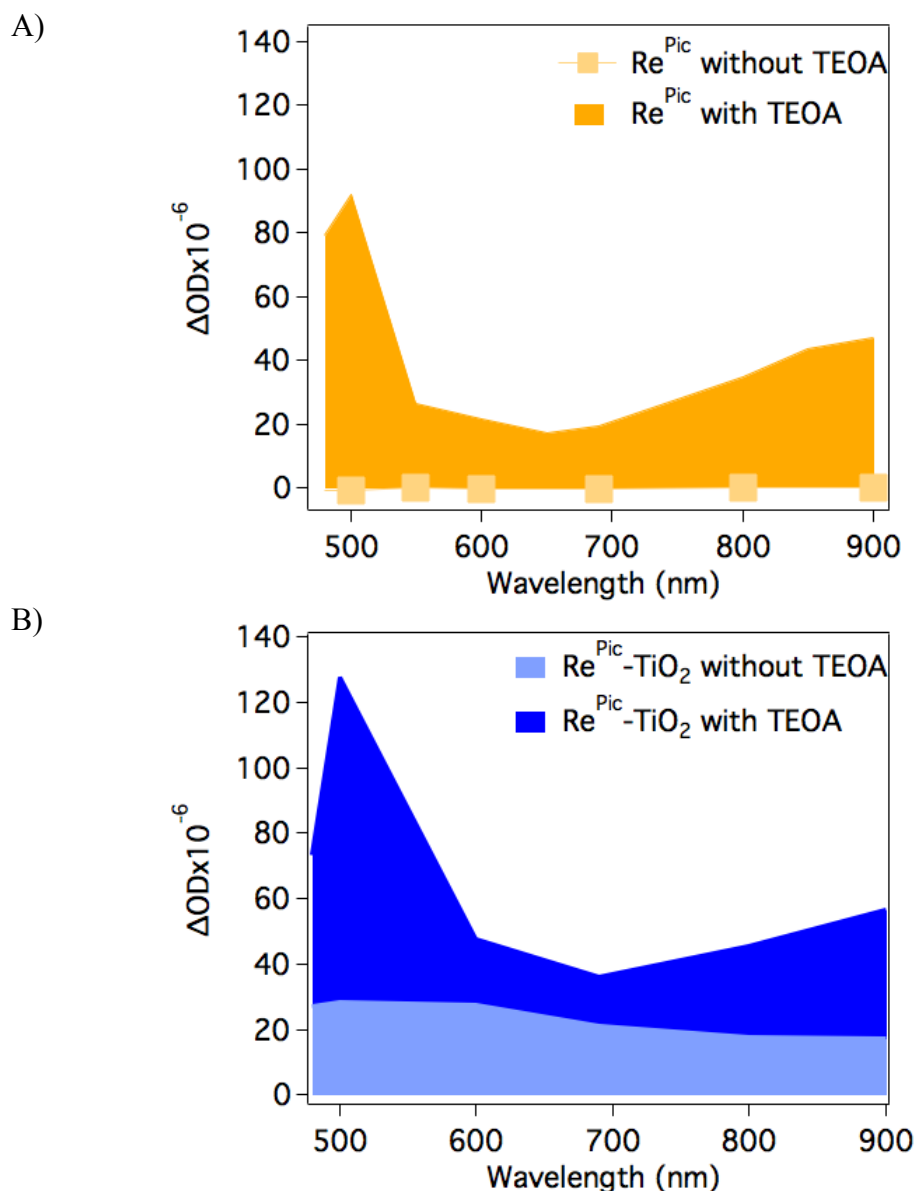


Figure 3-6 Transient absorption spectra measured 300 μs after photoexcitation with 415 nm light of A) 0.1mM Re^{Pic} and B) $\text{Re}^{\text{Pic}}\text{-TiO}_2$ with and without sacrificial electron donor, TEOA (1M). The amplitude ratio between the peaks at 500 nm and 900 nm is calculated taking the signal amplitude without TEOA as baseline so to account for the background noise.

The positive absorption features in Figure 3-6 are not observed in the absence of the sacrificial electron donor. This is indicative of the formation of the anion state of **Re^{Pic}** after reductive quenching by TEOA as shown by the equation scheme below:



The 500 nm maximum has previously been observed in other [Re(bpy)(CO)₃L] systems and has been assigned to the reduced complex [Re(bpy)(CO)₃L]⁻ in agreement with our reaction scheme.[12] Therefore, monitoring the decay kinetics of the light induced absorption of the 500 nm maximum is a probe of the reaction dynamics of the photocatalyst reduced intermediate (**Re^{Pic}**)⁻ both, in solution and immobilised onto TiO₂.

3.4.2. Intermediate dynamics under N₂ and CO₂

Figure 3-7A shows the transient decay under N₂ of the photoinduced absorption at 500 nm both in solution and anchored to TiO₂, in the presence of the sacrificial electron donor. The lifetime of the surface immobilised **Re^{Pic}** anion is found to be at least one order of magnitude bigger than that of (**Re^{Pic}**)⁻ in solution (*t*_{50%} > 1 s for **Re^{Pic}**-TiO₂ and *t*_{50%} = 60 ms for (**Re^{Pic}**)⁻ in homogeneous solution). The addition of CO₂ to the system results in a significant change in the decay dynamics as shown in Figure 3-7B. The lifetime of the **Re^{Pic}** anion on the surface of TiO₂ shortens to *t*_{50%} = 400 ms in the presence of CO₂, whereas (**Re^{Pic}**)⁻ in solution has a strong biphasic behaviour with a slow component in the 100 ms to 1 s timescale and a fast phase in the 1-10 ms timescale. Interestingly, the decay dynamics of the slow phase are very similar to those of the **Re^{Pic}**-TiO₂ system in the same timescale as shown in the inset of Figure 3-7B.

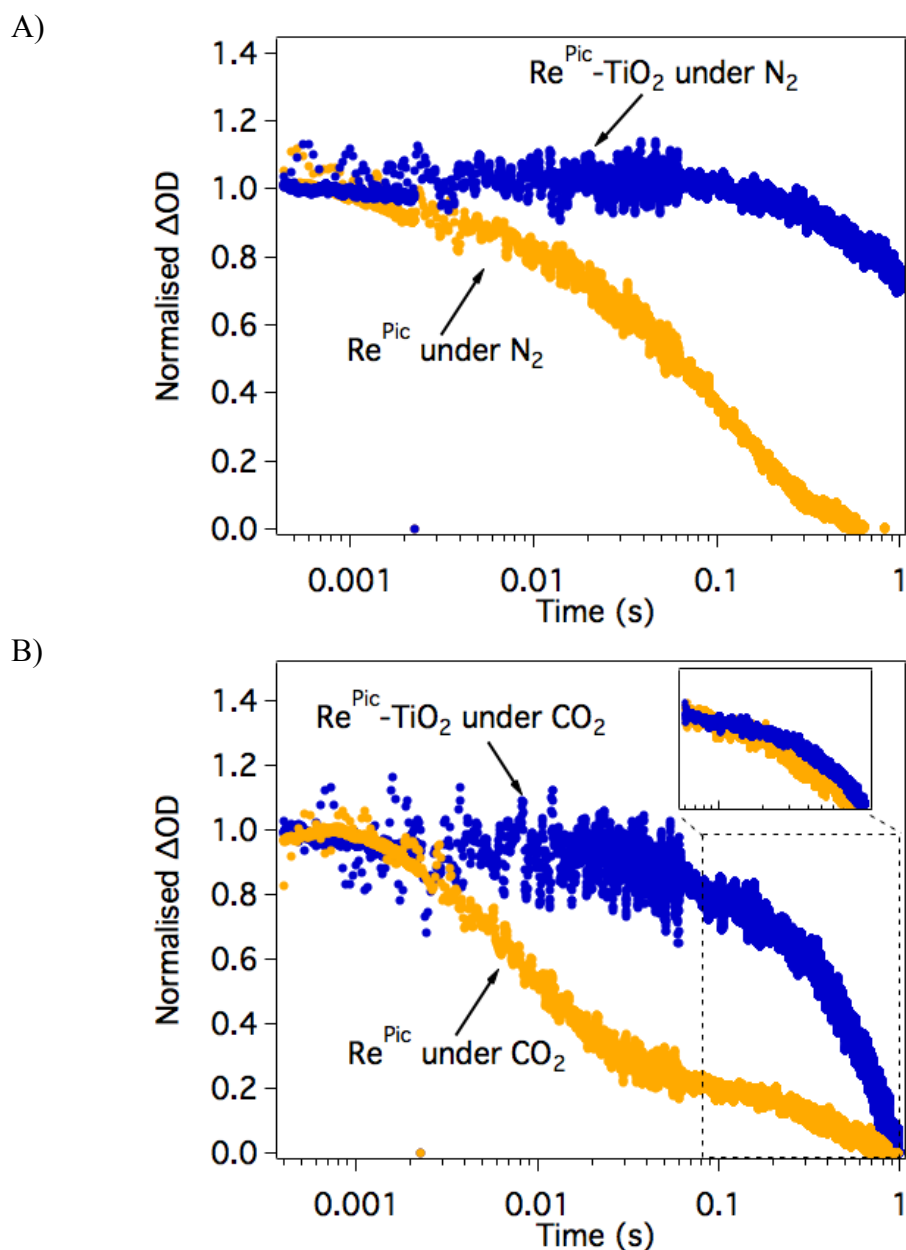


Figure 3-7 Transient absorption decays measured at 500 nm after photoexcitation of Re^{Pic} and Re^{Pic} anchored to TiO_2 in the presence of TEOA under A) N_2 and B) CO_2 .

3.5. Discussion

Following illumination with visible light, the excited state of the $\text{Re(I)}^{\text{Pic}}$ catalyst might: (i) inject electrons into the TiO_2 and/or (ii) react with the sacrificial electron donor. As shown in the inset of Figure 3-5, the excited state emission of Re^{Pic} is qualitatively the same when the molecule is anchored to TiO_2 and Al_2O_3 . Since the latter is an insulator, with a conduction band that does not allow electron injection (-4.2 V vs NHE),^[26] these results suggest that no (or negligible) electro injection occurs

in the $\text{Re}^{\text{Pic}}\text{-TiO}_2$ system. Conversely, the data shows that the excited state of the $\text{Re}(\text{I})^{\text{Pic}}$ undergoes rapid reductive quenching by TEOA ($\text{TEOA}^+/\text{TEOA} = 0.8\text{V}$ vs NHE) both, in the homogeneous and the surface immobilised system (Figure 3-5). This process has been observed for the excited state of many other $[\text{Re}(\text{bpy})(\text{CO})_3\text{L}]$ type molecules, which have typical reduction potentials $> 1\text{V}$ vs NHE, and results in the formation of an oxidised TEOA molecule (TEOA^+) and an anion radical ($\text{Re}^{\text{Pic}}\text{--}$). [12, 27] This anion radical has been proposed to be the specie that interacts with CO_2 in the reduction catalytic cycle. [12, 28, 29] In this reduced intermediate, the electron is localized in the *bpy* ligand rather than in the Re centre. The resulting electronic distribution allows the metal to remain sufficiently electrophilic to bind substrates such as CO_2 . [30-33] In addition to this, the preferable reduction of the *bpy* ligand, has also been proposed to be a key feature responsible for the better performance and selectivity of $[\text{Re}(\text{bpy})(\text{CO})_3\text{L}]$ type photocatalyst for CO_2 reduction. The *bpy* ligand is thought to act as an electron reservoir, which prevents the accumulation of 2 electrons in the Re. This renders the catalyst an electronic configuration ($\text{Re}^0(\text{bpy})\text{--}$) with low reorganization energies that favour the electron transfer (ET) to CO_2 . [24, 25] For these reasons, this catalyst anion is considered a key intermediate in the catalytic cycle and has been the subject of mechanistic studies. [23, 32]

We now turn to the study of the kinetics of the Re^{Pic} anion and, the influence of surface immobilisation on the lifetime of the intermediate.

Under N_2 the Re^{Pic} anion in solution decays within $t_{50\%} = 60\text{ ms}$ whereas the anion on the surface exhibits a very long-lived transient, with only a moderate decay long times ($t > 0.5\text{ s}$) as shown in Figure 3-7A. This decay in the absence of a substrate is assigned to the deactivation of the catalyst. This process has been proposed to occur via the formation of thermodynamically stable and often inactive diametric species and Re-formate complexes. [22, 29] These Re dimers are reported to have a transient absorption in the near-IR region. [32] Our transient spectra in the presence of TEOA show a band in this region (800-900 nm) for both systems studied (Figure 3-6), suggesting that dimers are formed in our system. However, the signal amplitude of the IR signal with respect to that of the anion absorbance (500 nm) is smaller for the $\text{Re}^{\text{Pic}}\text{-TiO}_2$ system than for the homogenous one. This is indicative of a lesser dimers formation per anion intermediate when the photocatalyst is anchored to TiO_2 . Such

behaviour is in agreement with the longer lifetimes measured on TiO₂ and is consistent with the restrictions imposed by surface immobilisation that are likely to hamper bimolecular reactions.

It is apparent from Figure 3-7A that the scaffolding provided by the metal oxide enhances the stability of the reduced reaction intermediate by preventing the formation of dimers. As such, it is reasonable to expect greater photocatalytic yields in this systems. Indeed, the heterogenised system shows a 26-fold increase in the yield of CO production, under visible light illumination ($\lambda > 420$ nm), compared to the homogenous system (Figure 3-1). Control experiments using variations of the photocatalyst without phosphonated ligands in combination with TiO₂ nanoparticles also show very poor activity. This suggests the need to covalently anchor the catalyst to the metal oxide in order to hamper the formation of dimers and achieve photocatalytic enhancement.

We can assign this enhancement in the photocatalytic activity for the heterogenised system to the increase in the stability of the reactive intermediate provided by the scaffolding. The longer-lived anion species formed in the **Re^{Pic}**-TiO₂ system have a greater probability of encountering and consequently reacting with CO₂ as well as undergoing the subsequent electron transfer required for the release of CO. This observation is in agreement with reports of enhanced electrochemical CO₂ reduction in modified electrodes and improved CO₂ photoreduction yields in a system composed of a Re phosphonated catalyst anchored to TiO₂ and activated for visible light absorption with a molecular dye.[3, 18] These results show that, the heterogenisation of CO₂ reduction catalysts is a powerful strategy to improve the stability and performance of CO₂ reduction systems both electrocatalytic and photocatalytic.

3.5.1. Mechanistic implications

So far we have studied the kinetics of the reactive intermediate under N₂. Now we turn to the effect of CO₂ in the kinetics.

As shown in Figure 3-7B, the addition of CO₂ to the system results in a change in the kinetics of the anion, both in solution and on the surface of TiO₂. In the homogenous system, a biphasic behaviour is observed composing of a fast (1-10 ms) and slow (100 ms to 1 s) phase. For the **Re^{Pic}**-TiO₂ system, the signal decays one order of magnitude faster than the analogous system under N₂. At early times a long-lived signal, identical to that observed under N₂, is monitored. The signal is followed by a fast decay from 100 ms to 1s. This final, fast decay can be assigned to the interaction of (**Ru^{Pic}**)⁻ with CO₂. Further evidence of this interaction is provided by the comparison of the kinetics of the (**Ru^{Pic}**)⁻ in solution and immobilised onto TiO₂. As shown in the inset of Figure 3-7, the kinetics of the slow phase in solution is identical to those of **Re^{Pic}**-TiO₂ suggesting they involve the same process. Hence, our results indicate that the interaction of the catalyst with CO₂ qualitatively takes place at the same timescale in the homogeneous and heterogenised systems. More importantly, this interaction is found to occur at relative long timescales (>10 μs). This observation is in agreement with previous mechanistic studies that reported, slow CO₂ reduction rate constants.[32] The similarity between the reaction in homogeneous and heterogeneous conditions is also supported by recent theoretical calculations; they show that Rhenium photocatalysts covalently anchor to TiO₂ with the metal centre exposed to the solution, this being the most optimum orientation for maximum reduction capacity. Due to the lack of steric hindrance effects in the heterogeneous system, the interaction of the anion with CO₂ is expected to be qualitatively similar in both the homogeneous and the heterogeneous system as our data shows.[20]

After interaction with CO₂ and formation of a CO₂-adduct, a second reduction must take place for CO to be evolved. The second reduction has been hypothesised to take place via the interaction of two singly reduced anion intermediates or via the reaction of a carbon radical formed upon the deprotonation of TEOA⁺ after the first reduction.[23] Little evidence is yet available about this step. However, the observation of high reduction yields in the heterogeneous system, where bimolecular reactions are restricted, suggests that the electron transfer is likely to precede though the interaction with the TEOA molecule, at least in this system. It is important to note that our transient studies cannot clearly differentiate between the interactions of CO₂ with the catalyst from the second electron transfer to generate CO. For the unequivocal elucidation of the intermediates in these steps, IR studies in combination

with NMR and mass-spectrometry are the most suited techniques. However, our transient studies do allow us to provide an estimate of the timescale at which the different steps of the mechanism take place. A summary of this timescales is shown in Figure 3-8.

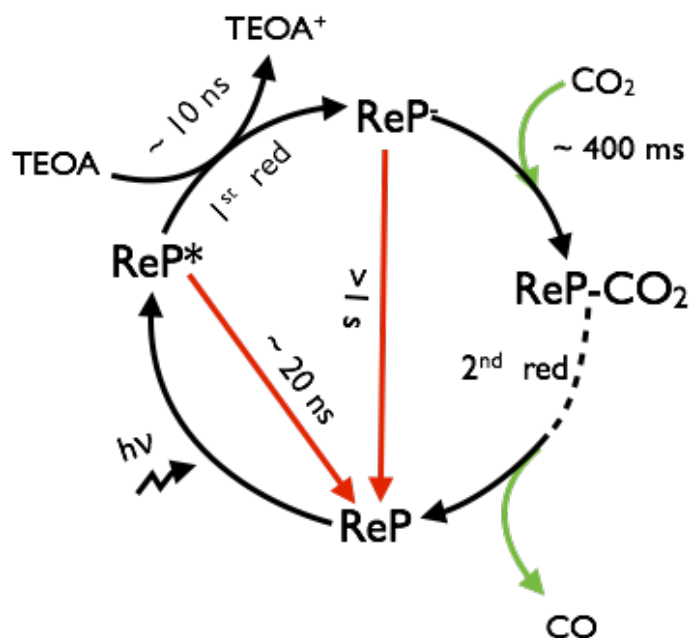


Figure 3-8 Proposed CO₂ reduction mechanism of a Re-based photocatalyst immobilised on TiO₂ under visible light illumination. The deactivation pathways are represented in red lines. The second reduction step (dashed line) was not observed by transient absorption spectroscopy measurements.

3.6. Conclusions

In summary, the transient studies presented in this chapter provide evidence that the surface immobilisation of a [Re(bpy)(CO)₃L] type photocatalyst for CO₂ reduction results in an increase in the stability of one of the key reaction intermediates. This increase in stability increases the probability of an intermediate encountering a CO₂ molecule and reacting with, and it directly translates into higher TON of CO production. This study also shows that the interaction of CO₂ and the photocatalyst occurs at long timescales both in the homogeneous and heterogenised system stressing the importance of generating long-lived intermediates. Using transient absorption spectroscopy and time-correlated single photon counting we have been

able to provide a timescale for the some of the key steps in the acceptor CO₂ to CO reduction mechanism.

3.7. In the next chapter

In this chapter it has been shown how heterogenisation can help increase the lifetime of reaction intermediates and therefore improve photocatalytic yields. In the next chapter the possibility of improving the catalytic efficiency by means of controlling the yield of electron transfers and the catalyst's activity is explored.

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Chapter Four

Kinetic study of a homogeneous proton reduction photocatalytic system

In this chapter, the mechanism by which the pH affects the performance of systems for the photocatalytic reduction of protons is studied. For this purpose a model system based on a Ruthenium photosensitiser, a Nickel bisdiphosphine electrocatalyst in aqueous solution with ascorbic acid as a sacrificial electron donor is studied. The results presented herein demonstrate that the electron transfer from the reduced photosensitiser to the catalyst is pH independent. At $\text{pH} < 4.5$ the performance of the system is limited by the yield of reduction of the photosensitiser by the ascorbic acid. At $\text{pH} > 4.5$ the efficiency of the system is limited by the poor protonation of the electrocatalyst. The results from this study show the potential of tuning the pH to control the kinetics of the multiple steps involved in these photocatalytic systems.

Part of the results presented in this chapter is included in the publication:

“Unravelling the pH-dependence of a molecular photocatalytic system for hydrogen production.” Chemical Science, 2015, 6, p.4855

4.1. Introduction

The light driven generation of H₂ as an energy carrier is considered to be one of the key steps towards a carbon neutral energy system. Thermodynamically all redox couples with a redox potential more reductive than that of the H₂O/H₂ pair ($E^{\circ} = 0 \text{ V}_{\text{RHE}}$; $-0.41 \text{ V}_{\text{NHE}}$ at pH=7) can reduce water. However, slow kinetics often hamper the reduction of protons.[1] Up to date the best electrocatalysts for H₂ evolution are based on noble metals such, Pt or enzymes like hydrogenases.[2-8] To replace, these expensive and fragile catalysts, synthetic efforts have focused on the design of H₂ evolution molecular catalysts based on earth-abundant elements such as Fe,[9-12] Co,[13-16] , Ni,[5, 17-21] Mo,[22-24].[25] Often these molecules are not light active, and they need to be coupled to a molecular dye in order to activate them for light-driven catalysis. [9, 11, 26]. Amongst the newly developed molecular systems, Ni based catalysts are attracting increasing attention, due to the abundance of this element and suitable catalytic properties. In particular diazacyclooctanes Ni catalysts have shown remarkable performances both as electrocatalysts and in photocatalytic systems.

4.1.1. bis(1,5-R'-diphospha-3,7-R''-diazacyclooctane)nickel(II) and catalytic activity of proton reduction catalysts

The design of catalysts has drawn inspiration on biological systems, not only in the choice of elements (Fe, and Ni are key components in the active sites of hydrogenases) but also in the chemical structure of the molecule. One example of a biology inspired catalyst is the Ni based H₂ evolution electrocatalyst developed by DuBois and co workers.[19] This electrocatalyst is composed of a Ni core with a second coordination sphere containing amine groups (see Figure 4-2 for an example of this type of this core structure). This structure was designed to mimic the [FeFe] hydrogenases' active site in which a pendant amine group is located next to the metal centre.[19] It is believed that these pendant bases act as a proton relays between the solvent and the metal facilitating the formation of H₂. In the same manner the amines in the electrocatalyst are thought to act as a proton pathway between the solvent and

the vacant coordination site at the metal.[27-29] Up to this date the DuBois catalyst remains one of the most efficient H₂ evolution catalysts however, it only operates in organic solvents. Synthetic work has been done to modify the outer sphere structure of the catalyst to increase its solubility in water. Recently Reisner and Co-workers reported a highly active DuBois type Ni catalyst soluble in water, the subject of this chapter. This catalyst was coupled with light harvesting unit to yield H₂ with a quantum yield of 10% at pH=4.5.[5]

The efficiency of H₂ evolving electrocatalytic and photocatalytic systems is often strongly pH-dependent.[27, 30-32] Typically photocatalytic systems combining a molecular dye and an electrocatalyst show a characteristic volcano type dependence of the TON (or TOF) with the pH with a sharp decrease in activity monitored at moderate-high pH. An example of such type behaviour is shown in Figure 4-1 for the Ni catalyst reported by Reisner and co-workers. The performance of this system increases towards pH~ 4 and at pH> 4.5 a sharp decrease in activity occurs. It is noteworthy that, contrary to that observed in the photoelectrochemical system, the activity of the Ni electrocatalyst is larger in very acidic (pH~2) conditions when used purely as an electrocatalyst. Interestingly this dependence of the system activity on the pH is observed in many photocatalytic systems independently of the dye, the sacrificial electron donor or the catalyst,[5, 30, 31, 33-35] yet little is known about its origin.

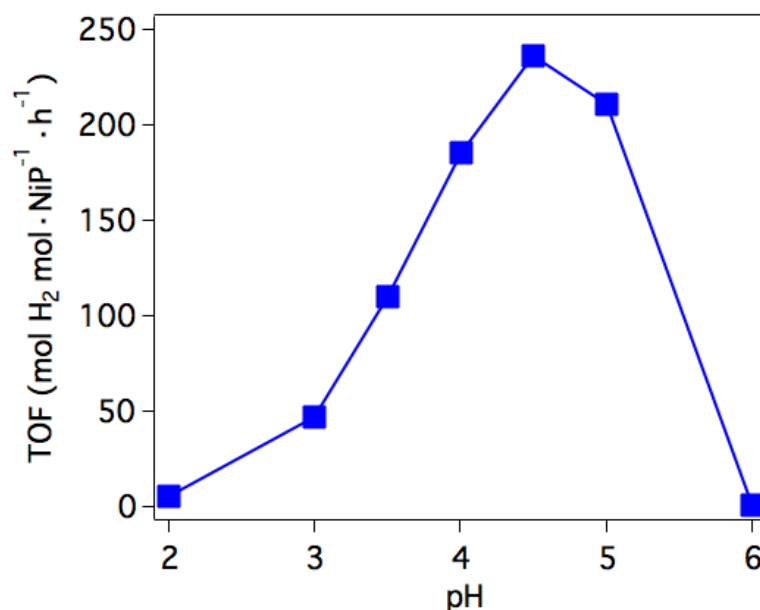


Figure 4-1 TOF_{NiP} (H₂) at different pH of the Ni-based photocatalytic system reproduced from reference. [5]

4.2. In this chapter

The pH is a key parameter for the performance of photoelectrochemical systems as it can influence key system properties like redox potentials. Indeed photoelectrochemical systems containing more than one component, such as a sacrificial donor a dye and an electrocatalyst are often pH sensitive. Such dependency has been speculated to arise from the influence of pH in the electron transfer reactions and the generation of reaction intermediates.[33] Despite its importance, little evidence is available in the literature about the effect pH in the electron transfer kinetics. In this chapter Transient Absorption Spectroscopy is used to study the effect of pH in the kinetics of intermediates as well as in the catalytic function of electrocatalyst itself. Kinetic studies are used to establish whether the observed pH dependencies arise from the function of the light absorber, the sacrificial electron donor or the availability of protons to the catalyst.

4.3. Experimental methods

The molecular electrocatalyst employed in this study was a modification of the DuBois type Nickel electrocatalyst reported in 2011 to allow water solubility. This was achieved by incorporating an outer coordination sphere containing phosphonic acid moieties. The complex was prepared by Manuela Groß (University of

Cambridge).[5] The photosensitiser used to activate the system for visible light absorption was a Ru(II) phosphonated bypyridine complex (Figure 4-2). In this chapter the Nickel electrocatalyst is referred as **NiP** and the Ruthenium photosensitiser as **RuP**. Further details can be found in the appendix to this thesis.

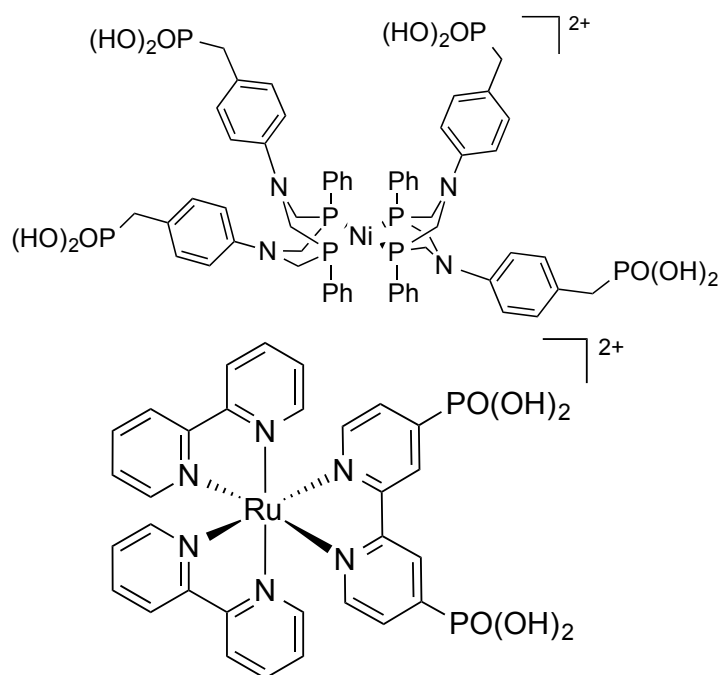


Figure 4-2 Structure of $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{PhCH}_2\text{P}(\text{O})(\text{OH})_2}_2)]$ (**NiP**) and $[\text{Ru}(\text{bpy})_2(4,4'-(\text{PO}_3\text{H}_2)_2\text{bpy})]$ (**RuP**) employed in this study.

The transient studies shown here were collected using the TA apparatus described in *Chapter 2*. For this particular experiment the excitation wavelength was chosen to be 355 nm, at a pulse rate of 0.8 Hz and an intensity of 350 $\mu\text{J}/\text{cm}^2$. Transient measurements were carried out in freshly prepared ascorbic acid (0.1M) aqueous solutions and the pH was adjusted by the addition of NaOH (0.1M) or HCl (0.1M). The samples were purged with N₂ before each experiment. Part of this experiments were performed in collaboration with Dr Anna Reynal (Imperial College London).

4.4. Results

4.4.1. Assignment of the H^+ reduction intermediates' kinetics

Figure 4-3 shows the steady state absorption spectra of the Ruthenium photosensitiser (**RuP**) and the proton reduction electrocatalyst (**NiP**). The photosensitiser has a strong absorption in the UV-VIS region with a peak centred at ~450 nm. The electrocatalyst, on the other hand, has a weak visible absorption with a maximum centred at ~500 nm.

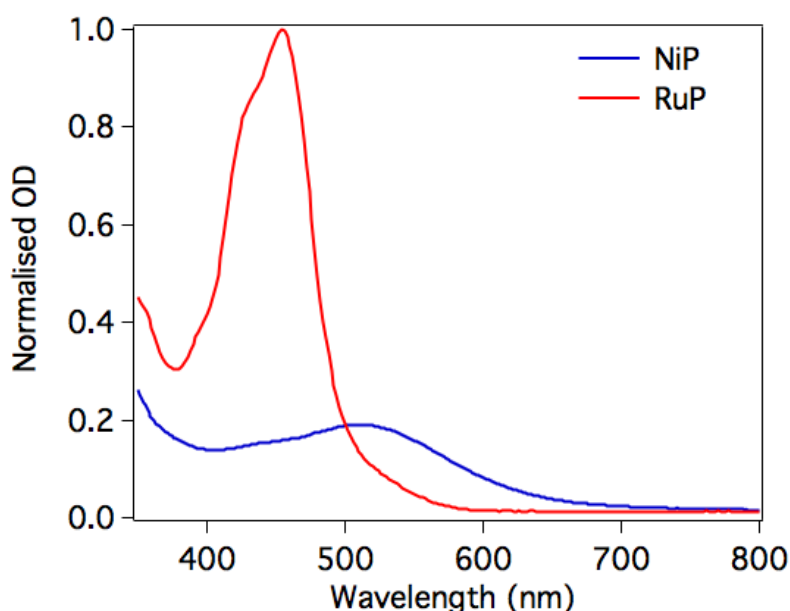


Figure 4-3 Steady state absorbance of **RuP** and **NiP** in methanol.

Pulsed optical excitation of the photosensitiser, **RuP**, with 355 nm light in the presence of ascorbic acid results in the appearance of a strong positive absorption feature centred at 500 nm corresponding to the absorbance of a new photogenerated state. (Figure 4-4 A)

The excitation of the system containing simultaneously the sensitiser and the electrocatalyst gives rise to a positive absorbance at 500 nm but also to a negative

change in absorbance at the same wavelength as shown in Figure 4-4 B. It is noteworthy that this negative feature appears only at long times ($t_{50\%} > 500 \mu\text{s}$) and that no signal at 500 nm can be measured upon the direct excitation of **NiP** in the absence of photosensitiser as shown in the inset of Figure 4-4B.

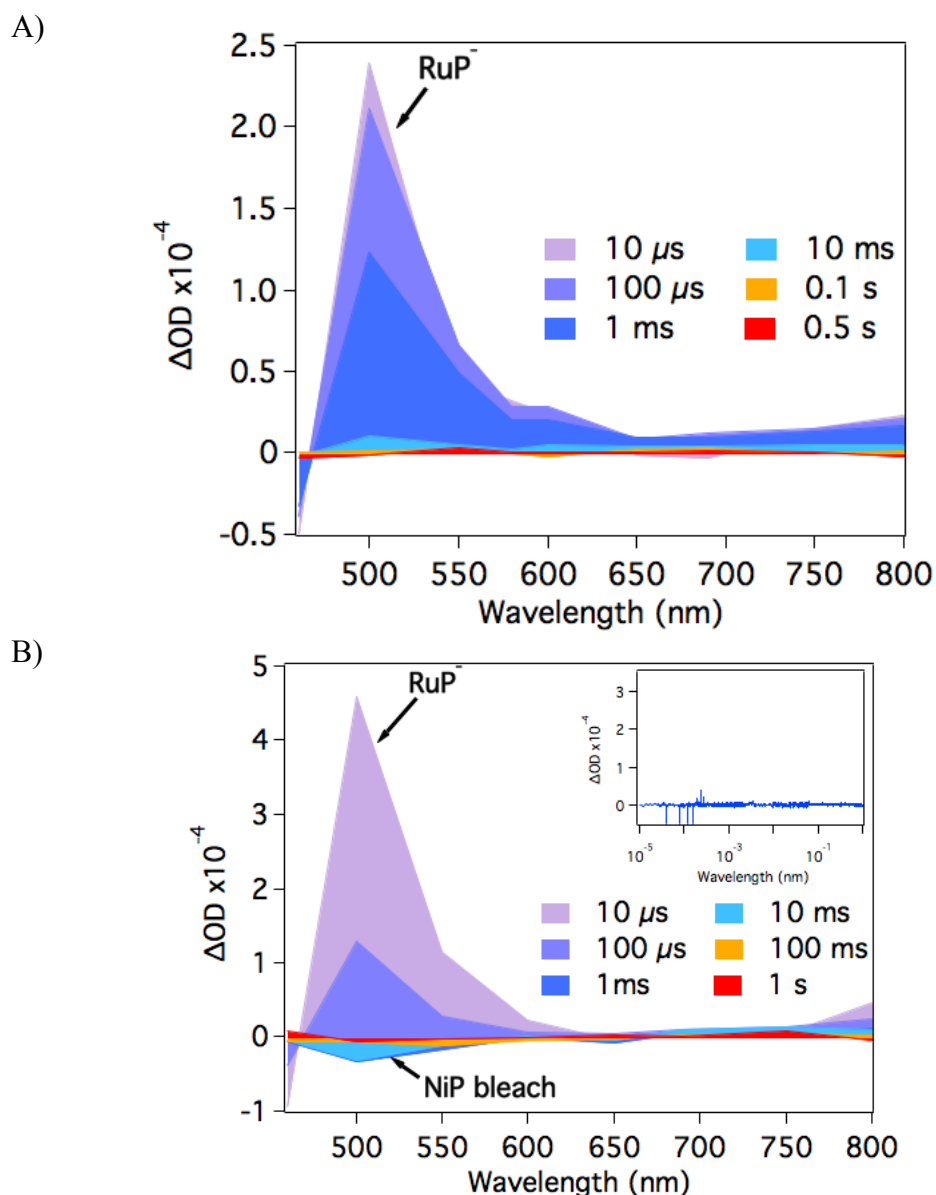


Figure 4-4 Transient absorption spectra as a function of time delay after photoexcitation with 355 nm light of A) **RuP** ($4\mu\text{M}$) and B) **RuP** ($4\mu\text{M}$) and **NiP** ($8\mu\text{M}$) mixture in the presence of ascorbic acid (0.1M) at $\text{pH} = 4.5$. The inset in B) shows the 500 nm signal after photoexcitation of **NiP** ($8\mu\text{M}$) in the same conditions.

The positive transient feature at 500 nm cannot be observed in the absence of ascorbic acid suggesting that it results from the interaction of the excited state of the

photosensitiser and the electron donor. Equally, the negative signal at 500 nm is only observed in the presence of both **RuP** and **NiP** (and SED), this being indicative that it results from the interaction of these molecules. This correlation is further exemplified in Figure 4-5 showing the kinetics of the 500 nm signal for **RuP** and **RuP+NiP**. In the absence of **NiP** a long-lived decay ($t_{50\%} \sim 500 \mu\text{s}$) is monitored. The addition of **NiP** results in a rapid quenching of the 500 nm signal leading to the appearance of a negative change in optical density.

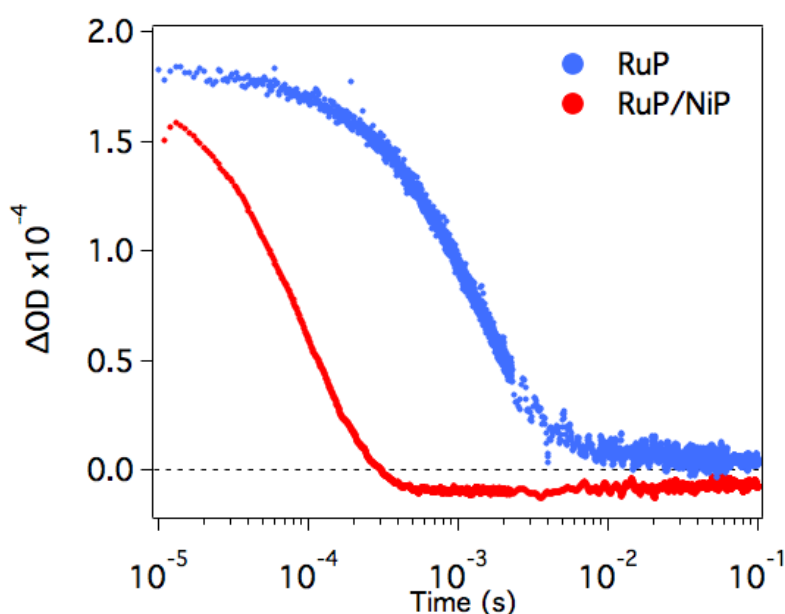


Figure 4-5 Transient absorption decay measured at 500 nm after 355 nm photoexcitation of **RuP** ($4 \mu\text{M}$) and a mixture of **RuP** ($4 \mu\text{M}$) and **NiP** ($8 \mu\text{M}$) in the presence of ascorbic acid (0.1M) at $\text{pH} = 4.5$.

4.4.2. Effect of the pH

Figure 4-6 shows the effect of the pH in the kinetics of the 500 nm features. In the absence of **NiP** the amplitude of the positive signal increases with increasing pH reaching a maximum at pH 5. The pH also affects the decay kinetics but not to a large extent. In the presence of **NiP** the amplitude of the negative signal also increases with increasing pH (to more negative values) with only slight changes in the ground state the recovery kinetics.

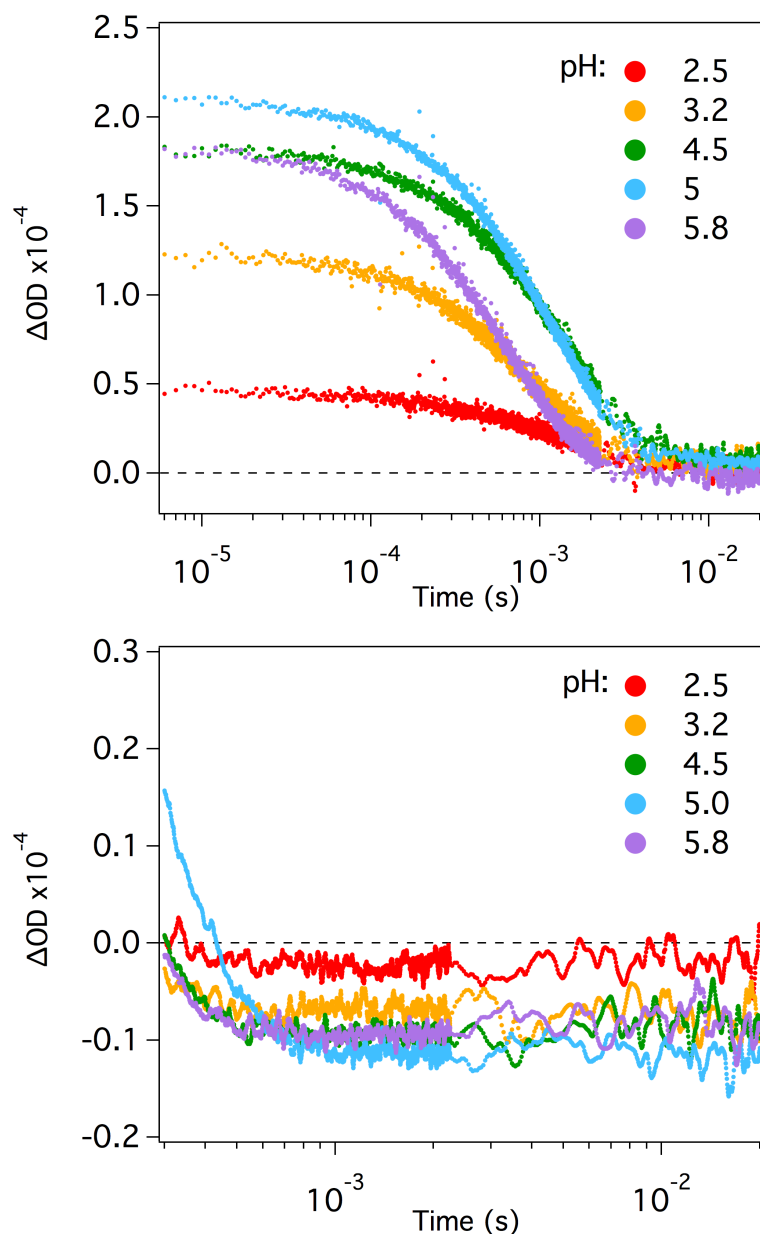
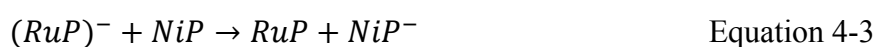
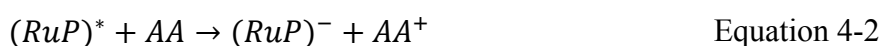


Figure 4-6 Transient absorption decay measured at 500 nm after 355 nm photoexcitation of A) **RuP** (4 μ M) and B) a mixture of **RuP** (4 μ M) and **NiP** (8 μ M) in the presence of ascorbic acid (0.1M) at different pH.

4.5. Discussion

Illumination of the Ruthenium photosensitiser with UV-VIS light induces a metal-to-ligand charge transfer that results in the formation of an excited state with triplet character. This state has a reduction potential (**RuP**^{*}/**RuP**[•]) of approximately 1.1V vs NHE and is therefore susceptible to undergo the reduction by sacrificial electron donors such as ascorbic acid ($E = 0.71$ V vs NHE). This interaction has been

previously reported to occur with relatively high efficiencies (~70%) within 250 ns in homogeneous solution leading to the formation of a reduced sensitiser.[5] The 500 nm maximum monitored in our transient studies (Figure 4-4) is only visible in the presence of both **RuP** and ascorbic acid, suggesting that it results from the interaction of these two molecules upon illumination. Indeed this feature has previously been assigned to the absorbance of the reduced photosensitiser (**RuP⁻**) following reductive quenching by ascorbic acid.[5, 36] On the other hand, the negative signal at 500 nm is only monitored in the presence of AA, **RuP** and **NiP** and only at long times ($t_{50\%} > 500$ ns). This suggests that the bleaching signal does not appear directly after photoexcitation and, that it results, instead, from the slow interaction between the **RuP** and **NiP**. Furthermore, the negative change in absorption coincides spectrally with the ground state absorption of **NiP** (Figure 4-3). This suggests that the feature tracks the optical change of the electrocatalyst. Based on these observations we have assigned the bleaching signal at 500 nm to the disappearance of the ground state absorption (hence negative) of **NiP** upon interaction with **RuP⁻**. The lack of change in absorbance upon direct excitation of **NiP** in the absence of sensitiser and AA supports this assignment (inset of Figure 3-5). Given that the positive absorbance assigned to the **RuP⁻** is quenched as a result of this interaction it is reasonable to assign the process to the 1-electron transfer from **RuP⁻** to **NiP** according to the reaction scheme below:



Hence monitoring the decay kinetics of the light induced absorption of the 500 nm is a probe of the reaction dynamics of the reduced photosensitiser (**RuP⁻**, positive signal) and the reduced electrocatalyst (**NiP⁻**, negative signal).

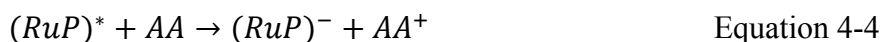
4.5.1. Effect of the pH

Having assigned the optical signals and being able to directly measure the reduced photosensitiser and indirectly the reduced electrocatalyst we now turn to examine the effect of the pH in (i) the electron transfer kinetics and (ii) the catalyst activity.

4.5.2. pH dependence of the electron transfer kinetics

The yield of **RuP⁻** production at different acidities can be obtained from the initial amplitude of ($\sim 10 \mu\text{s}$) of the **RuP⁻** transient signal monitored at 500 nm. From Figure 4-6 A it is apparent that the assay of this yield increases with increasing pH, reaching a maximum at pH $\sim$ 5. This pH dependency can be understood in terms of the reactivity of ascorbic acid at different pH. Ascorbic acid is a diprotic acid, which exists primarily in its undissociated form (H_2A) at low pH ($\text{pK}_a \sim 4.17$), whereas at higher pH the monoprotic ascorbate anion predominates ($\text{pK}_a \sim 11.57$). The ascorbate anion is stronger reducing agent than its protonated form and therefore it is reasonable to expect that the reductive quenching of the excited state of the photosensitiser (**RuP^{*}**) would be favoured at pH > 4 where the ascorbate anion is the dominating species.[20, 37, 38]

Favourable at higher pH



Following the formation of the **RuP⁻**, electrons are transferred to the catalyst (see Equation 4-3). As shown in Figure 4-5, in the presence of **NiP**, the positive absorbance assigned to **RuP⁻** at 500 nm is rapidly quenched leading to the appearance of a negative signal at longer times ($500 \mu\text{s}$ to 1 s). This signal is assigned to the ground state bleaching of **NiP** and is associated with the electron transfer (ET) from **RuP⁻** to **NiP**. In the absence of **NiP** or after direct excitation of **NiP** no signal is measured, further supporting our assignment. Alike with the photosensitiser, we can obtain the yield of ET from **RuP⁻** to **NiP** from the amplitude of the negative signal. In this context, a greater negative signal is indicative of more reduction of **NiP** to form **NiP⁻** (the more **NiP** reacts, the larger the loss of ground state absorbance). It is apparent from Figure 4-6 B that this assay of ET increases with increasing pH, reaching a maximum at pH = 5. Hence more reduced intermediate is formed at higher pH. It is noteworthy that the ET kinetics between the reduced photosensitiser and the catalyst are relatively fast, suggesting that this process is unlikely to be rate limiting in

the overall catalysis. On the other hand, the signal assigned to reduced **NiP** is relatively long lived suggesting its further reactivity might possibly be rate limiting.

Figure 4-7 compares the pH dependency of the 500 nm signals namely, the transient bleach assigned to the yield of reduced **NiP** (blue circles, in absolute value for clarity), the ratio of reduced **NiP** per **RuP**[−] molecules (black triangles, calculated as the signal ratio at 10 μs and 1 ms) as well as the TOF_{NiP} (H₂) per catalyst molecule (red squares) as measured previously by Reisner and co-workers.[5] It is apparent from Figure 4-7 that both the yield of reduced **NiP** intermediate and the TOF of the system are strongly pH-dependent however, the ratio **NiP**-to-**RuP**[−] is pH-independent. These results hence suggest that the electron transfer from **RuP**[−] to **NiP** is independent of pH.

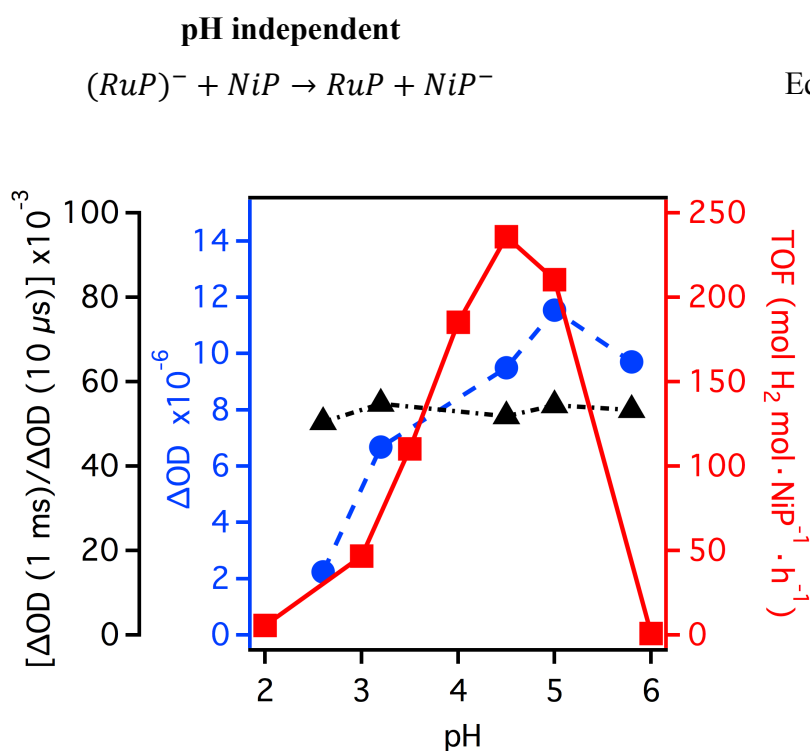


Figure 4-7 Absolute values of the transient absorption signal amplitude of the **NiP** bleach at 1ms (blue circles), transient absorption ratio of **NiP** at 1ms and **RuP** at 10 μs (black triangles) and TOF_{NiP} (H₂) (red squares) reproduced from reference [5]

4.5.3. pH dependence of the catalyst activity

The observed increase in the yield of reduced **NiP** and consequently in the TOF_{NiP} (H_2) can be directly assigned to the increase in the yield of reduction of **RuP** to **RuP⁻**, due to the pH dependence of the electron donating character of ascorbic acid. However, it is striking that at $\text{pH} > 4.5$ the TOF rapidly decreases despite the yield of reduced **NiP** remaining at its maximum. As discussed in the introduction to this chapter, this sharp maximum in performance has also been observed in many other photocatalytic systems. Given that the yield of the reduced **NiP** intermediate remains approximately constant at $\text{pH} > 4.5$, the sharp decrease in H_2 evolution at higher pH is indicative of decrease in the catalytic ability of the Niquel catalyst.

The mechanism of the catalysis is yet unknown, with even less evidence in aqueous media (relevant for this study).[39, 40] Following the reduction of the catalyst, protonation is expected to occur. This process might take place both in the metal centre or in the pendant amines; however recent DFT calculations suggest that the protonation of the amines might be more favourable.[39] This is also in agreement with acid concentration studies, which show that these amine groups with low pK_a might have a key role in the catalysis by acting as proton relays between the solvent and the metal centre.[27, 28, 41, 42] Interestingly, pH titration with NaOH (0.1 M) of the Niquel catalyst studied herein revealed two equivalence points at $\text{pH} \sim 5$ and $\text{pH} \sim 9$ due to the deprotonation of the pendant amines and the phosphate groups. These assignment were further confirmed by the titration of the analogous bis(diphosphine) Niquel complex with ethyl esters groups instead of the phosphonic acids.[43] An equivalence point at $\text{pH} \sim 5$ yields an approximate $\text{pK}_a \sim 3$ from the Henderson-Hasselback equation meaning that at $\text{pH} \sim 3$ half of the amines are deprotonated and at $\text{pH} > 5$ all amine groups are deprotonated. Since these groups have been reported to be key in the reduction of protons, it is reasonable to assign the low activity observed at $\text{pH} > 4.5$ to the poor protonation of the amines, that at sufficiently high pH inhibits the ability of **NiP** to reduce protons completely. It is important to note that the photosensitiser employed in this study also contains phosphonic acid groups, however the pK_a for these has been reported to be 1 and 12 and therefore the buffer capacity in the pH range here studied is limited.

These observations match with the strong pH-dependencies reported with other photocatalytic system employing sacrificial electron donors. Whereas at low pH the protonation of the sacrificial decreases the electron donating ability limiting the performance; at high pH when this ability is optimum, the poor protonation of the catalyst limits the catalytic process. Hence this study shows that the optimum pH of homogenous photocatalytic systems is a compromise between the electron donor ability of the sacrificial and the optimum working environment of the catalyst.

4.6. Conclusions

The transient studies presented herein provide evidence of the nature of the optical signals of a model photocatalytic system for H₂ evolution, consisting of a sacrificial electron donor, a dye and an electrocatalyst. The studies show how the acidity of the medium influences the yield of electron transfers in the system and ultimately controls the H₂ evolution activity. Therefore, these results help explain the pH dependency of these complex photocatalytic systems. Specifically it has been found that the electron transfer from the sacrificial donor to the dye is favoured at high pH and that the electron transfer from the reduced dye to the catalyst is independent of pH. The data shown here suggests that the performance of the system can be controlled by matching the rates of electron transfer reactions and the optimum protonation of the catalyst and that this can be achieved by tuning the pH of operation.

4.7. In the next chapter

In *Chapter 3* and *4*, heterogenisation and pH tuning have been explored as strategies to control the lifetime of intermediates and the catalytic activity. In the next chapter a solid-state photocathode is studied. Despite the obvious difference between molecular and solid proton reduction systems, they have similar challenges, namely the competition between recombination reactions and catalysis. As in molecular systems, in the solid-state electrodes long intermediate lifetimes and control of the catalytic activity is key to achieve high quantum yields, however the routes to achieve this might be different.

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Chapter Five

Kinetic study of a solid-state proton reduction photocathode

The key factors controlling the efficiency of a state-of-the-art photocathode for H_2 evolution are studied in this chapter. The photocathode is based on a Cu_2O light absorber, coupled to a proton reduction electrocatalyst (RuO_x) in a multi-junction structure. The experimental evidences presented herein show that, the buried junction controls the separation of charge in this system and that the onset of photocurrent is dictated by the energetics of this junction. Evidence suggesting the active role of the catalyst in preventing undesired recombination reactions is also provided. Furthermore, from the mechanistic point of view, the results suggests that, the nature of the rate-limiting step in the catalytic cycle has a significant impact on the recombination kinetics and that purely electrochemical techniques can be used to study photo-electrocatalytic mechanisms. The results presented in this chapter provide material design rules to aid the development of multi-junction photoelectrodes.

5.1. Introduction

Photoelectrochemical cells (PEC) containing semiconductor-based photoelectrodes are an alternative to homogeneous molecular catalysts. PEC are usually more robust than molecular systems and offer solvent flexibility as the electrode needs not be solubilised. Proton reduction in PECs has been achieved using relatively scarce materials like p-GaInP₂ and GaAs,[1] or p-InP.[2] However, if PEC cells are to be used in a large scale they must rely on earth abundant semiconductors and catalysts. In this context copper oxides are attractive as they are photoactive and based on elements already processed in large scales. p-type Cu₂O has recently emerged as a potential candidate for H₂ generation in PEC cells, with remarkable H₂ evolution performances, and reasonable stabilities being reported for a multilayer Cu₂O based photocathode. [3]

5.1.1. Cu₂O as a photocathode

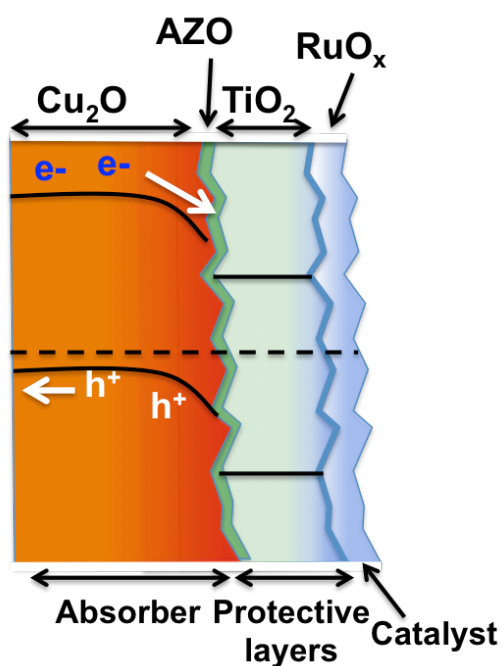
Cu₂O is a p-type semiconductor with a direct bandgap of 2-2.5 eV. Its p-character arises from Cu vacancies close to the valence band and its energy gap allows an integrated photocurrent of up to -14.6 mA cm⁻² under AM1.5 illumination.[3, 4] Due to these qualities Cu₂O has been explored as electrode for batteries,[5] solar-to-fuel conversion,[6-10] or photovoltaic applications.[11, 12] However Cu₂O has a major drawback; its conduction band is more reductive than the reduction potential for the reduction of Cu₂O to Cu⁰ and its valence band is more oxidative than the oxidation potential of Cu₂O to Cu^{II}O. This renders the material photounstable in water as photogenerated electrons and holes can react with the bulk material.[3]

The photo and electrochemical stability of this oxide has been reported to be dependant upon the exposed crystal facets, and hence upon the method of preparation. For example, O²⁻ terminated facets as opposed to Cu²⁺ facilitate the adsorption of protons, and thus increase the instability in water.[13] At the same time, the nature of the surface has also been reported to be a factor determining the efficiency of photoreduction reactions. Predominant (111) facet, usually obtained by electrodeposition methods, favour the reduction of protons to H₂ whereas (101) facets obtained by solvothermal methods facilitate de adsorption and reduction of CO₂

molecules.[6] For these reasons stabilising Cu₂O photocathodes whilst preserving its catalytic properties has proven extremely challenging.

In 2011 Grätzel and co-workers reported a highly active and stable Cu₂O photocathode (Figure 5-1A).[3] The architecture was composed of a p-type Cu₂O light absorber synthesised by electrodeposition conformably coated with protective layers, deposited by Atomic Layer Deposition (ALD). The overlayers were made of Al doped ZnO (Al:ZnO or AZO) and TiO₂. This photocathode produced currents of up to -7.6 mA cm⁻² under 1.5 AM illumination at 0 V vs RHE with an onset potential of 0.5 V vs RHE. The high H₂ evolution performance was achieved by deposition of Pt nanoparticles that acted as proton reduction catalysts. However, the performance of the cathode still decreased over time due to the dislodging of Pt during photolysis. In order to address this problem, the Pt catalyst was replaced by a layer of RuO_x (x<2), a well-known water oxidation and reduction catalyst.[14] In the presence of this oxide the stability of the film significantly improved and large photocurrents were achieved (~ 5mA cm⁻²) with a similar onset of photocurrent (0.5 V vs RHE). Figure 5-1B shows the performance of the photocathode in the presence of the RuO_x catalyst. More recently MoS_{2-x} was reported as an earth abundant alternative to the RuO_x, achieving similar performances.[15]

A)



B)

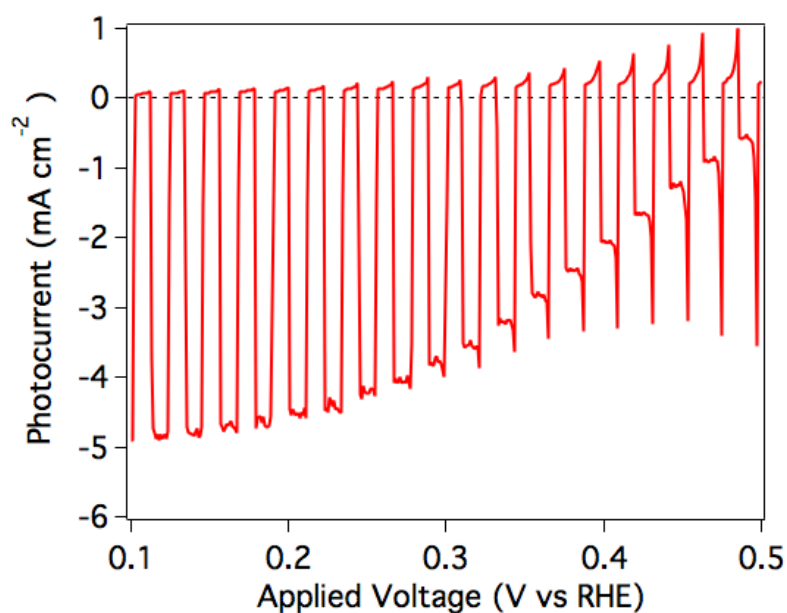


Figure 5-1 A) Schematic representation of the Cu_2O photocathode with RuO_x and B) Current-Voltage characteristics of a Cu_2O photocathode with RuO_x under light chopping at 1 sun measured in a pH 5 phosphate-sulfate electrolyte.

5.1.2. Semiconductor coatings

The idea of passivating the surface of a material with poor stability such as Cu_2O has been previously explored.[10, 16] However, due to the development of deposition

techniques such as ALD and CVD, this approach is becoming increasingly popular.[16] Recently semiconductor protective coatings have been employed on p-Si and p-GaP as well p-InP photocathodes for H₂ evolution.[17-19] Overlayers have also been used to protect photoanodes such as n-Si and n-GaP.[20] Even molecular catalysts and chromophores have been stabilised by Al₂O₃ coatings prepared by ALD.[21]

Besides its role in improving stability, overlayers have also been employed to enhance the performance of solar fuels systems. Fe₂O₃ photoanodes for O₂ evolution have been improved by the deposition of Al₂O₃ overlayers.[22] Anatase TiO₂ coatings have been used to improve p-CuFeO₂ and rutile TiO₂ for water reduction and oxidation respectively.[23, 24] Notably not only oxides have been explored; TiO₂ has also been used to coat CuInS₂/CdS electrodes resulting in better performances.[25] Often the improvements gained with the overlayers are attributed to the reduction of recombination reactions and improvement of charge separation. However, especially in photocathodes, little evidence is yet available supporting this. Moreover the importance of the buried junction between materials and the role of added catalysts is relatively unexplored.

5.1.3. Charge recombination in PEC cells

As discussed in *Chapter 1*, recombination reactions are considered a major loss pathway in PEC systems. This problem arises from the mismatch between the timescales of charge photogeneration and catalysis.[26] In Fe₂O₃, a very intensively studied photoanode, recombination reactions occurring in the picosecond to nanosecond timescale compete with the oxidation of water reported to occur in the millisecond to second timescale.[27] Consequently in order to achieve meaningful quantum yields the photoelectrodes must be capable of retaining separated charges long enough for them to react.

PEC cells rely on the semiconductor/electrolyte junction to separate photogenerated charges. After photoexcitation the electric field in the space charge layer helps separating the electrons and holes and avoid bulk recombination. Following that process, the majority carriers are extracted through the external circuit and the

minority carriers accumulate at the interface before they react. These accumulated charges can still recombine before they react with the electrolyte, a process often termed 'surface' or 'back electron / hole' recombination.[28]

Charge separation and back electron hole recombination have been extensively studied in semiconductors used in solar-to-fuels applications.[26] The role of surface defects and the space charge layer in the semiconductor/electrolyte interface has also been carefully investigated.[29] However, often these studies were limited to bare semiconductors (namely, without overlayers) and there is little information on multi-layer materials describing the role of the buried junctions with regards to charges separation and recombination.

5.2. In this chapter

The use of protection layers and multiple p-n junctions structures has emerged as a promising route for the development of efficient photoelectrodes. These architectures are thought to provide system robustness and also aid the catalytic process. Despite these advantages, preparation of such architectures is non-trivial and often relies on the use of non-abundant materials. Understanding the role of the junctions in the kinetic and catalytic process can help discern what material properties and functions are essential to performance. Ultimately it can help tailor device fabrication to specific needs. The $\text{Cu}_2\text{O}/\text{AZO}/\text{TiO}_2/\text{RuO}_x$ photocathode is an example of a high efficient multi-layer photocathode; however its onset of photocurrent is 400 mV cathodic from its apparent ideal value and its catalytic properties are yet not well understood. Studying the electron transfer reactions occurring within this structure can help elucidate the factors controlling the onset of photocurrent and the nature of catalytic reaction and thus, help further improve the efficiency of the photocathode. In this chapter Transient absorption Spectroscopy is used to study the role of the p- $\text{Cu}_2\text{O}/\text{n-Al:ZnO}$ buried junction as well as that of the TiO_2 and the catalyst layers. The effect of these layers on charge separation, back electron hole recombination and catalysis is studied in order to gain insight into the key factors limiting the function of a state-of-the-art photocathode.

5.3. Experimental methods

The photocathode employed in this study consisted of a Cu_2O light absorber coated with Al:ZnO and TiO_2 . The electrode was activated for proton reduction with a RuO_x ($x < 2$) catalyst layer (see band diagram in Figure 5-9). The samples were prepared by Dr. David Tilley (École Polytechnique Fédérale de Lausanne) as previously reported.[14] Structural information details can be found in the appendix of this thesis. Details on the thickness of the samples and its electrical properties are shown in Table 1

Table 1 Details of the Cu_2O photocathode employed in this study. The values were obtained from reference [30]

<i>Layer</i>	E_{fb} (V/RHE)	Thickness (nm)	N_D (cm^{-3})	N_A (cm^{-3})	Type
Cu_2O	+0.8	400	-	5.0×10^{17}	p-type
AZO	-0.330	20	1.6×10^{21}	-	n-type (deg.)
TiO_2	-0.1	100	4×10^{20}	-	n-type
RuO_2	+0.4	-	-	-	metallic

The measurements described in this chapter were carried out using the photoelectrochemical set up described in *Chapter 2* (PIA set up). The measurements were conducted in a 3-electrode cell containing a pH 5 phosphate-sulphate buffer. The Cu_2O photocathode was the working electrode and platinum gauze was used as a counter electrode. The potentials were applied against a Ag/AgCl reference electrode saturated with KCl ($E = + 0.197 \text{ V}$ vs NHE) and were converted to reversible hydrogen potential (RHE) according to the Nerst equation (Equation 2-13). Illumination of the sample was through the electrolyte/semiconductor interface unless otherwise stated and the illumination area was determined to be $\sim 0.5 \text{ cm}^2$. Sample integrity between measurements was assessed by measuring the photocurrent response of the photocathode before and after the experiment. Steady state absorption of the studied samples was also measured and compared between experiments.

5.4. Results

5.4.1. Optical Signals

Figure 5-2 shows the steady state spectra of bare Cu_2O as well as that of Cu_2O with additional overlayers. The spectra were calculated from the transmission data (as $-\log(T)$). All samples have a similar absorption profile characterised by a strong absorption in the UV region indicative of a virtually pin-hole free structure. All spectra are dominated by the strong absorption of the Cu_2O phase, which is the thickest layer. The addition of thin overlayers does not cause a significant change in the absorption edge compared to that of Cu_2O that renders a bandgap of ~ 2.5 eV, expected for Cu_2O . [3, 31] The apparent absorbance at wavelength greater than 600 nm is caused by reflections at the sample due to the high quality interfaces (the effect of this reflections is discussed in *Chapter 6*).

Unless otherwise stated, in the following sections the architecture composed of $\text{Cu}_2\text{O}/\text{AZO}/\text{TiO}_2$ is referred as “ Cu_2O photocathode”.

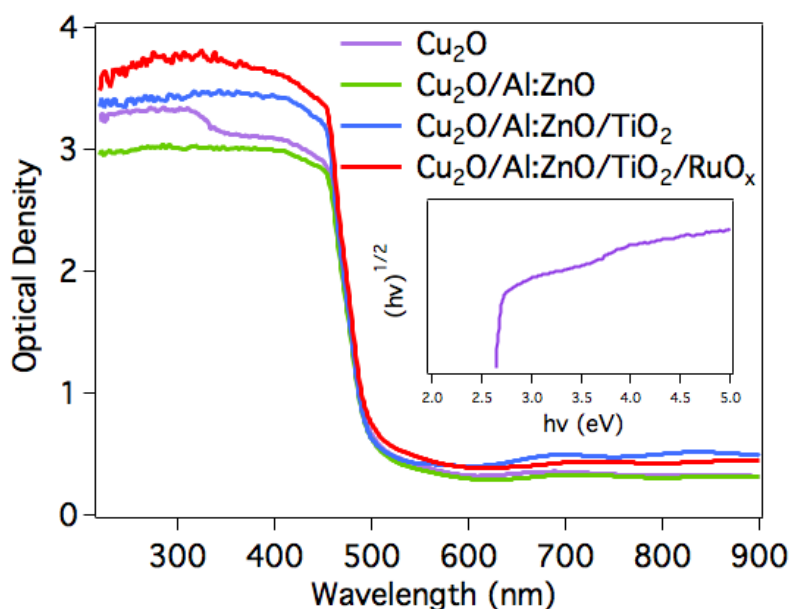


Figure 5-2 Steady state absorbance of a Cu_2O thin film and electrodes composed of Cu_2O with different protective layers (Al:ZnO and TiO_2) and the catalyst (RuO_x). The inset shows the tauc plot of Cu_2O .

Figure 5-3 shows the steady state JV response of the photocathode under low light conditions.[14] These conditions are chosen to reproduce those of the PIA measurements (see *Chapter 2* for details) and maintain sample stability. In the absence of RuO_x no catalytic current is observed. Upon the addition of the catalyst a catalytic current is monitored (red line). A current of -1 mA cm^{-2} is achieved at approximately 0.35 V vs RHE. Negligible photocurrent is monitored in the dark.

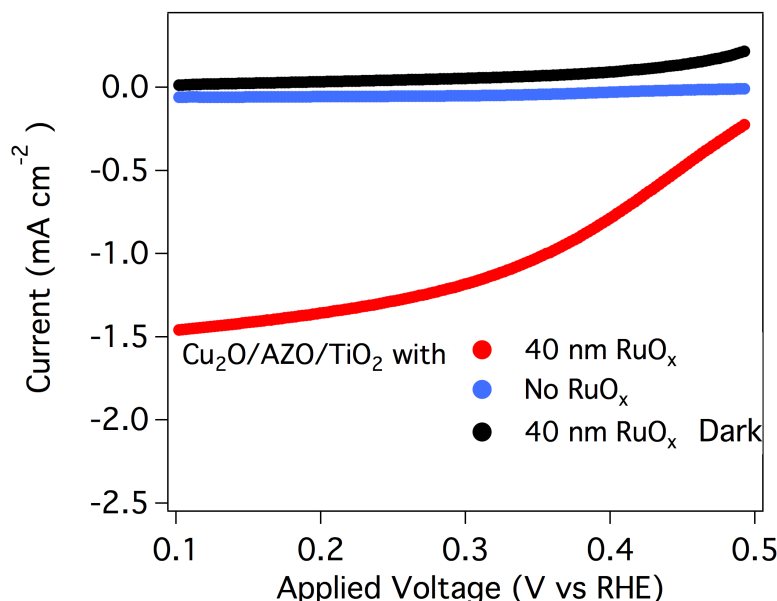


Figure 5-3 Current densities in mA cm^{-2} of a Cu_2O photocathode tested in a pH 5 phosphate-sulfate electrolyte, measured in the dark (black line) and under light with and without the presence of catalyst (red and blue lines), shown as a function of applied potential. The illumination conditions are chosen to match those of the photoelectrocatalytic experiments.

In order to gain insight into the kinetics of charge carriers under operation-like conditions in a photoelectrochemical cell, we performed Photo Induced Absorption (PIA) measurements. These measurements differ from transient absorption measurements in the source (an LED as opposed to a laser) and length of the excitation pulse. Changes in optical signal are recorded during and after long ($> 2 \text{ s}$), continuous illumination pulses. The electric current passing through the electrode is simultaneously measured. This method enables the analysis of (i) charge accumulation under illumination and (ii) the decay of these charges after the light is switched off. [32]

The steady state PIA signal obtained at 5 s after front illumination (365 nm) of the system ($\text{Cu}_2\text{O}/\text{AZO}/\text{TiO}_2$) with and without the catalyst (RuO_x) is shown in Figure 5-4A. In both cases an increasing absorption towards the IR is observed. Notably, the size of the signal for the sample containing RuO_x is larger than that without it. A similar spectrum is obtained for the photocathode containing Pt rather than RuO_x (Figure 5-4A inset). Interestingly, when the sample is illuminated through the back (i.e. through the FTO glass), a negative signal is observed at all wavelengths and steady state is only reached after 15 s of illumination (Figure 5-4B).

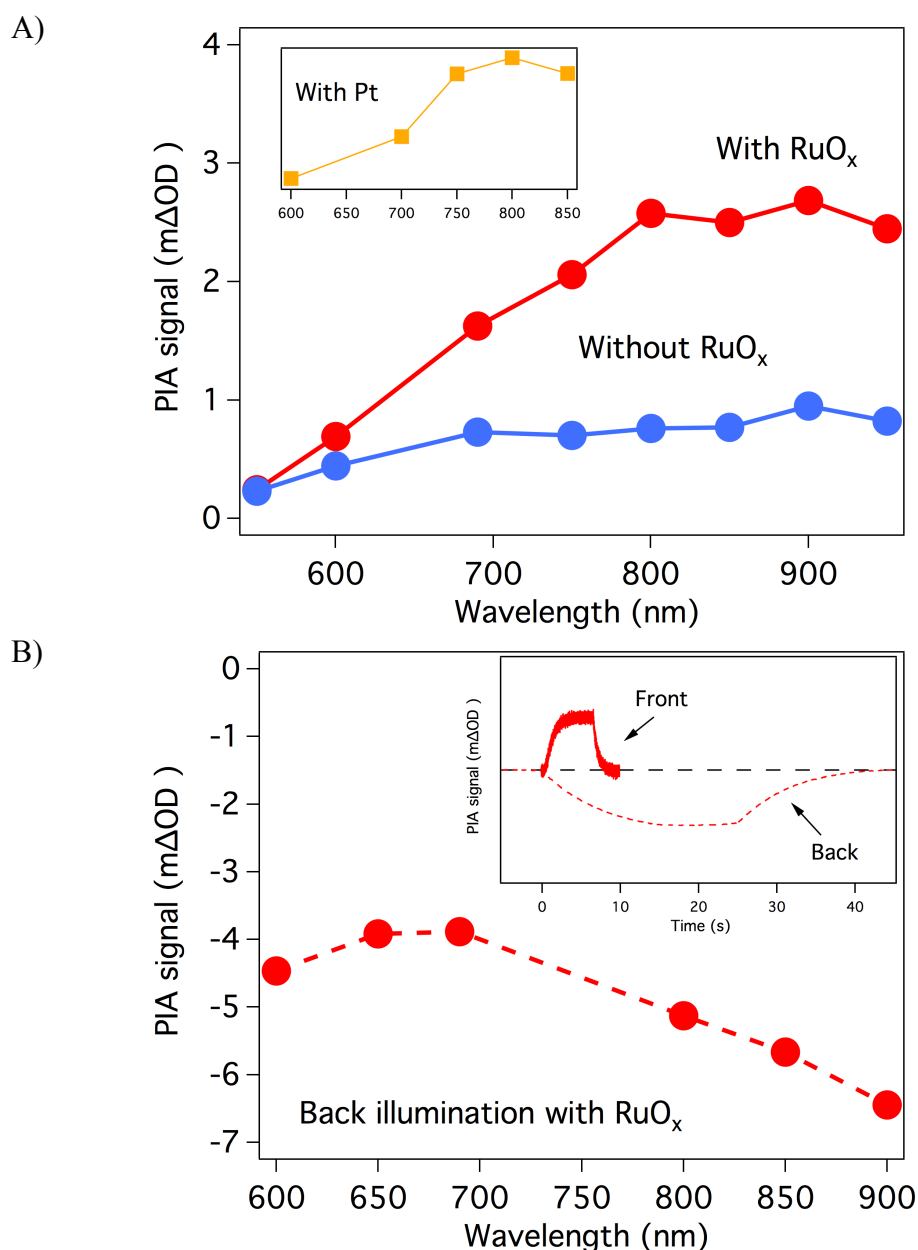


Figure 5-4 Photoinduced absorption spectra of A) the Cu₂O photocathode with and without the H₂ evolution catalyst (RuO_x or Pt-inset) and B) the Cu₂O photocathode with RuO_x after back illumination. The samples were held at 0.3 V RHE (with RuO_x) and 0.1 V (without RuO_x and Pt, to avoid damage) in a pH 5 phosphate-sulfate electrolyte and the points shown are acquired at the equilibrium plateau attained during illumination. The inset in B shows a normalised example of the PIA signal as a function of time for a photocathode with RuO_x measured though front an back illumination; a significant difference in the time is required to achieve a steady state value.

Figure 5-5 shows PIA spectra collected with front illumination of the photocathode at different applied potentials. A positive signal is obtained at potentials cathodic of 0.4 V vs RHE whereas a negative signal is obtained at potentials anodic of 0.3 V vs RHE. For all cases, a cathodic photocurrent was measured as expected from the JV curve. This photocurrent was found to be stable during the course of the different measurements as shown in the Figure inset.

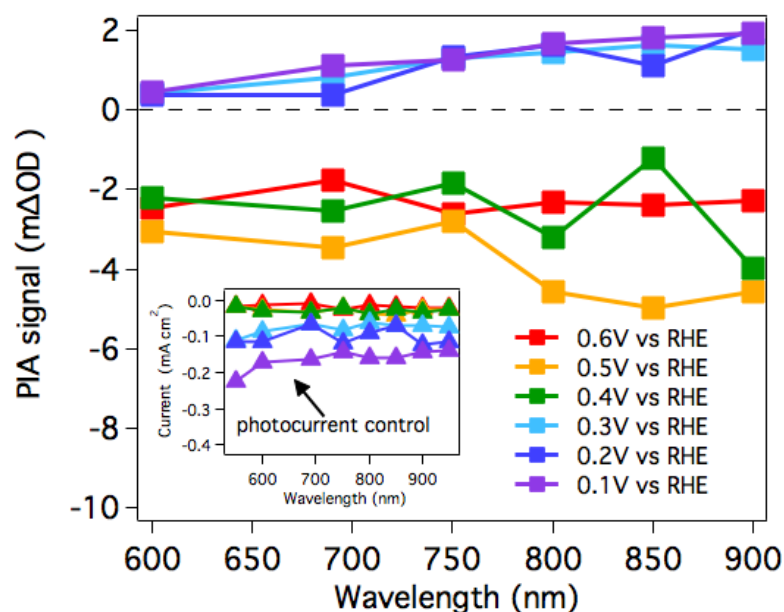


Figure 5-5 Photoinduced absorption spectra of the Cu_2O photocathode with the H_2 evolution catalyst (RuO_x) measured at different applied potentials. The samples were measured in a pH 5 phosphate-sulfate electrolyte and the points shown are acquired at the equilibrium plateau attained during front illumination. The inset shows the photocurrent plateau measured simultaneously with the optical signal at different wavelengths.

5.4.1.1. Signal assignment

The photo induced absorption spectra measured at steady state during a ~ 6 s illumination pulse shows an absorption band increasing towards the near-IR. (Figure 5-4A) This increase in absorption is observed in the sample without catalyst ($\text{Cu}_2\text{O}/\text{AZO}/\text{TiO}_2$) as well as when the sample contains RuO_x or Pt ($\text{Cu}_2\text{O}/\text{AZO}/\text{TiO}_2/\text{RuO}_x$ or $\text{Cu}_2\text{O}/\text{AZO}/\text{TiO}_2/\text{Pt}$). This suggests that the positive optical feature does not result only from the absorption of the catalyst layer, but primarily from the Cu_2O or the TiO_2 layer. This claim is further supported by

spectroelectrochemical studies of RuO_x under applied potential showing little absorption in this region at moderate applied potentials.[33]

Previous reports of the transient absorption spectra of Cu_2O and TiO_2 have shown that electrons in these materials absorb in the near-IR nm region.[6, 34-36] Cu_2O electrons have been reported to have a narrow absorbance signature at wavelength longer than 700 nm. At shorter wavelengths, the ground state bleach of the Cu_2O dominates the transient spectra. Conversely, TiO_2 electrons have been shown to have a broad spectral signature, with absorption from ~ 500 nm onwards, similar to the one monitored in our experiments. Based on the larger similarity of our PIA spectra with that of TiO_2 electrons, we tentatively assign the absorption feature around 900 nm to the absorption of electrons accumulated in the TiO_2 layer.

It is noteworthy that the direct generation of charges in the TiO_2 , upon front excitation cannot be excluded. However, due the small absorbance of the thin (~ 100 nm) TiO_2 layer at the excitation wavelength this contribution is expected to be small. Indeed, we do not observe the characteristic strong absorbance at 550 nm associated with photogenerated TiO_2 holes. Hence, the optical signals studied herein are considered to be predominantly due to charges generated in the thick Cu_2O layer. In order to confirm our optical assignment, a PIA spectra of bare Cu_2O and the Cu_2O with Al:ZnO in the absence of TiO_2 would be necessary. However, the instability of the samples under photoelectrochemical conditions without the Al:ZnO/TiO_2 protection layer hampers these assignments.

5.4.2. The effect of the catalyst

Figure 5-6A shows the PIA signal at 900 nm of the photocathode in the presence and absence of the catalyst (RuO_x), under the same illumination conditions and strong cathodic bias (0.1 V vs RHE). A positive PIA signal is observed in both cases reaching a steady state value within 2-4 s. The amplitude of the signal without RuO_x is half of the one obtained with RuO_x indicating a smaller density of accumulated electrons (see also spectra in Figure 5-4). As expected, in both cases, the positive absorbance decays when the illumination is interrupted (from ~ 6 s onwards) and the pre-pulse state is recovered. Figure 5-6B shows the photocurrent change measured

simultaneously with the optical signal. When the pump light is turned on (time 0 s) a negative photocurrent spike is measured. This current peaks are indicative of a reduction reaction and have previously been assigned to recombination processes.[37] The size of this negative photocurrent spike is greater for the sample without the catalyst. In the presence of RuO_x the current rapidly reaches a steady state value while, in the absence of the catalyst, it decays to an almost negligible value. The photocurrent at steady state value is approximately 5 times smaller without the catalyst. When the light is turned off, a positive current spike is observed in both samples. This signal has also been previously assigned to a recombination reaction.[37] The height of this positive photocurrent spike is greater for the sample without the catalyst.

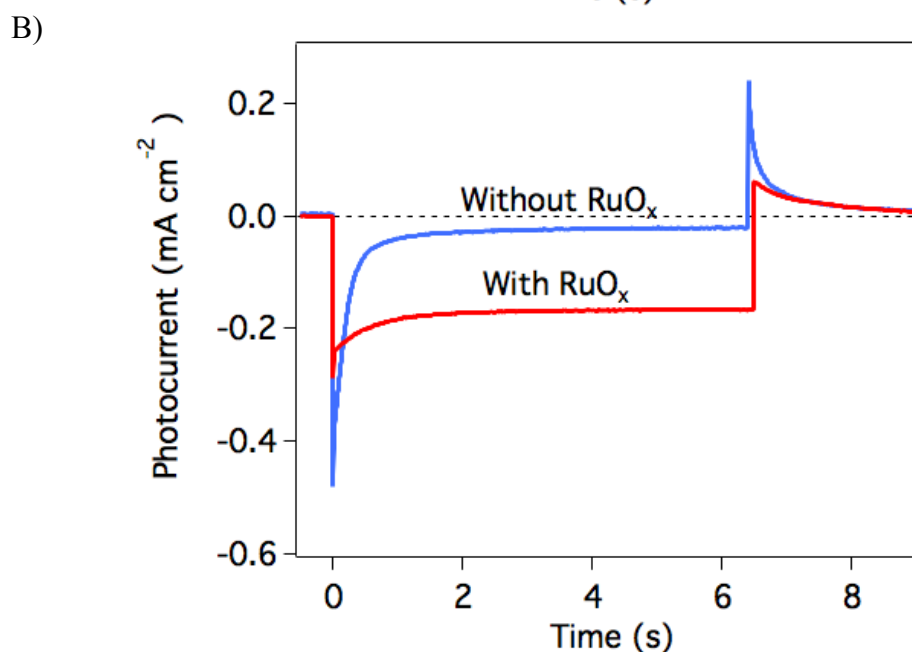
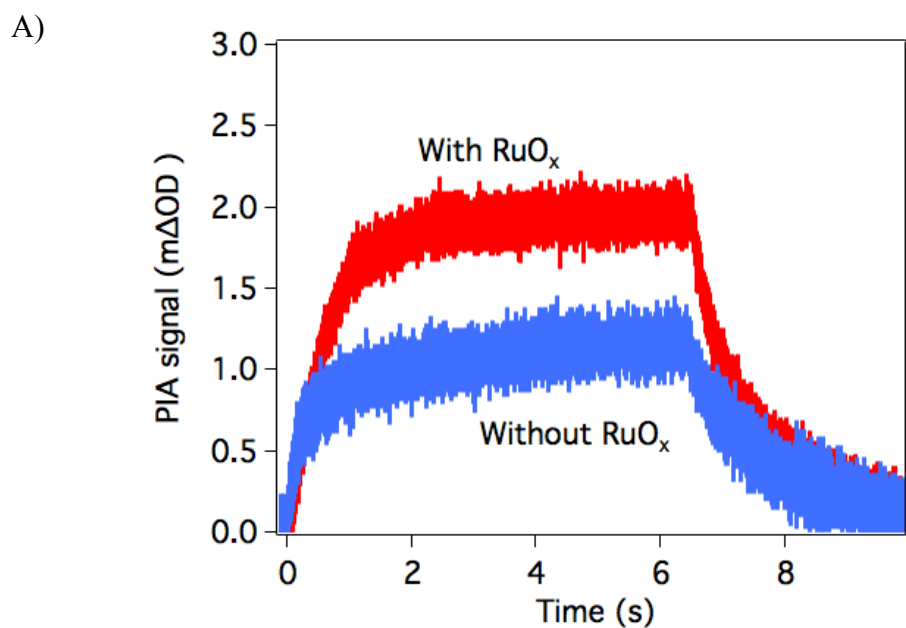


Figure 5-6 Time resolved A) PIA signal at 900 nm and B) photocurrent measured simultaneously for the Cu₂O photocathode with and without the catalyst (RuO_x) during ~5s illumination (0.9 mWcm⁻²) at 365 nm at 0.1 V vs RHE.

Our transient measurements suggest that recombination reactions, assayed through the transient photocurrent spikes, occur more in the photocathode without RuO_x. This is consistent with the lower photocurrents observed for this system.

5.4.3. Effect of applied potential and illumination intensity

Figure 5-7 shows the photocurrent measured at different applied potentials with and without the catalyst. From this figure we can make the following observations:

- (i) Both the positive and negative photocurrent spikes are significantly higher for the sample without catalyst for all applied potentials.
- (ii) In the sample without RuO_x , a shift in the applied potential from 0.3 V to 0.1 V vs RHE slows down the photocurrent decays, both when the light is turned on and when it is turned off.
- (iii) In the sample with RuO_x , the effect of applied potential on the transients is smaller, with only significant changes between 0.3 V and 0.2 V vs RHE.

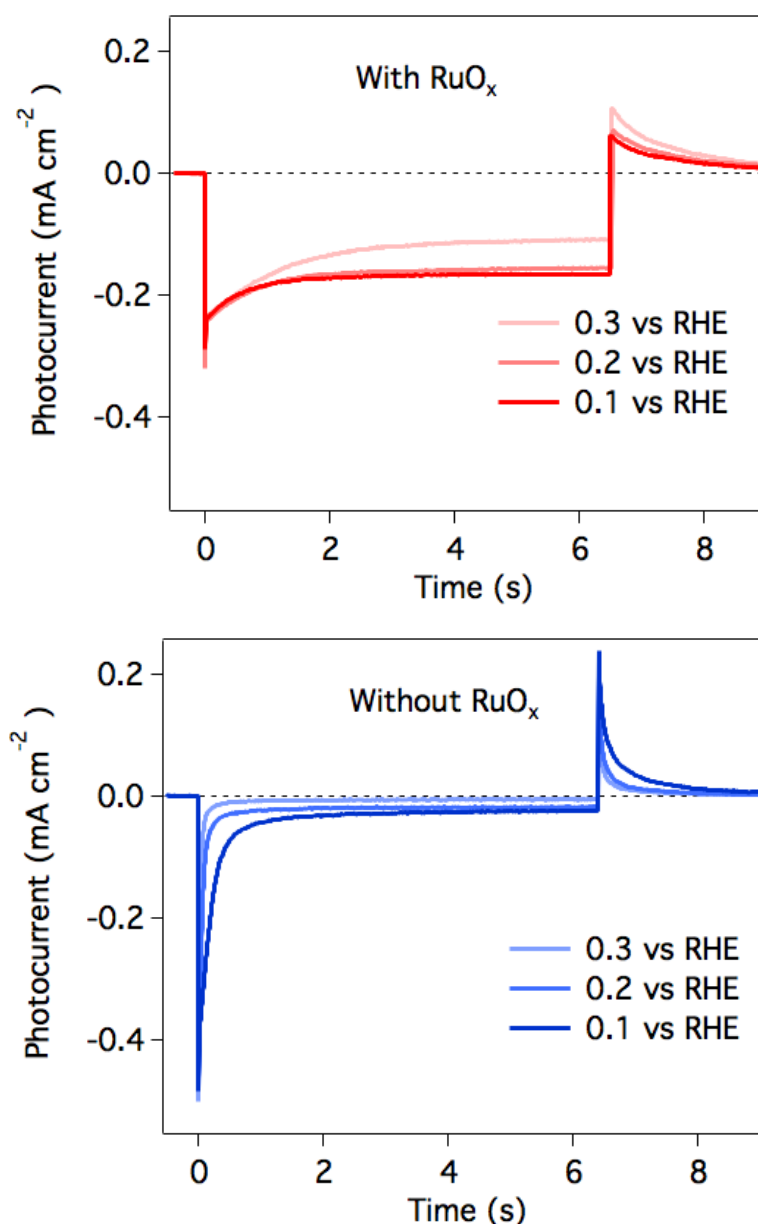


Figure 5-7 Photocurrent transients measured at different applied potentials for the Cu₂O photocathode A) with and B) without the catalyst (RuO_x). The samples were measured during a ~6 s illumination pulse with 356 nm light (0.9 mWcm⁻²)

These observations further support the hypothesis of recombination reactions taking place to a larger extent in the system without catalyst. This unwanted process appears to occur at all studied applied potentials, slowing down at stronger cathodic biases. Under these conditions, larger steady state photocurrents can be measured. However, these are still modest compared to the system with catalyst.

Figure 5-8 shows PIA signal (A) and the photocurrent (B) of a Cu_2O photocathode measured at different light intensities. Both photocurrent and accumulated electron density (PIA signal) are found to increase with increasing light intensity. If we focus on the photocurrent, we observe that: (i) at low light intensities, it rapidly ($t < 1$ s) reaches a steady value whereas (ii) at high light intensities, a pronounced photocurrent spike occurs and the initial photocurrent partially decays until it reaches a steady state. In all cases, when the light is turned off a reverse current peak occurs.

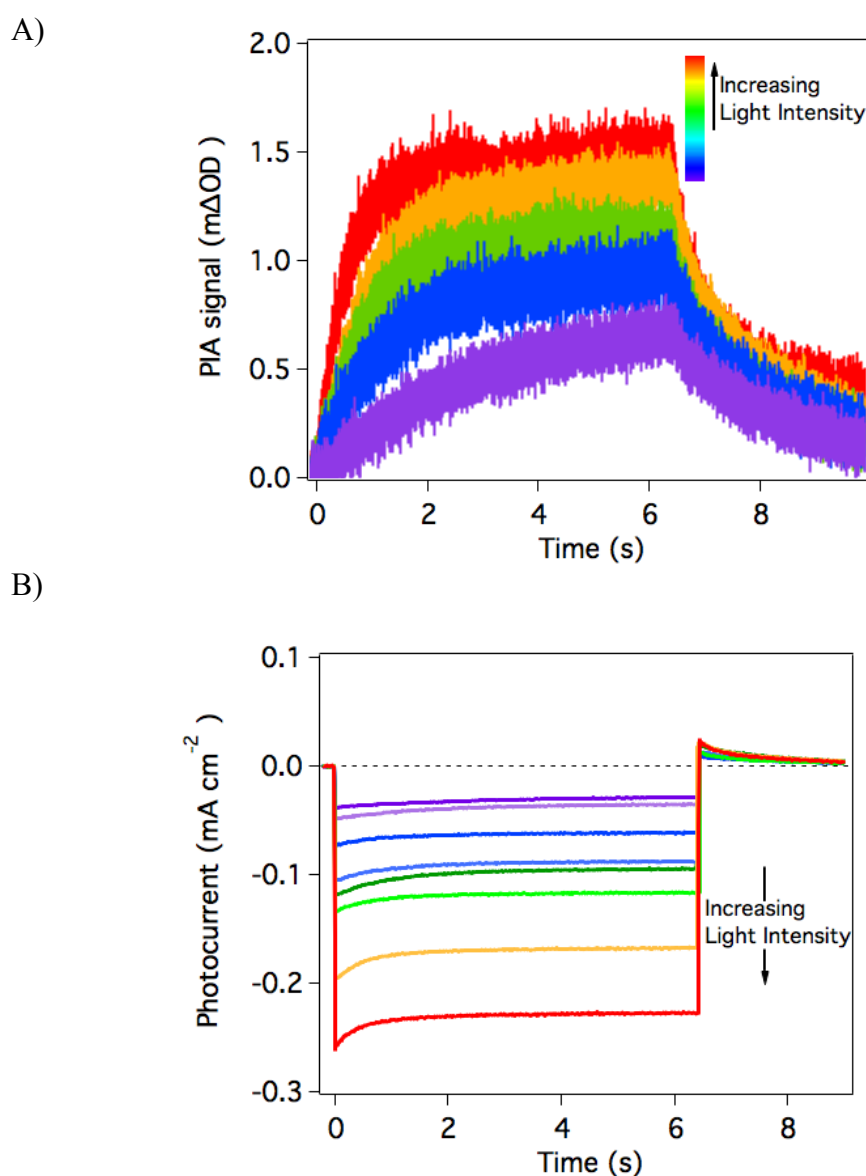


Figure 5-8 Time resolved A) PIA signal at 900 nm and B) photocurrent measured simultaneously at different light intensities (0.5 to 1 mWcm⁻²) for the Cu_2O photocathode with the catalyst (RuO_x) during a ~ 6 s illumination pulse with 365 nm at 0.1 V vs RHE. Some of the optical signals have been omitted for clarity.

These results suggest that in the system with RuO_x , larger catalytic currents are obtained at higher photon fluxes. Under these conditions recombination processes appear to turn on more significantly.

5.5. Discussion

5.5.1. Charge separation in the Cu_2O layer

We now turn to investigate the behaviour of accumulated photocharges following light excitation. The first step after illumination and generation of electron-hole pairs in the Cu_2O phase, is the charge separation in the $\text{p-Cu}_2\text{O/n-Al:ZnO}$ interface. The efficiency of this process is expected to be controlled by the quality of this junction as well as by the electric field present. [16]

When illuminating the photocathode through the FTO layer (back illumination, Figure 5-4B) a negative signal is observed. Under these conditions, negligible photocurrent is monitored, suggesting that the majority of photogenerated electrons are not transferred to the electrolyte. A similar signal has been observed for other materials and has been assigned to the trapping of photogenerated charges. This trapping process results in the loss of the ground state absorption of trap states near the band edges causing a negative change in absorption [38, 39] In our system, following back illumination charges are generated away from the $\text{Cu}_2\text{O/Al:ZnO}$ interface. This is likely to hamper their extraction and the transfer of electrons to TiO_2 and consequently to the electrolyte. We tentatively assign the negative signal observed in our system to the trapping of charges photogenerated in the bulk of the Cu_2O layer; trapped charges do not reach the TiO_2 layer and consequently do not lead to photocurrent. This is consistent with the low electron diffusion lengths measured for this Cu_2O (25-60 nm) and is agreement with the low IPCE monitored upon back illumination.[40] Hence, a negative signal in the Cu_2O photocathode is indicative of poor charge separation in the $\text{Cu}_2\text{O/Al:ZnO}$ interface.

Figure 5-5 shows the PIA spectra at different applied potential upon front illumination. At strong cathodic potentials (< 0.3 V vs RHE), a positive PIA signal is monitored, assigned to accumulated electrons in the TiO_2 following charge separation. On the other hand, at anodic potentials close to the onset of photocurrent (> 0.3 V vs RHE) a large negative signal is observed despite the reductive current (Figure 5-5 inset). Similarly to what occurs upon back illumination, this negative PIA signal can be attributed to the trapping of charges within the Cu_2O phase. Figure 5-9 shows the band diagram of the photocathode at different applied potentials based on previous literature.[15, 30] At strong cathodic, applied potential, the band bending in the $\text{Cu}_2\text{O}/\text{Al}:\text{ZnO}$ interface allows charge separation by favouring electron transfer to the AZO/TiO_2 and hole extraction through the external circuit (Figure 5-9A). On the other hand, at potentials closer to the onset of photocurrent a small charge layer that develops in the $\text{Cu}_2\text{O}/\text{Al}:\text{ZnO}$ interface resulting in a small band bending (Figure 5-9B). Under these conditions the large energy barrier for the transfer of charges from the Cu_2O disfavours charge separation with respect to charge trapping and recombination.

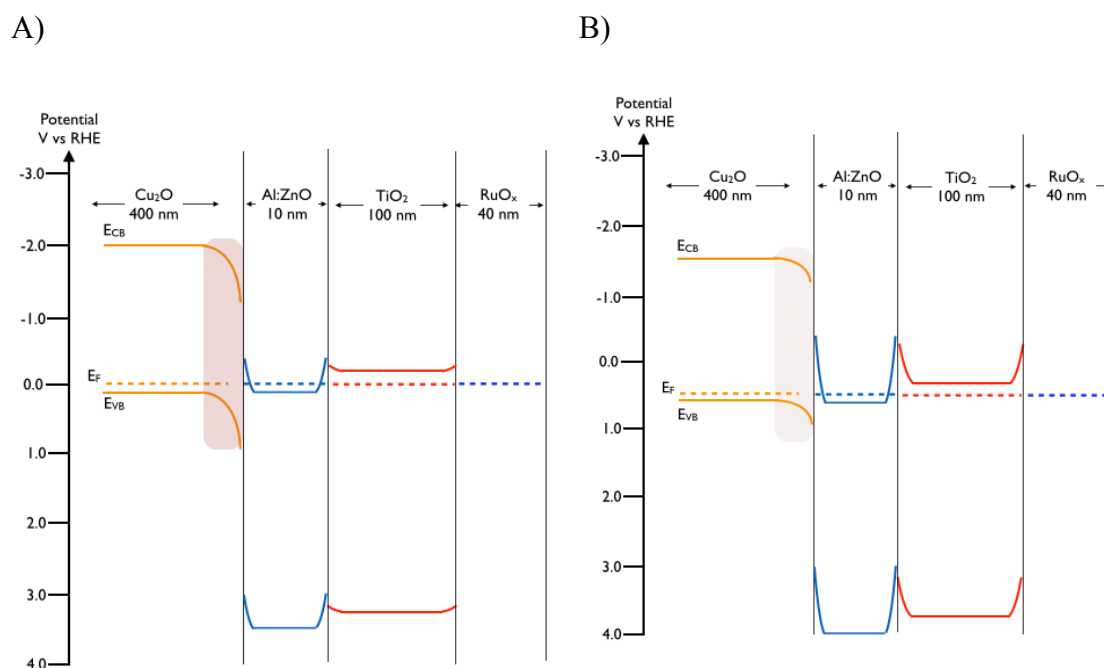


Figure 5-9 Band energy positions for the Cu_2O photocathode with the n-Al:ZnO, n- TiO_2 protective layer and RuO_x as a catalyst at two applied potentials A) 0 V vs RHE and B) 0.5 V vs RHE. At mild cathodic potentials vs the flatband of Cu_2O (~ 0.8 V) the small electric field in the $\text{Cu}_2\text{O}/\text{Al:ZnO}$ junction is likely to hamper the efficient charge separation and thus favour charge trapping. On the other hand, at stronger cathodic potentials (A), the larger depletion layer is likely to favour the separation and extraction of more charges (electrons and holes) and disfavour trap assisted recombination thus leading to a greater accumulation of more electrons in the TiO_2 (monitored as a negative PIA signal). The energy values have been obtained from the literature and RuO_x has been considered to have metallic character as first approximation.[6, 30]

Our model suggest that the potential at which charge separation occurs is determined by the bulk heterojunction between p- Cu_2O and n-Al:ZnO and therefore, that the overpotential for proton reduction in this system is controlled by the nature of the junction and its photovoltage. In agreement with this model, the built in voltage of the p- $\text{Cu}_2\text{O}/\text{n-Al:ZnO}$ buried junction has been previously determined to be 0.5-0.6 V vs RHE matching with the photocurrent onset we observe as well as the ones reported for the Cu_2O based photocathode with different catalysts including Pt or MoS_{2-x} . [3, 14, 15, 30] Previous studies have also shown that the performance of the photocathode is dependant on nature of the junction.[30] A recent report by Domen

and co-workers, showed that the replacement of the Al:ZnO layer by a Ga₂O₃ buffer layer results in a dramatic improvement of the photocurrent onset.[41] The observed cathodic shift was attributed to the larger energy offset between Cu₂O and Ga₂O₃ favouring electron transfer and inhibiting recombination. It was assumed that the diffusion of Ga in Cu₂O lead to an improvement of the interface and its transport thus aiding charge separation.[41]

The results presented herein suggest that control of the buried junction is key in order to achieve good charge separation and control the onset of photocurrent in these structures. Hence, as in traditional bulk heterojunction solar cell, optimisation and tuning of this junction is key to achieving larger photovoltages.

5.5.2. Back electron hole recombination

5.5.2.1. The effect of the catalyst

We now turn to study the reaction kinetics of photogenerated electrons with protons at strong cathodic bias. In this context Photo Induced Absorption spectroscopy is a powerful technique as it allows us to monitor the reactivity of charges accumulated under constant illumination. In our particular case, it allows us to monitor the density of charges in the TiO₂ layer as well as the simultaneous photocurrent. Therefore PIA can provide insight into the nature of the reaction of accumulated electrons with protons and the competing recombination reaction with Cu₂O holes.

Figure 5-6B shows the photocurrent transient monitored upon ~ 6 s illumination of the photocathode, with and without the catalyst at 0.1 V vs RHE. In the sample without catalyst, cathodic and anodic photocurrent peaks dominate the transients when the light is turned on and off respectively. This photocurrent behaviour has been understood in terms of accumulation of charges in the semiconductor electrolyte interface and their subsequent recombination with extracted charges (back recombination).[28, 37, 42-44] These assignments have been reported for photoanode materials often consisting of single layer acting both as the light absorber and the catalyst. In our particular case, the assignment can be understood considering six overall steps (see also Figure 5-10):

- 1) Photogeneration of charges in the Cu_2O layer;
- 2) Charge separation aided by the built in potential in the $\text{Cu}_2\text{O}/\text{Al:ZnO}$ junction; in this process electrons flow towards the interface and holes are extracted through the external circuit.
- 3) Charge transfer to the TiO_2 layer and
- 4) Accumulation of electrons in the TiO_2 layer.

The accumulation of negative charges in the TiO_2 /catalyst interface can induce a back flow of positive charges (holes) from the external circuit leading to the:

- 5) Recombination of accumulated electrons with bulk holes in the Cu_2O (surface recombination or back electron hole recombination) or
- 6) The electron transfer to the RuO_x and the electrolyte.

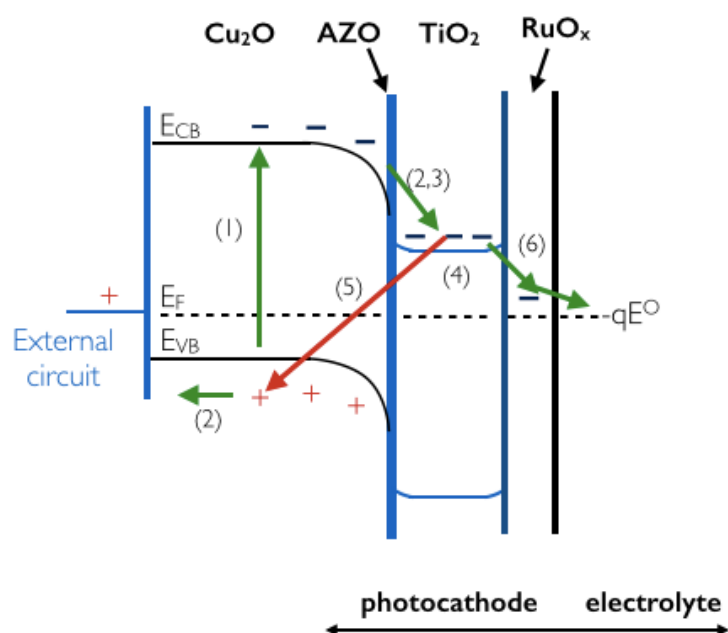


Figure 5-10 Schematic representation of the processes occurring in the Cu_2O photocathode after photoexcitation.

As shown in Figure 5-6B, when the light is turned on a cathodic photocurrent peak is observed for the samples with and without RuO_x , suggesting that a build-up of accumulated electrons is generated during the light pulse.[37] The extent of this accumulation in TiO_2 can also be observed in the PIA transient monitored at 900 nm

(Figure 5-6A). The amplitude of the optical signal without RuO_x is half of that obtained with RuO_x indicating that less electron accumulate in the TiO_2 . This lesser accumulation of charges in the photocathode without RuO_x can be attributed to faster back electron hole recombination in this system. As shown in the photocurrent transients, in presence of the catalyst the photocurrent rapidly reaches a steady state value ($t_{50\%} < 0.5 \text{ s}$) whereas, in the absence of RuO_x the photocurrent decays to a negligible value ($t_{50\%} > 1\text{s}$). This rapid decay of the photocurrent during illumination is caused by a back flow of holes that re-enter the system to recombine with the separated electrons.

Further evidence of back electron-hole recombination can be inferred from the anodic current measured when the light is switched off. Under these conditions the flow of electrons from the Cu_2O to the TiO_2 (cathodic current) is instantaneously interrupted; consequently holes flow back from the external circuit into the photocathode (anodic current) to recombine with the remaining electrons. This gives rise to a characteristic net change in the direction of the current and a subsequent decay to pre-pulse level. As shown in Figure 5-6B, a larger recombination current during the dark phase is observed for the sample without catalyst in agreement with the behaviour observed during illumination.

The data presented herein suggest that the catalyst layer has a double role: (i) *a catalytic effect*: it favours the proton reduction kinetics and consequently, for the same density of accumulated electrons larger photocurrents are drawn with RuO_x , and (ii) *an effect on the recombination*: it slows down the back recombination of accumulated electrons in the TiO_2 with Cu_2O holes thus allowing a larger density of electrons to participate in the reduction of protons.

Similar behaviour with regards to recombination has been observed in photoanodes used in combination with catalysts. For example, the improved water oxidation (increased photocurrent and cathodic shift of photocurrent onset) in BiVO_3 and Fe_2O_3 using CoO_x or Ga_2O_3 catalyst (or co-catalysts) has been attributed to the retardation of electron-hole recombination aided by the catalyst layer.[45, 46] In these systems, the catalyst has been found to primarily slow down the recombination of charges rather than enhance the water oxidation kinetics.[47] Conversely, in the Cu_2O photocathode,

our data suggests that the catalyst layer has a role both in reducing recombination and favouring the proton reduction kinetics.

Figure 5-11 illustrates our proposed model. The catalyst employed in this study consists of a 40 nm layer of hydrous and amorphous RuO_x with very large pores. This morphology, with high surface area, allows proton intercalation and has been shown to render better photostability compared to the system with Pt nanoparticles.[14] It is reasonable to assume that the facile diffusion of protons through the catalyst might:

- (i) Allow a larger local proton density in the RuO_x , which is likely to facilitate the catalytic reaction and help sustain higher catalytic currents.
- (ii) Allow sufficiently large number of protons to locate close to the interface with TiO_2 (Figure 5-11) [48]. This layer of protons can effectively screen the electrons accumulated in TiO_2 helping compensate the electrostatic field induced and consequently reduce the driving force of the back electron hole recombination.

It is noteworthy that our PIA measurements at 900 nm do not monitor electrons accumulated in the RuO_x prior to the reaction with protons. Although electron accumulation in RuO_x might occur, it is likely that due to the large number of active sites in RuO_x electrons present in this layer quickly react with adsorbed protons. Hence, the majority of charges are likely to accumulate in the TiO_2 . Nonetheless charge accumulation in RuO_x would contribute towards the stabilisation of electrons and the retardation of surface recombination.

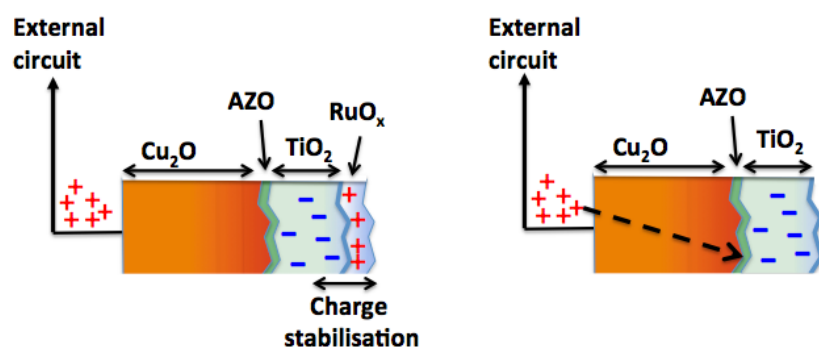


Figure 5-11 Model describing the effect the catalyst on the back electron hole recombination. In the presence of RuO_x accumulated electrons are stabilised by charge compensation from intercalated protons, which effectively reduces the back recombination with extracted holes.

5.5.2.2. The effect of the applied potential

According to the model developed in the previous section, the catalyst layer plays an important role in preventing the recombination of accumulated electrons before they react with protons. In order to identify the best operation conditions, it is interesting to study the effect of applied potential on the kinetics of recombination and catalysis.

Figure 5-7 shows the photocurrent transient at three applied potentials for the system with catalyst and without catalyst. The potential range studied (0.1-0.3 V vs RHE) has been chosen to allow sample stability during the measurement (anodic of 0 V vs RHE) and to avoid charge separation limitations (cathodic of 0.4 V vs RHE). In the system without RuO_x , an increase in the overpotential results in a retardation of the fast back electron hole recombination, as inferred from the slower decay of the current under illumination and in the dark. Despite this improvement low photocurrents are monitored suggesting that, in the potential range studied, accumulated electrons still recombine before they can react with protons. In the system with RuO_x , an increase in the overpotential results in a retardation of the recombination during the light pulse and also in an increase in the steady state photocurrent. Hence in this system, a stronger cathodic applied potential helps reduce recombination and improve the catalytic rates. Further evidence of this can be found in the current transients when the light is turned off. Figure 5-12 shows the

integration of the current decay when the light is turned off. This is a measure of the number of charges remaining in the film when the illumination is interrupted. Whereas in the sample without RuO_x an increase in the applied potential results in an increase accumulated charge density, the inverse trend is observed in the sample with RuO_x (Figure 5-12).[37]

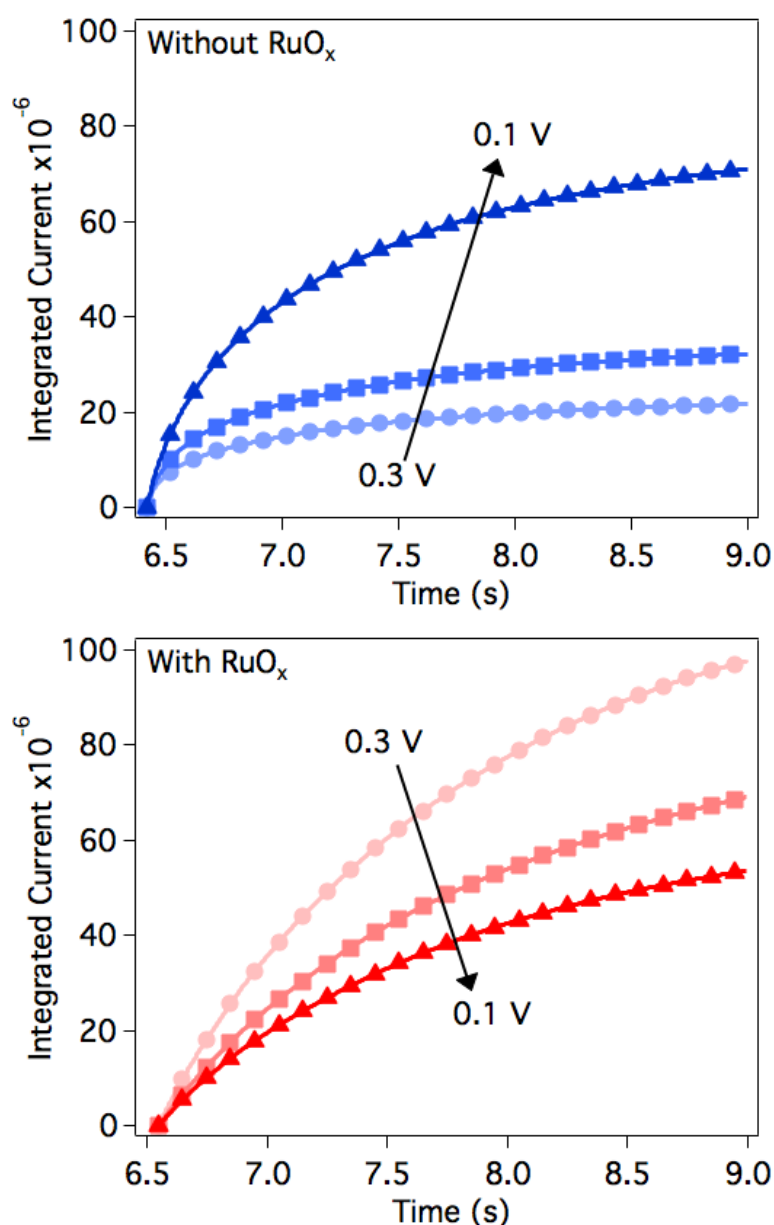


Figure 5-12 Number of accumulated charges remaining during the dark phase at 3 different applied potentials (vs RHE) for the system A) without and B) with the RuO_x catalyst. The number of charges was calculated from the integral of the anodic photocurrent decay caused by the flow of extracted holes back into the photocathode when the light is switched off. Plotted 1 every 20 points.

We can rationalise this by taking into account two factors:

- (i) At stronger cathodic potentials the depletion layer within the Cu_2O increases (Figure 5-9), this not only helps charge separation as previously discussed, but also increase the potential barrier holes need to overcome in order to recombine with accumulated electrons.
- (ii) The energy barrier between TiO_2 and the RuO_x that electrons need to overcome in order to react with proton decreases with increasing cathodic potential (see Figure 5-9).

Therefore, applying a stronger cathodic potential is expected to have a double effect namely, reduce the back electron hole recombination and favour the transfer of electrons to the catalyst. The retardation of the recombination is observed in both photocathodes, with and without RuO_x . However, the increase in accumulated charges does not translate into an increase in photocurrent in the absence of catalyst due to proton reduction kinetics on TiO_2 (compared to RuO_x) as inferred from the low photocurrents. This is shown in the integrated currents at strong cathodic potentials; in the absence of RuO_x more charges remain in the film when the light is tuned off due to the reduced back recombination. On the other hand, in the presence of RuO_x fewer charges remain in the films when the light is switched off as more participate in the proton reduction reaction.

5.5.3. Proton reduction on RuO_x

So far, we have studied the factors controlling charge separation and the recombination of accumulated electrons in the Cu_2O photocathode. Our model suggests that the buried heterojunction controls charge separation and that both, the applied potential and the catalyst, determine the extent of the back recombination. Despite this, efficient H_2 generation only occurs when the RuO_x is present. In this section, we explore the nature of the HER on RuO_x .

5.5.3.1. Rate law analysis of proton reduction

We now focus on the rate of proton reduction with accumulated electrons to reduce protons. Figure 5-8 shows the PIA signal and the simultaneous photocurrent obtained at different illumination intensities at 5 s (steady state). As expected higher intensities result in a larger accumulation of electrons in the TiO₂ as well as larger photocurrents of proton reduction.

We can consider a simple kinetic model relating the concentration of accumulated electrons in the catalyst interface (n_{cat}) and the photocurrent.[32] The change in electron density in the catalyst is equal to the incoming electron flux minus the outcoming flow due to the proton reduction:

$$\frac{dn_{cat}}{dt} = J_{photo} - k_{wr} \cdot n_{cat}^{\alpha} \quad \text{Equation 5-1}$$

Here, J_{photo} is the electron flux towards the catalyst, k_{wr} is the proton reduction rate constant and α is the reaction order with respect to accumulated electrons. This model assumes 100% faradaic efficiency and that H₂ is evolved even at low current densities. This is a reasonable assumption for the photocathode containing RuO_x as previously shown.[14] At steady state, such as in our PIA measurements, the density of accumulated electrons does not change with time. Moreover, under these conditions charge equilibrium must exist between the TiO₂ and the RuO_x. Hence Equation 5-1 can be simplified to:

$$J_{photo} = k_{obs} \cdot n_{TiO_2}^{\alpha} \quad \text{Equation 5-2}$$

Where k_{obs} is the rate constant monitored in our experiments.

Figure 5-13 shows a plot of the photocurrent (J_{photo}) as a function of electron concentration per cm² (n_{TiO_2}). The different electron concentrations has been obtained from the absorption at 900 nm (PIA signal at different light intensities) employing an extinction coefficient of 840 M⁻¹cm⁻¹ previously reported. [49] It is noteworthy that this conversion to electron density merely allows a visual representation of the electron accumulation for comparison with other materials, but it does not change the

outcome of the analysis. The figure shows two experimental sets (solid and fill circles). A reaction order (α) of approximately 2 can be obtained from the slope of the log-log plot independently from both sets.

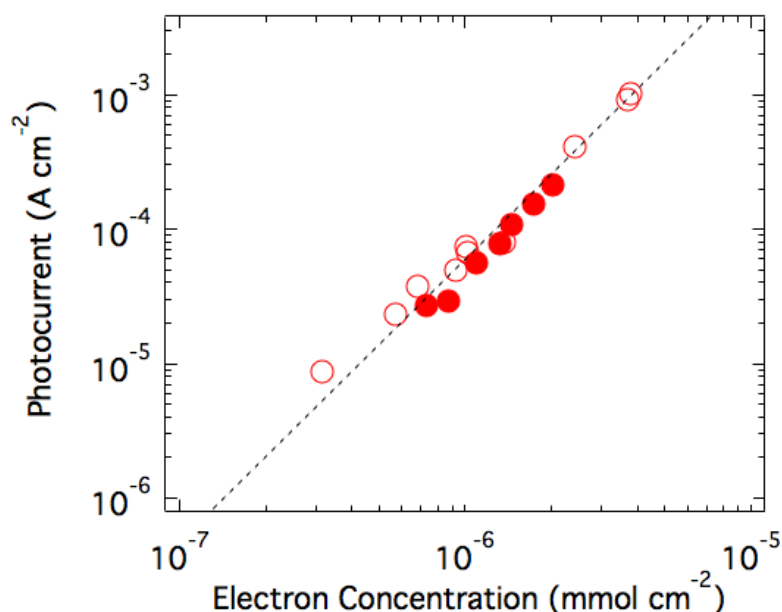


Figure 5-13 Relationship between photocurrent and accumulated electron density. The steady state photocurrent is plotted against the electron concentration, obtained from the PIA amplitude measured at different light intensities (from 0.7 to 70 mWcm⁻²). The sample was held at 0.1 V RHE in a pH 5 phosphate-sulfate electrolyte. Two datasets obtained with different samples and experimental arrangements, are included (solid and fill circles). A reaction order in electron concentration of approximate 2 was obtained for each set independently. The sets have been normalised in order to be represented in the same graph.

5.5.3.2. Mechanistic implications

A second order in electron concentration has important mechanistic and operational implication. The HER using RuO₂ has been studied electrochemically, and the catalysis has been proposed to occur via Volmer-Heyrovsky (V-H) mechanism.[50, 51] In this mechanism first a proton and electron react to form a Ru-OH₂ intermediate (Volmer reaction[52]). In the following step, a solvated proton and an electron react with the intermediate to form a H₂ molecule. This mechanism differs from others proposed [51] in that the rate-limiting step is the electrochemical desorption of H₂ (Heyrovsky reaction) rather than the non-electrochemical H₂ desorption. A schematic

representation of the V-H mechanism is shown in Figure 5-14. This mechanism, predicted for the RuO_2 acting as an electrocatalyst, is in good agreement with the results obtained for the Cu_2O photocathode with RuO_x . In particular our data, showing a 2nd order reaction in electron density, points to a mechanism in which the rate limiting step varies with the electron density such as occurs in the Heyrovsky reaction. Hence, our data supports that proton reduction in RuO_x proceeds through to the same mechanism when the catalyst is used as an electrocatalyst than when in part of a more complex photocatalytic system. The photo-electrochemical reaction has been found to occur via the same mechanism than the electrochemical one. This suggests that the reaction pathways of electrocatalysts incorporated in photocathode electrodes may be directly rationalised from the electrochemical behaviour of the catalyst.[50] However, further comparison of catalysts is required to confirm this.

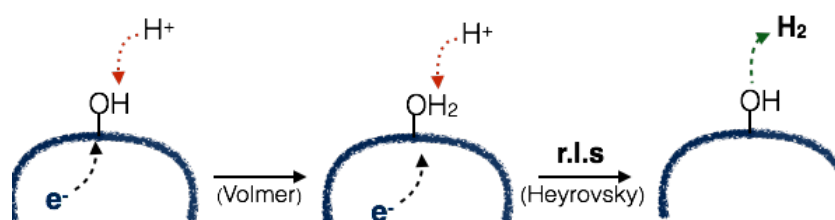


Figure 5-14 Mechanism of proton reduction on the surface of RuO_2 based on Volmer-Heyrovsky reaction scheme in which the latter is rate limiting.

In this context it is interesting to consider the Cu_2O photocathode containing Pt as a catalyst. At high overvoltages Pt (110) has been shown to operate via a Volmer-Tafel mechanism in which the Tafel reaction is rate limiting.[52] This step is a homolytic reaction in which two adsorbed protons react to form H_2 (Figure 5-15A). It is therefore a non-electrochemical step and consequently at high overvoltages the current will remain constant; this would imply a zero order in electron density. In our measurements, the steady state photocurrent of the photocathode with Pt is found to plateau at high photon fluxes (Figure 5-15B). From this, a zero order in electron density can be obtained (Figure 5-15B). It is important to note, that the Cu_2O photocathode with Pt suffers from poor stabilities due to the dislodging of Pt. Consequently the measurements in Figure 5-15 are limited by the stability of the system. Nonetheless, the data presented herein, appears to point to a Volmer-Tafel

type mechanism for the Pt based photocathode with a non-electrochemical rate-limiting step at high current densities.

Comparisons of the kinetic analyses of Pt and RuOx suggest that the latter may be more suited to operate at high current densities. In a second order reaction, the density of accumulated electrons required to achieve a fixed current is reduced compared to a zero order reaction. The higher transfer rate kinetics can also help mitigate the impact of back electron hole recombination, potentially leading to better quantum yields.

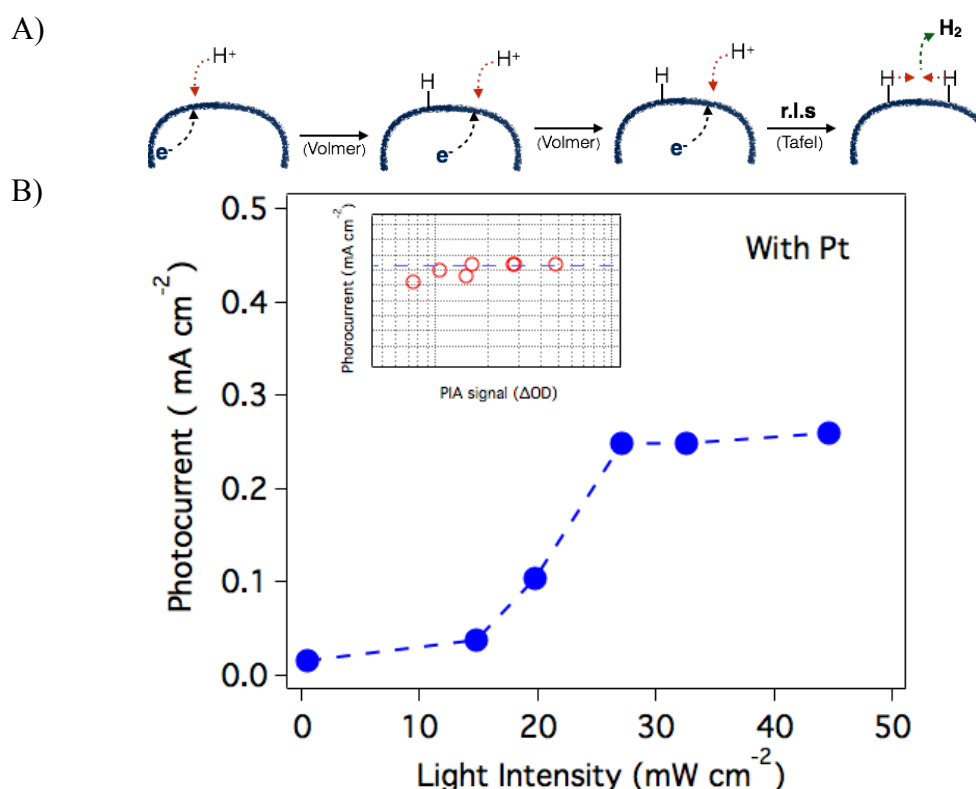


Figure 5-15 (A) Mechanism of proton reduction on the surface of Pt based on Volmer-Tafel reaction scheme in which the latter is rate limiting. (B) Steady-state photocurrent of the Cu₂O photocathode with Pt as a function of illumination intensity. The inset shows the plot of the photocurrent against the electron concentration (PIA signal).

5.6. Conclusions

In summary, the transient studies presented in this *Chapter* show that the charge separation of photogenerated carriers in Cu₂O is controlled by the buried junction between p-Cu₂O and n-Al:ZnO and that the energetics of the junction dictate the onset

of photocurrent. Following charge separation, the recombination of accumulated electrons before they can react is found to dominate in the system without catalyst due to the slow proton reduction kinetics on TiO_2 . However, the presence of an electrocatalyst slows down the back electron hole recombination by electrostatically stabilising accumulated electrons resulting in larger photocurrents. Our data also suggests that the nature of the rate-limiting step in the catalytic cycle might have an impact in the recombination kinetics, with higher orders in electron density likely to result in greater proton reduction efficiencies. Furthermore, we find that the proton reduction reaction proceeds through the same mechanism when the catalyst is used as part of a photoelectrode and as an electrocatalyst. This suggests that purely electrochemical techniques can be used to predict the mechanism of electrocatalyst when incorporated in photocatalytic systems. The results presented in this chapter provide evidence of the key factors affecting the efficiency of a multi-layer photocathode and highlight the possible routes for improvement in this type of systems.

5.7. In the next chapter

In *Chapter 3* and *4* Transient Absorption Spectroscopy was used to study the kinetics of solar-to-fuel conversion system. In this chapter a modification of this technique (PIA) has been used to study a Cu_2O photocathode. The studies of the latter using classical TAS prove to be more puzzling than anticipated. The assignment of the optical signals was hampered by the observation of (apparent) inconsistent signal. Figure 5-16 exemplifies this problem.

In Figure 5-16A the TAS spectra of a Cu_2O sample and a $\text{p-Cu}_2\text{O/n-TiO}_2$ sample after excitation of the Cu_2O phase is shown. The bare Cu_2O , has a transient peak centred around 1100 nm. Addition of n-TiO_2 changes the spectrum of the excited state. This observation may suggest that the addition of the n-TiO_2 layer causes a change in the properties, and probably in the kinetics of the system. Given the nature of the junction, electron transfer from $\text{p-Cu}_2\text{O}$ to n-TiO_2 could be a plausible explanation for this observation. However, the measurement of a bare $\text{p-Cu}_2\text{O}$ sample of different thickness (comparable to that of the complete device: $\text{p-Cu}_2\text{O} + \text{n-TiO}_2$), reveals an unexpected change in optical density. Remarkably, the two bare $\text{p-Cu}_2\text{O}$

samples measured have completely different transient spectra despite differing only in their thickness (Figure 5-16B). This apparent inconsistency questions the validity of assignments made in the presence of overlayers, as addition of a new layer, not only may change the kinetics, but it also changes the overall thickness of the sample.

This thickness dependence of our transient spectra, and the inconsistencies observed between samples lead us to think that our transient measurements were affected by some sort of optical interference effect, perhaps enhanced by the high optical quality of our samples. In the next chapter the impact of optical interferences in Transient Absorption Measurements is explored and its implications discussed, which then allow us to elucidate the ultrafast recombination losses in Cu_2O photoelectrodes.

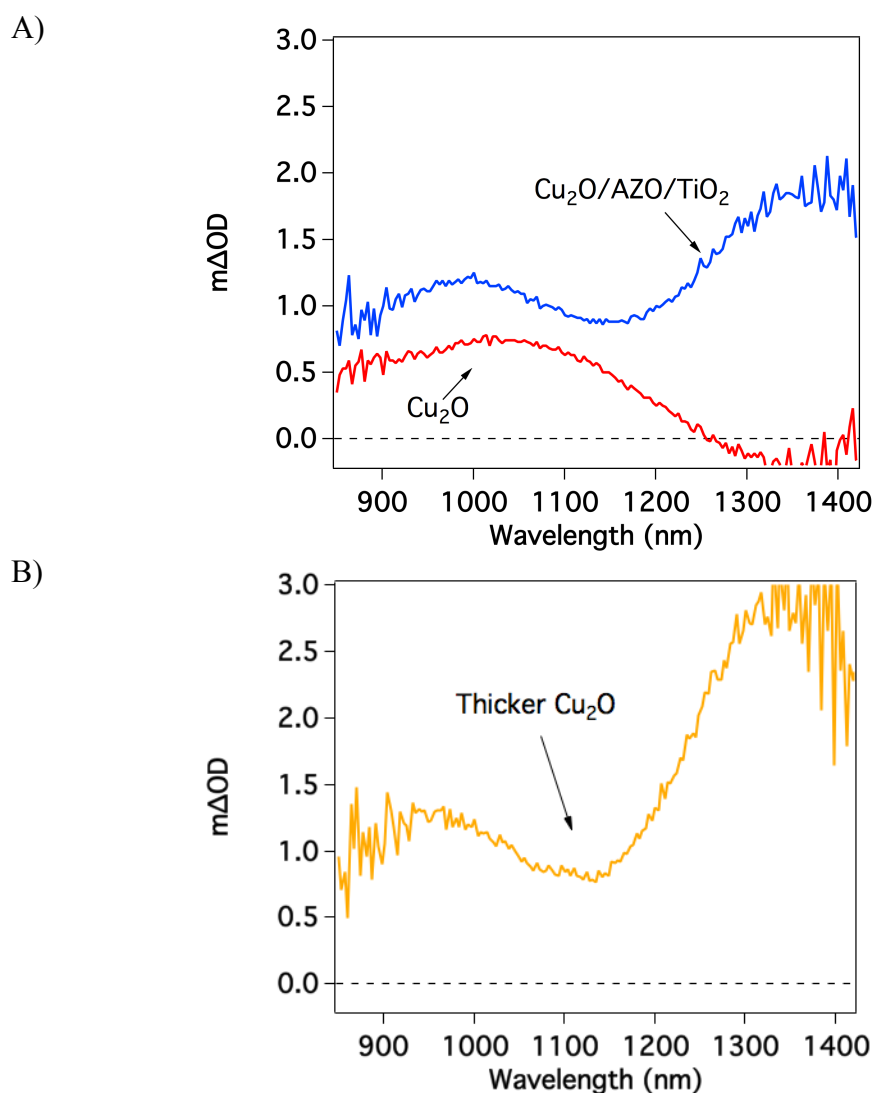


Figure 5-16 A) Transient spectra of a Cu_2O and a $\text{Cu}_2\text{O}/\text{AZO}/\text{TiO}_2$ at 2 ps time delay. B) Transient spectra of a Cu_2O sample of thickness equal to that of the $\text{Cu}_2\text{O}/\text{AZO}/\text{TiO}_2$ film at 2 ps time delay. The excitation wavelength was 500 nm, to selectively excite the Cu_2O phase.

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Chapter Six

Deconvolution of charge carrier kinetics from transient optical interference effects in Cu_2O photocathodes

Our initial studies of charge carrier kinetics by TAS of Cu_2O photocathodes appeared to be complicated by optical interference effects. In order to understand the kinetics of photocharges, first, it was necessary to assess the impact of such effects on the Transient Absorption Spectrum of Cu_2O . For that purpose, in this chapter, the light interferences in Cu_2O films, as well as in TiO_2 films and a $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite device are studied. The results show that light interference fringes in these materials can dominate their transient absorption spectra and consequently complicate their interpretation. A method to obtain relevant kinetic information from the transient spectra, based on a Fourier transform analysis is here presented. The potential of these interferences effects to extract other optical information from the system such as the change in the refractive index induced by the light pulse is also discussed.

6.1. Introduction

The kinetics of photogenerated charges of a Cu₂O photocathode have been studied in *Chapter 5*. Our studies reveal that electron hole recombination hinders the performance of the system, especially in the absence of a catalytic layer. The recombination of photogenerated charges competing with the catalytic reaction is a problem affecting the performance of many solar-to fuel materials, occurring on timescales from picoseconds to milliseconds.[1-5] Indeed, previous studies of Cu₂O have indicated that electron hole recombination in this system primarily occurs on ultrafast timescales.[6] In order to further improve the performance of the Cu₂O photoelectrode studied herein, it is important to understand the nature and timescale of the recombination process in this material.

Our transient absorption experiments of Cu₂O in the picosecond to nanosecond timescales, shown in Figure 5-16, appear to suffer from optical interference effects. Such effects are not unexpected given the nature of the sample (a high refractive index material with high quality interfaces) and the experiment (an absorption technique). [7] However, they hamper the assignment of the optical signals and thus, the resolution of the recombination kinetics. In order to elucidate the charge carrier dynamics in Cu₂O, first we need to address the impact of any optical interference effect in TA experiments.

Optical interference effects are widely understood and have multiple applications. For example, the interference of light in samples is used to determine the thickness of materials and assess their surface properties. [7, 8] Light interferences are also used in spectroscopic techniques, such as Transient Grating Spectroscopy, to study the kinetics of excited states.[9] As an optical technique, TAS measurements are susceptible to such optical effects. Despite this, little reference is made to this problem in the literature and there is no assessment of how it might affect the interpretation of transient data. As such it is interesting to study the impact of optical interference effects in the TAS of the Cu₂O photocathode studied in this thesis.

6.1.1. Light interference effects

When a beam of light strikes one of the front surfaces of a material of thickness d , the incident radiation will be reflected, absorbed or transmitted through the material. When the transmitted light reaches the back surface of the material again part of the incident light will be reflected, absorbed or transmitted further out of the material. Due to its wave like character the light reflected from the front and back surfaces will interfere. Depending on the phase of the waves this interference will be constructive or destructive.

A system formed by a film of thickness d , a refractive index $\tilde{n}$ on a transparent substrate of refractive index $\tilde{n}_{\text{subs}}$ is shown in the inset of Figure 6-1. This simple description is representative of systems like the one based on Cu_2O or TiO_2 described in this thesis. The transmission spectrum for this latter sample is shown in Figure 6-1. It is apparent that a large number of interference fringes are present. The presence of the interferences is indicative of thickness uniformity and low surface roughness of the sample.[8] Poor thickness uniformity or high surface roughness normally results in a smooth curve in the transmission, as all possible interference effects are destroyed (dotted line, T_2). In a typical absorption spectrum of a semiconductor film, three main regions can be distinguished: (i) a strong absorption region where the interference fringes disappear; (ii) a weak absorption region where the interference start to gain visibility and (iii) a transparent region where no absorption occurs and interference fringes dominate. The presence of the interferences is a function of the length and speed with which the wave travels through the material, namely of the thickness and the refractive index of the material.[7]

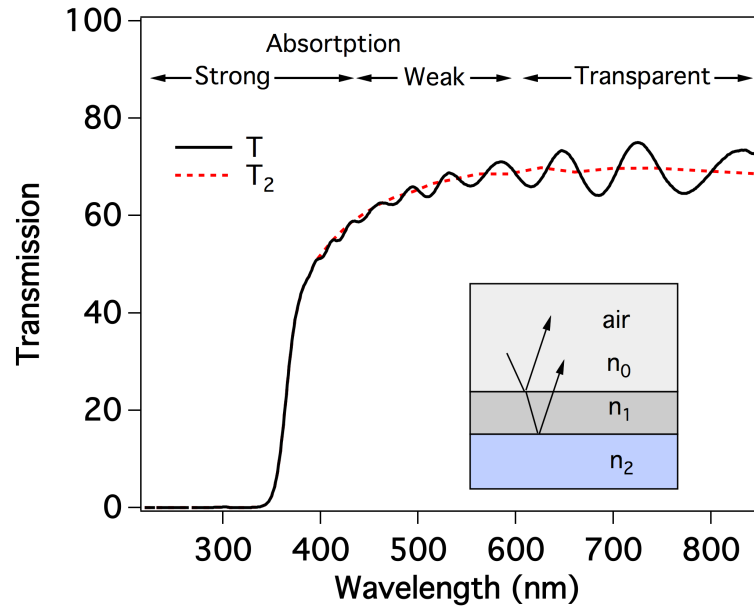


Figure 6-1 Transmission of a typical semiconductor (such as TiO_2) over a wide wavelength range. If the material has uniform thickness interference effects will be visible. An increase in absorption will dampen these interferences. If the material is not uniform, little or no interference effects will be visible.

In the field on solar energy conversion, semiconducting junctions are an integral part of the device architectures ensuring efficient charge separation and charge blocking.[10, 11] The development of synthetic methods has allowed the preparation of junctions with high quality interfaces that are beneficial for device performance, but in which optical interferences effects might occur. Furthermore, the materials brought to contact, not only have differences in their electronic properties but they almost inevitably differ in their optical properties. Thus junctions of materials with different refractive indices are fabricated. These can give rise to optical interference effects that in some cases can be used to improve, for instance, light harvesting by the devices.[12, 13] Surprisingly, the existence of these interference effects in the transient absorption spectroscopy of these materials has normally been ignored. This is evident in the extensive amount of transient spectroscopic work done on organic, hybrid, quantum dot and perovskite solar cells as well as semiconductors for solar fuels synthesis, where, to the best of my knowledge, there is no mentioning of interference effects.

6.1.1.1. Interference effects and optical properties

Interference effects arise from the interaction of light and matter. Because of this, they carry information of the sample's optical and electronic properties. Optical properties are closely related and thus, it is possible to obtain important properties such as the dielectric constant or the absorption coefficient from others such as the absorbance. Importantly, this is not limited to ground state properties of the material but is also applicable to the excited state. In this section the relationship between optical properties is discussed.

The dielectric constant, often termed ϵ , describes how an electric field (such as that created by the propagation of an electromagnetic wave) affects a material. Since electric fields polarise dielectric materials, the dielectric constant is a measure of the polarisability of a material in the presence of an electric field.

It is possible to obtain these important properties (n and ϵ) through the transmission, the absorbance and the absorption coefficient. Consider an electric field caused by an electromagnetic wave (such as light) travelling through an isotropic medium.[14] The time and spatial dependence of the electric field of a wave travelling in the z direction with angular frequency ω is:

$$E = E_0 e^{i(\tilde{n}kz - \omega t)} \quad \text{Equation 6-1}$$

Where E_0 is the amplitude at $z = 0$, k is the module of the wave vector, t is the time and $\tilde{n}$ is the complex refractive index. This later relates to the real refractive index by:

$$\tilde{n} = n + i\kappa \quad \text{Equation 6-2}$$

Where the imaginary part κ is the *extinction coefficient*.

As $k = 2\pi/\lambda = \omega/c$ the electric field can be rewritten in the form of:

$$E = E_0 e^{-\kappa \frac{\omega}{c} z} e^{i\omega \left(\frac{n}{c} z - t \right)} \quad \text{Equation 6-3}$$

An important conclusion from Equation 6-4 is that the first term containing the extinction coefficient acts as a damping factor of the electric field. Considering only this term, the intensity of the electric field ($I = |E|^2$) is

$$I = I_0 e^{-2\kappa \frac{\omega}{c} z} \quad \text{Equation 6-4}$$

If we compare this to the Lambert-Beer law:

$$I_0 e^{-\alpha x} = I_0 e^{-2\kappa \frac{\omega}{c} z} \quad \text{Equation 6-5}$$

We can obtain the extinction coefficient directly from the absorption coefficient as

$$\alpha = \frac{4\pi}{\lambda} \kappa \quad \text{Equation 6-6}$$

Hence, the exponential decay predicted empirically by the Lambert-Beer law, when a light beam is absorbed by the material, can be understood in terms of the dampening of the intensity of the electric field created by the electromagnetic wave propagating through the material.

The dielectric constant is related to the complex refractive index by $\varepsilon = \tilde{n}^2$. [14] It follows that the dielectric constant is also a complex magnitude and that

$$(n + i\kappa)^2 = (\varepsilon_1 + i\varepsilon_2) \quad \text{Equation 6-7}$$

The real and imaginary terms of the dielectric constant are: $\varepsilon_1 = n^2 - \kappa^2$ and $\varepsilon_2 = 2n\kappa$ respectively.

Hence, there is a close relationship between the different magnitudes discussed. For example, by measuring the absorption coefficient of a sample (α) as a function of frequency it is possible to obtain the extinction coefficient (κ). Simultaneously, from the latter, the real refractive index (n) can be obtained using the Kramers-Krönig relationship, which relates the real and imaginary parts of a function. [14] Therefore, it

is possible to obtain the frequency dependence of the dielectric function by means of simple absorption measurements.

In pump-probe type experiments, such as transient absorption, a light pulse is used to induce a perturbation in the sample. The absorbance of the photogenerated excited state over time is further examined using a second light beam. The absorption coefficient of the excited state (α) is directly related to its population (N) (see Equation 2-4). Consequently TA is a useful technique to study the time evolution of the excited state. A change in absorption of the system will also trigger a change in other optical properties of the sample, such as the refractive index and the dielectric constant, and therefore it is tempting to explore if Transient Absorption Spectroscopy can be used to assay the time changes in these properties and therefore help provide a broader picture of the interaction of light and matter.

6.2. In this chapter

Understanding the kinetics of photogenerated carriers in Cu_2O is key to improve the performance of Cu_2O based materials. Transient Absorption Spectroscopy can be used to perform such studies. However, optical interference effects in the TA spectra of Cu_2O hamper the interpretation of the data. This phenomenon, which may be enhanced by the high quality interfaces of our Cu_2O samples, is well understood in steady-state absorption measurements. However, little is known about its relevance to transient absorption measurements. In this chapter the impact of light interference effects in Cu_2O is investigated. In order to assess whether the interferences in transient absorption are unique for this material or not, we have also studied TiO_2 films and a $\text{CH}_3\text{NH}_3\text{PbI}_3$ device. These materials are representative of the type of systems often used in solar energy technologies. TiO_2 is used in solar-to-fuel conversion systems and has been the subject of study in other chapters of this thesis. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite device has recently emerged as a promising material for solar cells. The potential of interferences TAS to obtain information about optical magnitudes such as the refractive index and the polarisation of the media is also explored.

6.3. Experimental methods

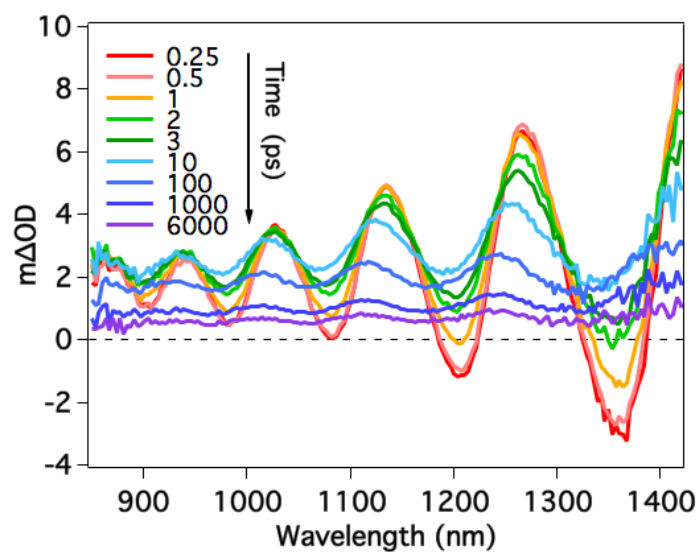
Three materials are studied in this chapter; two metal oxides: (i) Cu_2O (same as used in Chapter 5, but without an Au back contact in order to simplify the optical modelling) and (ii) dense, $\sim 1.2\ \mu\text{m}$, anatase TiO_2 (prepared by CVD by Dr Andreas Kafizas, Imperial College London as reported before [15]) and a (iii) $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. The latter was studied in the form of a bare, $\sim 0.3\ \mu\text{m}$, film deposited on FTO (prepared by Kim Jinhyun from Imperial College London as reported in: [16]) and as a $\sim 0.3\ \mu\text{m}$ perovskite device containing a layer of spiro-OMeTAD ($\sim 0.35\ \mu\text{m}$) and $\sim 0.5\ \mu\text{m}$ mp- TiO_2 (prepared by Dr. Chunhung Law from Imperial College London as reported in: [17]). The perovskite samples were encapsulated under N_2 . Spectroscopic experiments were carried out using the setup described in *Chapter 2*. The ultrafast transient measurements were done in air exciting the samples at 575, 500, 355 or 740 nm with an intensity of $\sim 0.2\ \text{mJ cm}^{-2}$ (details below) and probing in the near-IR.

The modelling and analysis of the optical data has been done in collaboration with Dr. Paul Stravrinou from Imperial College London.

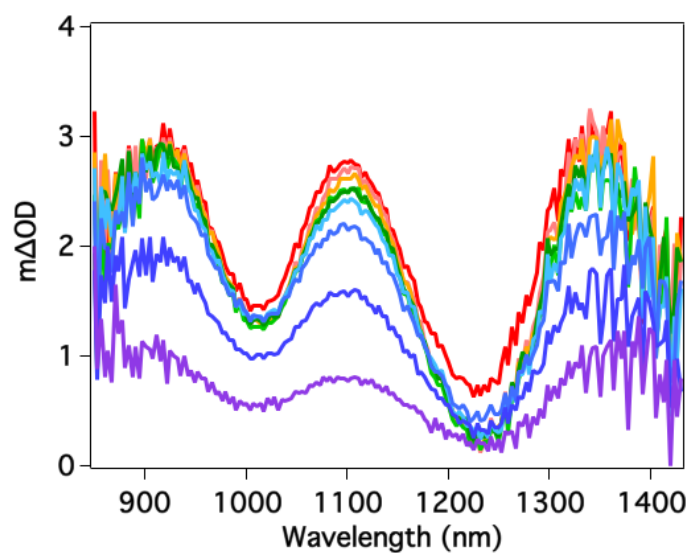
6.4. Results

Figure 6-2 shows the transient absorption in the NIR after band gap excitation of a Cu_2O , TiO_2 films and a $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite device. It is immediately apparent that the spectra are dominated by an oscillating signal. The amplitude of the oscillation increases with increasing wavelength and in the case of Cu_2O and the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite negative amplitudes are recorded (see for example 1350 nm in Cu_2O). Notably, the amplitude of the oscillation changes with time and its time dependence appears to be different for each sample. Whereas in Cu_2O and the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite almost no oscillation can be inferred at 6 ns, in TiO_2 the oscillating signal is clearly visible at this timescale. Furthermore, the oscillating signal is superimposed over a positive background signal this can be seen, for example, in Cu_2O at 6 ns, where a finite change in optical density is monitored despite no oscillation being observed. This offset signal is also found to be time dependent.

A)



B)



C)

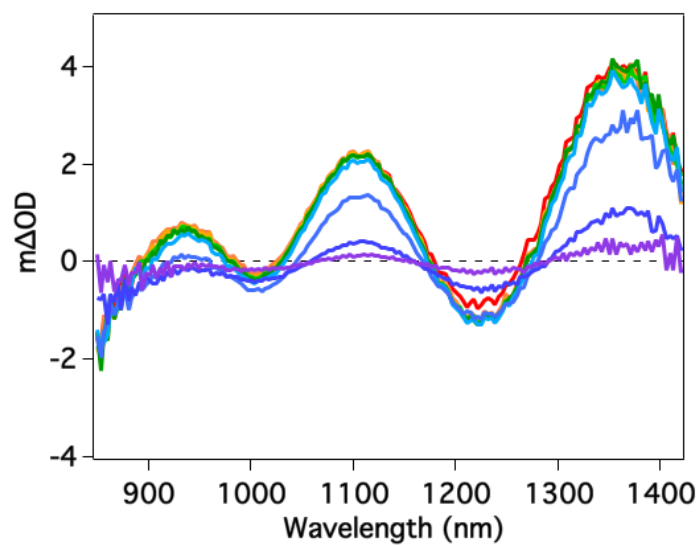


Figure 6-2 Transient absorption spectra of Cu_2O (a) , TiO_2 (b), and $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite (c) films at different times after photoexcitation. The samples were excited at 500 nm, 355 nm and 740 nm respectively.

In order to gain insight into the nature of these unexpected changes in optical density we examined the optical properties of the samples. Figure 6-3 shows the transmission of the three samples as well as that of the FTO substrate in the 220 -1400 nm region. It is noticeable that a large interference pattern is present in these samples. This phenomenon has been previously observed in these materials.[18, 19] As discussed in the introduction to this chapter, this pattern arises from the interference of light reflected from the sample in and out of phase. Such interference leads to peaks and troughs in the transmission. As expected, the amplitude of the interferences is found to be greater in the NIR region than in the visible region where the samples absorb.[7] Most notably, the interference pattern in the steady state spectra resemble those of the oscillations in our transient measurements suggesting these two phenomena are somehow related.

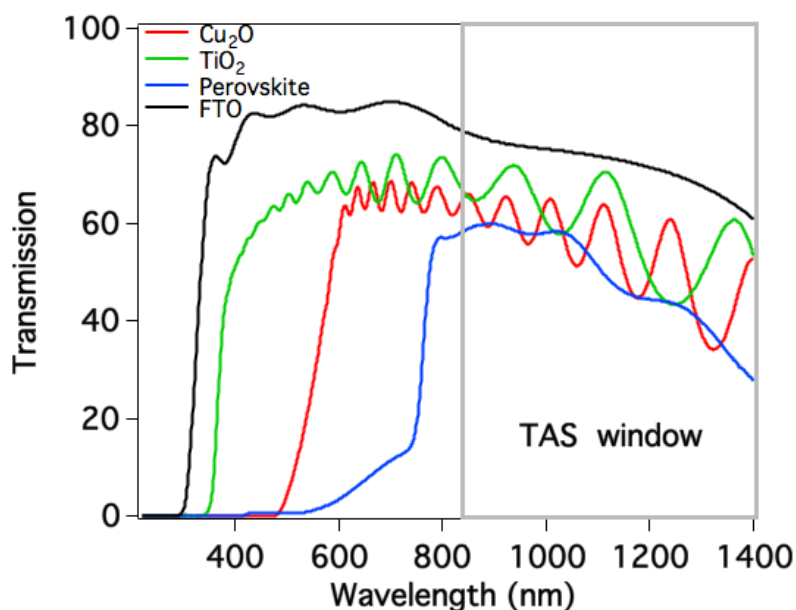


Figure 6-3 Steady state transmission spectrum of Cu₂O , TiO₂ , the CH₃NH₃PbI₃ perovskite device and the glass substrate measured in an integrating sphere.

In order to establish whether the oscillations observed in the transient spectra are unique for the NIR region we measured the TAS spectra of a thick TiO₂ sample in the Visible region. TiO₂ is chosen, as it is the sample with less absorption in the visible region and the one that displays an interference pattern that can be observed at wavelengths shorter than 400 nm. Figure 6-4 shows the transient absorption spectrum

of TiO_2 in the visible region as well as the transmission in this region (light green line). It is apparent that the spectrum is dominated by an oscillating signal such as that observed in the NIR and that this signal matches the inverse of the interference pattern in the transmission of the sample.

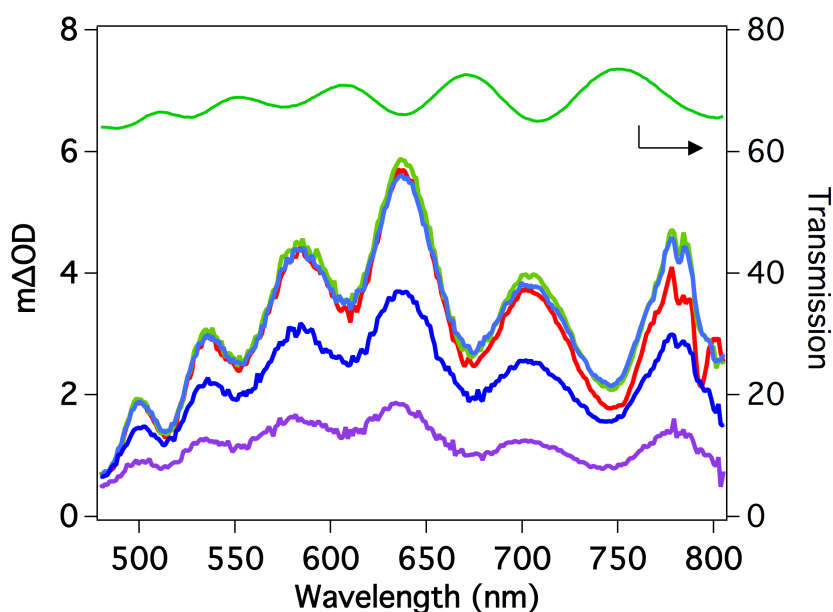


Figure 6-4 Transient absorption spectra of TiO_2 at different time delays (250 fs to 6 ns, top to bottom) after band gap excitation at 355 nm. The steady state transmission of the sample is included for reference (light green line).

To further examine the interference and the oscillations, we measured the steady state transmission of Cu_2O samples of different thicknesses. As shown in Figure 6-5, an increase in the thickness of the sample results in an increase in the number of interference peaks. The thinnest sample shows no clear interference pattern; on the other hand the thickest film shows a large number of peaks and troughs throughout the spectra.

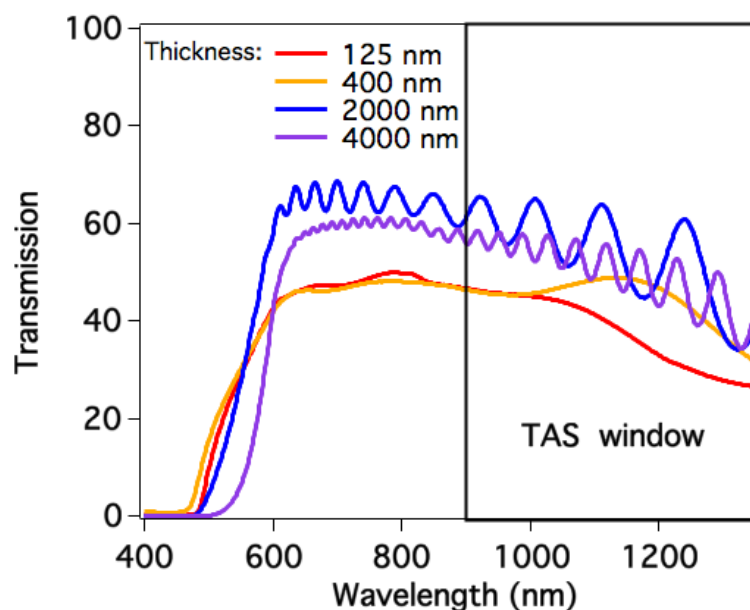


Figure 6-5 Steady state transmission spectrum of Cu₂O films with different thicknesses. Indicated in the figure is the wavelength range measured in our transient measurements.

Figure 6-6 shows the transient absorption spectra of Cu₂O samples of different thicknesses. As in the steady state transmission a change in thickness causes a dramatic change in the spectra. A large number of peaks, similar to those in the transmission spectrum, can be measured in the thick sample, with broader peaks being monitored for the thinner samples. Interestingly, the position of the TA peaks in the thin samples is also thickness dependent. Whereas in the ~125 nm sample a TA band with a maximum at 1100 nm is measured in the ~400 nm sample this band is displaced to longer wavelength with a TA maximum centered at 1350 nm.

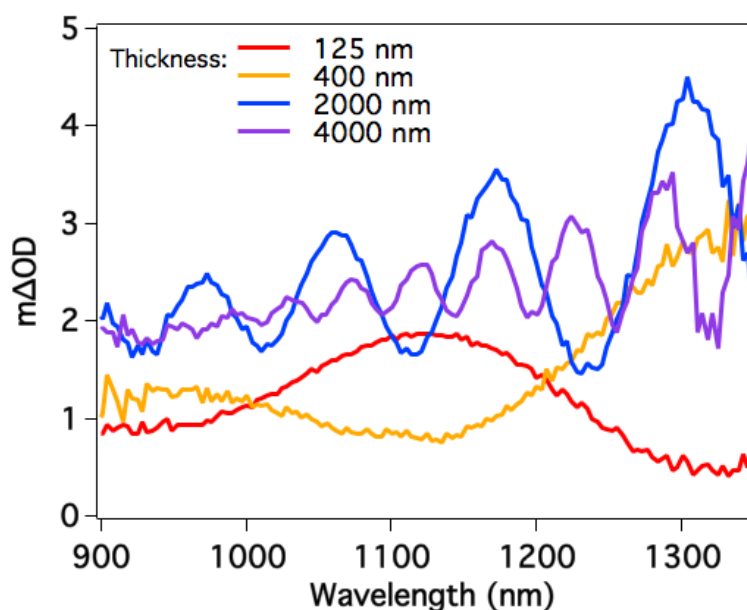


Figure 6-6 Transient absorption spectra of Cu_2O films with different thicknesses. The traces correspond to the transient absorption at 2 ps time delay after excitation at 500 nm.

The data above show that the steady state transmission and the transient spectra can change by altering the thickness of the sample. In the light of these results it is interesting to explore the effect of the film architecture in these measurements. This is important in order to test if for instance, device encapsulation, widely used in solar cells to prevent degradation, has any effect in optical measurements. Figure 6-7 shows the steady state transmission and the transient spectrum of a ~ 300 nm $\text{CH}_3\text{NH}_3\text{PbI}_3$ sample deposited on FTO and glass; the sample is sealed with a thin glass cover. A polymeric sealing gasket allowing a separation of ~ 25 μm between the perovskite and thin glass cover is used in order to avoid contact between these components.

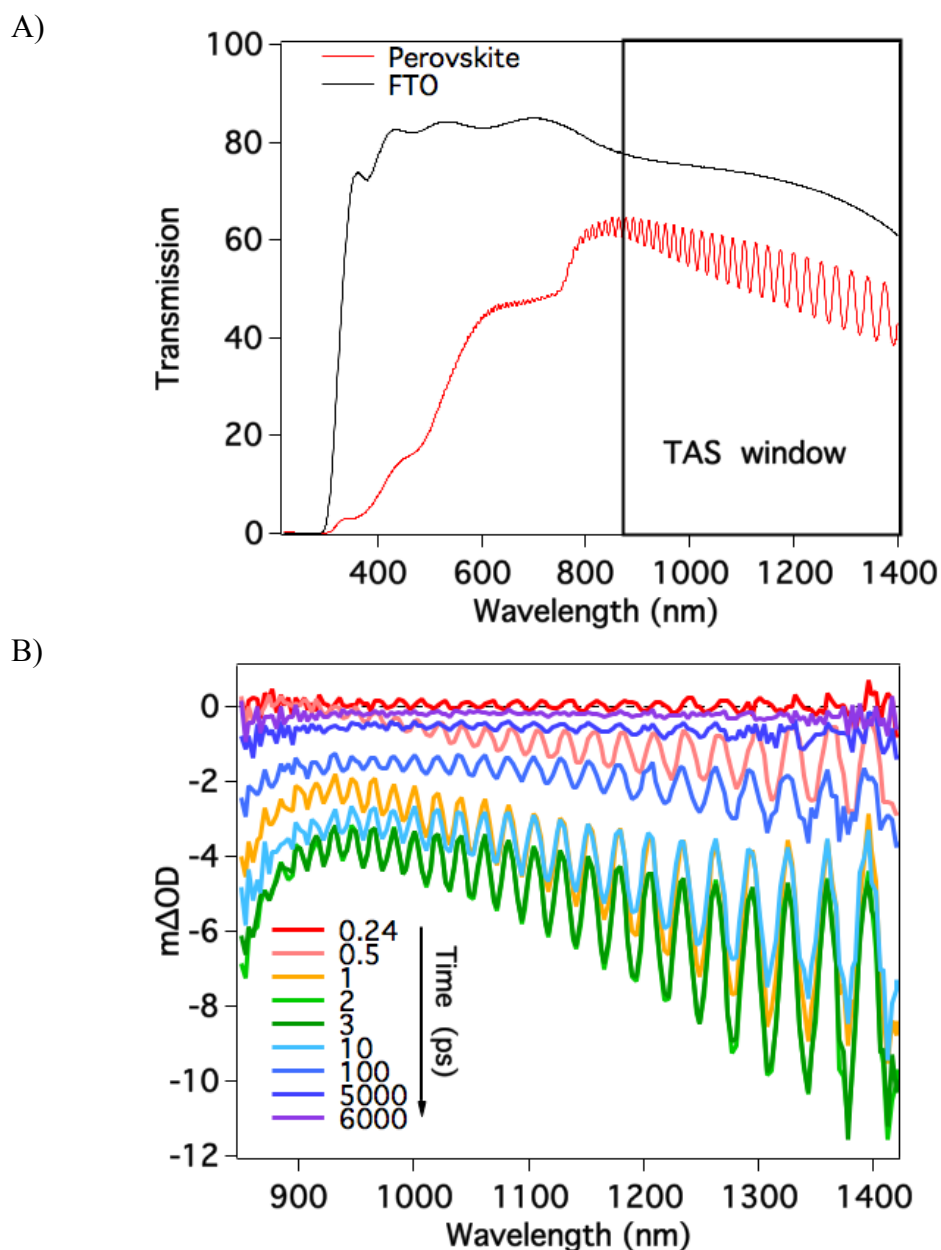


Figure 6-7 Steady state transmission spectrum of an encapsulated bare $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite and the glass substrate (A) and the corresponding transient absorption spectra after 575 nm excitation.

The transmission spectrum in Figure 6-7 is dominated by a high frequency interference effect. The amplitude of the interferences increases towards the NIR and decreases towards the visible where the sample absorbs. The peak-to-peak separation is approximately of 24 nm (peaks at 1148 nm and 1172 nm). The overall transmission in the visible region is typical of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. Similar to the steady state transmission spectrum, the transient spectrum is dominated by a high frequency interference growing towards the IR. The peak-to-peak separation is approximately of

28 nm (peaks at 1152 nm and 1179 nm). Interestingly, the negative change in optical density is monitored across the spectral region. Moreover at early times (~ 240 fs), a zero absolute change in optical signal is measured however an oscillating signal is monitored (solid red trace).

6.5. Discussion

Figure 6-2 shows that the transient spectra of Cu_2O , TiO_2 and a $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite are composed by of a series of transient peaks. These TA peaks are unlikely to correspond to the absorbance of photocharges or excited states in a semiconductor as these often appear as broad bands rather than a regular peak pattern. Similarly, the negative change in optical density in the NIR observed in our transient spectra is also unlikely to be due to a loss of ground state absorbance or stimulated emission as the bandgap of the samples occurs in the UV and visible regions. These features are however reminiscent of optical interference effects arising from the interaction of reflected light in and out of phase in an optical cavity. Such thin-film interference effect is clearly visible in the steady state transmission of the samples (Figure 6-3). As expected, the steady state interference fringes disappear in the region of strong absorption (UV-VIS) and increase towards the region where the sample is transparent. The appearance of such interference pattern is a good indicator of thickness uniformity and low surface roughness of the studied films. In our case, such prominent fringes indicate high quality interfaces between the semiconductor and air and the semiconductor and the conductive glass. Given the large coincidence between the oscillations observed in our transient spectra and the thin film interference fringes in the steady state it is reasonable to assume that these phenomena are directly related.

6.5.1. Thin film interferences in TA studies

The presence of thin film interference effects in the steady state transmission is well established and is often used as a method to calculate sample properties such as thickness, surface roughness and refractive index.[7, 8] On the other hand, their appearance in transient absorption spectra is less explored and the extent to which they occur in our transient measurement is striking.

In transient absorption measurements the change in optical density (ΔOD) can be calculated from the transmission (T) as $-\frac{\Delta T}{T_0}$. It follows that the presence of interference effects in the transmission in the sample before the pump (T_0) will result in the appearance of interference like fringes in the transient spectra. In order to exemplify this, we modelled the change in optical density of the Cu_2O film from the original transmission. Two extremes were modelled from the transmission (T_0) of Cu_2O : (A) a uniform ESA (excited state absorption) across the spectral range and (B) a Gaussian ESA centred at 800 nm with a standard deviation width of 100 nm. Figure 6-8 shows the change in optical density obtained for increasing values of the excited state absorbance (ESA) for the two cases; the original transmission (T_0) is included for reference. As expected from $-\frac{\Delta T}{T_0}$, the optical density change signal follows the inverse of the transmission before the excitation event (T_0). In both cases, an increase in the absorbance of the excited state results in an increase in the change in optical density as well as in the amplitude of the oscillations. Notably, these features increase simultaneously and therefore no isobestic point is observed. Furthermore, only in the spectral regions where the ESA occurs a finite ΔOD signal is monitored.

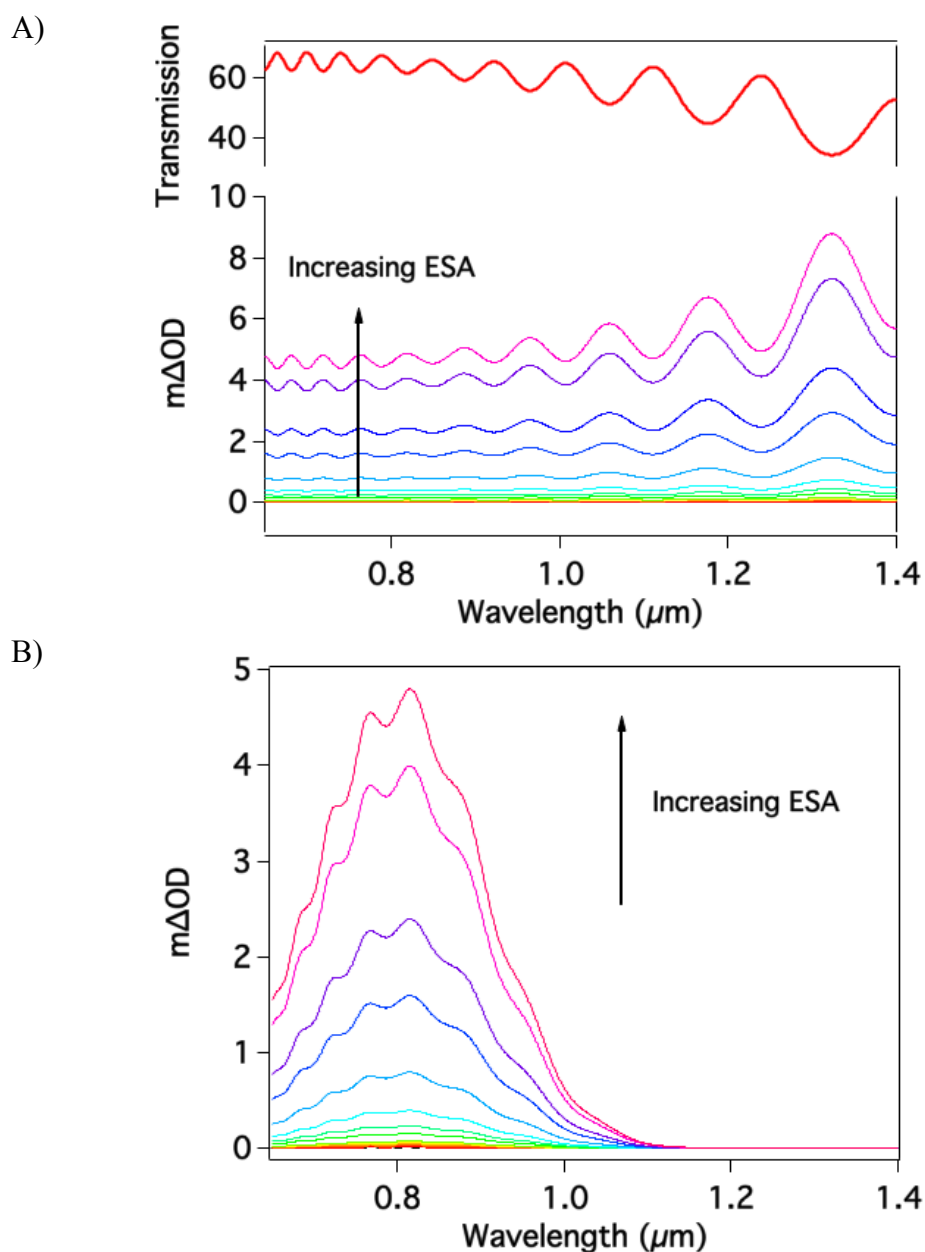


Figure 6-8 Modelled change in optical density expected for a Cu₂O sample when photoexcitation results in excited state absorbance constant across the whole spectral range (A) or a Gaussian shaped excited state absorbance centred at 800 nm (B). The steady state transmission of Cu₂O is shown in A for reference.

The modelled change in optical density confirms that interference effects should be present in transient absorbance spectra when they are present in the steady state transmission, as we observe. Therefore, interference fringes are to be expected in the transient spectra of materials with high quality interfaces and little surface roughness.

Notably, the effect of interferences will be stronger in the region where the material is transparent, however as shown in Figure 6-4, they can also be present in regions of weak absorbance (such as the visible region for TiO_2). Furthermore, as can be inferred from the model, higher excited state absorbance (ESA) will enhance the visibility of the interferences.

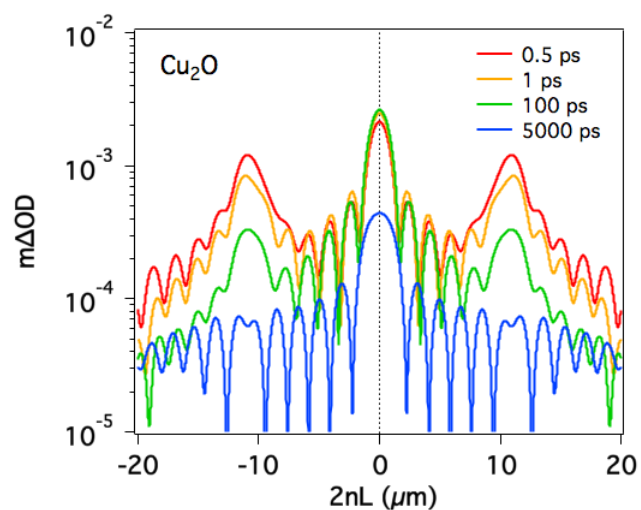
Interestingly, a direct comparison of the modelled change in optical density for Cu_2O with the experimental values (Figure 6-2) reveals that the modelled data does not reproduce well the empirical spectrum. Our transient data shows that (i) the oscillating signal decays faster than the background signal, this leading to isobestic points and (ii) in the modelled spectra, the oscillations are small in amplitude relative to the broad ESA increase, whilst in experimental data, the oscillations can dominate the spectrum, resulting for example in negative signals in regions where no ground state bleach or stimulated emission is expected. It appears that the transient data herein presented cannot be understood as simple change in transmission due to an ESA, but that other underlying factors affect the final change in optical density.

6.5.2. Composition of a transient absorption spectrum: Fast Fourier Transform

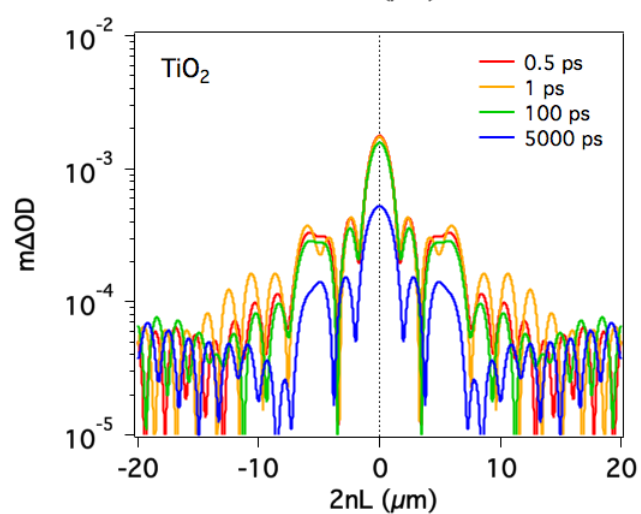
In order to identify the different components present in our transient data a Fast Fourier Transform (FFT) analysis was performed. Figure 6-9 shows the FFT magnitude spectra at different times for the samples studied. Due to the presence of thin film interference effects in the transient spectra it is convenient to express the frequency domain as a function of a simple optical cavity with a refractive index n , and length (sample thickness) L . In all cases a peak at $2nL = 0 \text{ } \mu\text{m}$ is observed, corresponding to the constant parameter in the Fourier series (A_0). In addition to this, within the resolution of these measurements, a fundamental harmonic (A_1) is observed at $2nL = 11 \text{ } \mu\text{m}$, $5.8 \text{ } \mu\text{m}$ and $6 \text{ } \mu\text{m}$ for Cu_2O , TiO_2 and the perovskite sample respectively, consistent with the optical cavity length of these samples. Hence at each time delay our optical signal is composed of two contributions, a constant non-oscillating component (A_0) and an oscillating one (A_1).

Based on the modelled data described in the previous section, we can understand the A_0 component as the background change in optical density due to the Excited State Absorbance (ESA), and the A_1 component as the oscillating signal caused by interference of light in the sample (optical cavity). It is noteworthy, that this analysis assumes that the nature of the ESA is independent of wavelength.

A)



B)



C)

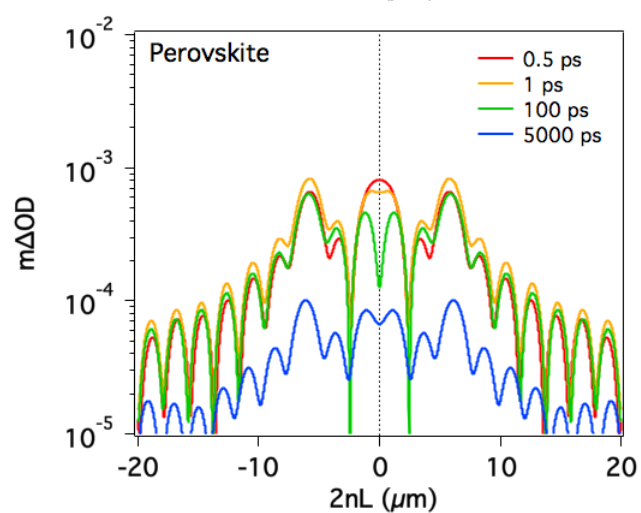


Figure 6-9 Fast Fourier magnitude spectra of A) Cu_2O B) TiO_2 and C) the perovskite device calculated from the transient spectra in Figure 6-2.

By calculating the Fourier Transform of the transient spectra at different time delays, it is possible to obtain the time dependence of each component. The time evolution for each sample is shown in Figure 6-10. In Cu_2O the component associated to the interference (A_1) decays significantly faster than the one due to the ESA (A_0). Contrarily, in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite device, the component associated to the ESA decays faster than the interference. Only in TiO_2 do both components decay simultaneously, as would be expected when the changes in optical density arise from a simple change in transmission due to an ESA. It is evident from the FFT analysis that the transient spectrum of Cu_2O and the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite is not controlled singly by a change in the absorbance of the sample but that an additional property of the system must be changing.

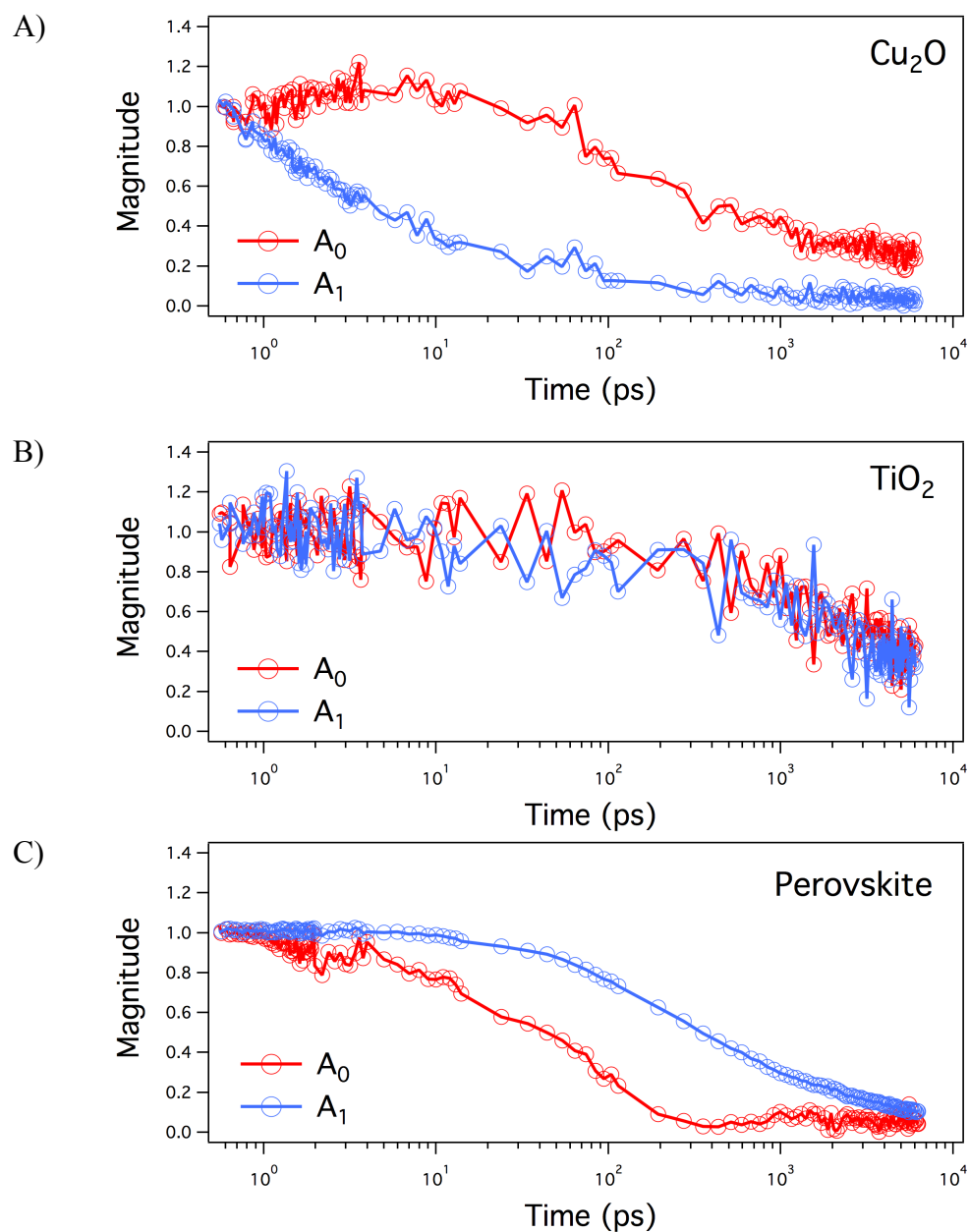


Figure 6-10 Time evolution of the two main components (A_0 and A_1) extracted from the Fast Fourier Analysis of Cu_2O (A), TiO_2 (B) and the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite device.

As discussed in the introduction to this *Chapter*, a close relationship exists between the refractive index of a sample, its dielectric function and its absorbance.[14] In simple terms, a change in absorbance will result in a change in the refractive index. Following photoexcitation two changes in absorbance occur: (i) the loss of the ground state absorption of the sample or bleaching and (ii) the appearance of a new absorbance due to the photogenerated excited state or ESA. Both these changes in absorbance will induce a change in the refractive index to a certain extent. Given the predominance of light interference effects in our measurements and given that these are controlled by the refractive index of the material, it is reasonable to explore the effect that a small variation of the refractive index might have in the transient absorption.

Figure 6-11 shows the modelled change in optical density of a thin film caused by a Gaussian shaped excited state absorbance centered at 800 nm with and without an index change of $(+10^{-3})$. This change in index is consistent with the change in the ground state absorbance of a thinner sample as calculated from the Kramers-kröning equation (calculated by *P. Stavrinou*). The presence of an ESA causes a positive change in optical density around 800 nm with very little signal at longer wavelength. The interference fringes, present in the sample's steady state transmission (T_0), are apparent in the TA spectra, with the oscillations being more prominent in the region of maximum excited state absorption. Strikingly, the inclusion of a small change in the refractive index results in a dramatic change in the interference pattern. A change in the index causes the amplitude of the interference fringes to increase across the entire spectral range so that they are visible even at wavelength with no ESA. Most notably, the index change results in negative changes in optical density even at wavelength without ESA.

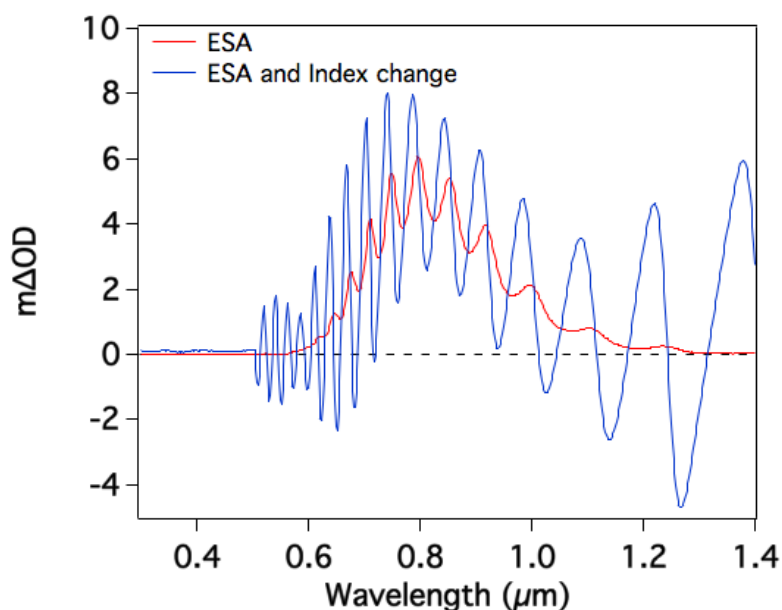


Figure 6-11 Modelled change in optical density caused by a Gaussian shaped Excited State Absorbance (ESA) with and without a change in the refractive index.

Figure provides evidence that the overall transient spectrum is composed of at least two contributions: an absorption change due to the ESA and a refractive index change. In particular, the appearance of negative signals in regions without ESA or where a loss of absorption is not expected is a clear indication that a change in the refractive index occurs after the excitation event.

6.5.3. Nature of the change in refractive index

The nature of the change in refractive index and its impact in the transient spectra is currently under scrutiny. However, based on the data herein presented and the current modelling it is possible to suggest a very tentative explanation.

As discussed above, the refractive index and the absorbance are directly related; a change in absorbance causes a change in the refract index. Our modelled data suggests that the large amplitude of the oscillations we observe in the transient measurements and the appearance of negative features in regions where no ground state absorbance of stimulate emission is expected are, in part, due to a change in

refractive index. This change in refractive index is likely to arise from a change in the absorbance after photo excitation. The latter can occur in two forms: (i) a change in the ground state absorption of the sample (ground state bleach) and (ii) a change due to the newly generated excited state (ESA). While both these changes in absorbance can contribute to the change in refractive index, the change in the ground state absorbance is likely to be the largest contribution, as it is located in the spectral region where the sample absorbs strongly (sub bandgap). Hence, we propose that the changes in the ground state bleach can induce changes in the refractive index across the spectral range. These changes in turn can affect the TA spectrum. This effect is consistent with a recent report on the spectroscopy of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskites, suggesting the contribution of refractive index changes to the TA spectrum, at least in the visible region.[20]

The observation of a different behaviour between the ESA and the interference fringes suggest that the way light interferes in the sample following photoexcitation changes at a different rate than the excited state absorption. In other words, after the excitation event the pattern of constructive and destructive interferences changes differently than the change in the ESA. As suggested by our model (Figure 6-11), a change in the way light interacts is predicted to arise from a change in index as no other physical properties of the sample, such as thickness, change after excitation. In Cu_2O , this change in index appears to cause the interference fringes to disappear faster than the ESA whereas the opposite is observed in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite device. In the TiO_2 sample both the ESA and the oscillation decay simultaneously. This indicates that in this material, at this excitation wavelength, there is no significant change in the index or that this one cannot be distinguished from the ESA.

It is important to note that more work is needed to assess the validity of our very tentative explanation and to define the extent of the index changes. The influence of the excitation wavelength as well as the importance of the ground state bleach in defining the overall transient signal are still under investigation. Nonetheless, it is apparent that through the use of transient absorption spectroscopy we might be able to gain insight into physical properties such as the refractive index changes in addition to the kinetics of the excited state.

6.5.4. Implications for the interpretation of transient data

The observation of large interference effects poses a conundrum for the interpretation of transient data. In particular, the interpretation of spectral features and its assignment to relevant process is significantly complicated by the presence of interference fringes in the transmission of the sample.

Figure 6-5 and Figure 6-6 show the steady state transmission and the transient spectra of a Cu_2O sample with different thicknesses. As expected, a change in the sample thickness equivalent to a change in the length of the optical cavity, results in different interference patterns. This phenomenon directly translates into differences in the transient absorption spectrum between samples. Completely different TA features are obtained for these samples despite the underlying process being likely to remain unchanged, namely charge generation and recombination. Importantly, only in the thickest samples do the optical interference become obvious.

In a similar way to thickness variations, the interface of two or more materials, such as a donor and acceptor layers in a solar cell, might significantly affect the transmission of the samples. As shown herein a change in the transmission spectrum will directly translate into changes in the transient spectra. Consequently the comparison of transient spectra of materials in different conditions in order to assay light induced processes may be misleading. This can explain the optical inconsistencies observed when measuring Cu_2O and $\text{Cu}_2\text{O}/\text{AZO}/\text{TiO}_2$ in *Chapter 5*. (Figure 5-16) As such, changes in the material of interest might have an impact in the TA spectra. The device architecture is likely to contribute to the overall signal as well. One example of this is the encapsulation of devices. This process might result in the appearance of a new optical cavity formed between the device and the thin glass cover the size of which will be determined by the thickness of the sealing gasket. The sealing method employed to encapsulate our $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskites results in a gap between the sample and the glass of approximately 25 μm . This gap acts as an optical cavity and can be directly monitored in the form of a high frequency interference

patter appearing both in the steady state transmission and the TA spectrum (Figure 6-7).

The presence of interference fringes significantly complicates the assignment of transient peaks to transient species and photophysical processes. This is particularly critical in the spectral range where the samples do not absorb and hence, where the interferences might dominate. For example in Cu_2O or $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskites, this corresponds to the Near-IR region. In this context, optical effects might explain the small number of reports of TAS and of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskites in this region, compared to reports in the UV-VIS.[21-24] Interestingly, the TA of semiconductors in the near-IR has often been assigned to photogenerated free charges in theses material and thus, understanding this signal is key to unravel the kinetics of charges in solar energy conversion devices.

In order to assign transient peaks in the TA spectra, a careful comparison with the steady state transmission spectra in the region of interest is necessary. Additionally, transient studies at different thickness might prove useful to assay if the observed peak in the TA spectra results from the defined absorbance of an excited state species or form an optical interference. The same applies when studying the effect of bringing materials into contact. However, in this case multiple complications arise as the nature (and quality) of the interfaces might change during the synthetic process. In such cases, the assignment of light induced process such as quenching or electron transfer reactions via spectral comparison is not appropriate and the comparison of kinetic traces might prove more useful, albeit only when the process can be time resolved. Alternatively, measuring samples where the interference effect is clear and unambiguous in combination with a Fast Fourier Transform Analysis, as the one described above, might prove the easiest and most reliable method to extract information relevant to the excited state kinetics as it is possible to decouple the ESA and the interference. Irrespective of the method used to interpret the data, careful consideration of the steady state transmission is paramount.

6.5.5. Charge carrier Recombination kinetics

Figure 6-10 shows the kinetics of the A1 and A0 components obtained from the FFT analysis of the transient spectra. We have associated the decay of the A0 component to the decay of the transient absorbance due to photogenerated species. For the three materials studied we observe that:

- (i) In the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskites device with an mp- TiO_2 layer (Figure 6-10C), the A0 signal is initially constant and rapidly decays from 1-2 ps with a $t_{50\%} < 100$ ps. This decay of photogenerated charges is faster than the one previously reported for similar perovskites containing TiO_2 in the same conditions.[22] However, these measurements are not sufficient to fully establish exact the nature of the reaction taking place.
- (ii) In TiO_2 (Figure 6-10B), the A0 signal is initially constant and decays at longer times decays with a $t_{50\%} > 1\text{ns}$. This behaviour has previously been observed and assigned to the recombination of charges.[3] Indeed, slow recombination kinetics, such as the ones we obtain in our FFT analysis, have been proposed to be the reason behind the low overpotential for water oxidation of TiO_2 photoanodes.[3]
- (iii) In bare Cu_2O (Figure 6-10A), the A0 component is initially constant and decays from 10 ps with a $t_{50\%} \sim 100$ ps. This is a relatively fast decay of photogenerated charges compared to TiO_2 , and is consistent with previous reports of the transient absorption of Cu_2O . [6] It is also in agreement with the kinetics reported for the $\text{Cu}_2\text{O}/\text{AZO}/\text{TiO}_2$ photocathode upon back illumination in *Chapter 5*. Under these conditions, in which charges are generated away from the $\text{Cu}_2\text{O}/\text{AZO}$ interface, no photocurrent was obtained. Fast electron-hole recombination kinetics in the Cu_2O can compete with electron transport to the interface and consequently hamper kinetics of charge separation in this material.

It is important to note, that this kinetic study is limited in its extent. Previous studies of charge carriers in photoelectrodes have shown that the applied potential or the

excitation intensities can have a significant effect in the kinetics of photocharges.[2-4, 25] Hence, intensity excitation studies and bias dependence studies of the Cu_2O photocathode are required to elucidate the behaviour its charge carriers. Nonetheless, these results show the potential of the FFT analysis to obtain relevant kinetic information, consistent with previous reports and highlight the need to further study the recombination of charges in solar energy conversion systems in order to improve their performance.

6.6. Conclusions

In summary, the results presented in this chapter provide evidence that light interference effects might have a significant impact in transient absorption spectroscopy. TA interference fringes are likely to dominate the transient spectra of materials with moderate-high refractive indices and especially high quality interfaces. Importantly, the presence of the interference fringes might complicate the interpretation of transient spectra, especially in thin films and complete devices. However, it has been found that these interferences might be used to gain insight into the physical properties of the system under study. A Fast Fourier analysis of the transient data has been used to decouple the interference from the TA of photogenerated species. The analysis of the photocharge absorbance component revealed that fast electron-hole recombination occurs in Cu_2O in the picosecond timescale. This recombination is likely to hinder charge separation and charge collection and thus, be detrimental for the performance of Cu_2O based materials, such as the $\text{Cu}_2\text{O}/\text{AZO}/\text{TiO}_2$ photocathode. The analysis of the interference component revealed that a light induced refractive index change can contribute to the overall TA of Cu_2O and a $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite device. Whilst the nature of this change is still under study, the results here presented herein show that Transient Absorption Spectroscopy can potentially be used to explore properties of solids other than the excited state absorption.

6.7. References

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Chapter Seven

Conclusions and future work

A review of the work presented in this thesis and its relevance to the development of efficient solar-to-fuel conversion devices is given in this chapter. Finally, possible future lines of work are also introduced.

7.1. Conclusions

It has been the main aim of this thesis to investigate the kinetics of reaction of intermediates in systems for solar-to-fuel conversion using Transient Absorption Spectroscopy and electrochemical techniques. For this purpose three systems, for CO₂ or proton reduction, have been studied. The systems were either molecular, hybrid or purely solid based. Our goal was to study the kinetic competition between recombination reactions and the catalysis. We aimed to identify the factors controlling the lifetime of these intermediate, explore ways to control their kinetics and obtain evidence of their role in the catalytic cycle.

Chapter 3 and *4* dealt with molecular and hybrid systems. These systems are advantageous for solar-to-fuel conversion because molecular catalysts, especially those based on transition metals, offers great flexibility to drive complex reactions. However, these systems often suffer from poor robustness and low efficiencies. It was shown that the control of the yield of reaction intermediates, their lifetime and the ability of the catalyst to react with the substrate is key to system performance. Furthermore, it was shown that such control could be achieved merely by means of heterogenisation and pH tuning. In *Chapter 3*, the performance of a Re based CO₂ reduction photocatalyst was found to be limited by a dimerisation side-reaction. Immobilisation of the photocatalyst on the surface of TiO₂ blocked this side reaction resulting in greater intermediate's lifetimes and a better CO₂ conversion performance. In *Chapter 4*, a homogeneous system consisting of sacrificial electron donor, a catalyst and a dye was studied. It was found that electron transfer between the dye anions and the electrocatalyst is pH independent. However, the generation of dye anions by the sacrificial electron donor and the catalytic ability of the catalyst were found to have opposite pH-dependencies; these must be simultaneously adjusted to maximise performance.

In *Chapter 5*, a purely solid-state inorganic system was studied. This system based on p-Cu₂O and a series of protection layers offers great robustness and outstanding performance. However, the device has a complex structure and its modification is synthetically challenging. It was found that the choice of materials, especially the nature of the catalyst layer can have a significant impact in the recombination kinetics

and performance of the system. Specifically, it was found that charge separation, and consequently the photocurrent onset, is controlled by the p-n junction between Cu_2O and Al:ZnO . The catalyst layer was found to be key in slowing down the recombination of separated charges and thus in helping achieve high quantum yields.

In *Chapter 6*, the kinetics of charge carriers on the ultrafast timescale was addressed using TAS. In order to do so, first the occurrence of optical interference effects in TAS measurements was considered. Optical interference effects were studied and their potential to obtain new information was explored. It was found that interference effects dominate the transient spectra of materials with high refractive index and high quality interfaces. If unnoticed these interferences can hinder the interpretation of transient spectra. However, they can also provide information about the change of the refractive index in the material and hence about the nature of the polarisation induced by the excitation event. A method to extract kinetic information based on a Fast Fourier Transform Analysis was presented. Employing this method it was found that ultrafast recombination of charges dominates in Cu_2O . Recombination of photogenerated charges in fast timescale can potentially hamper charge separation in Cu_2O based materials.

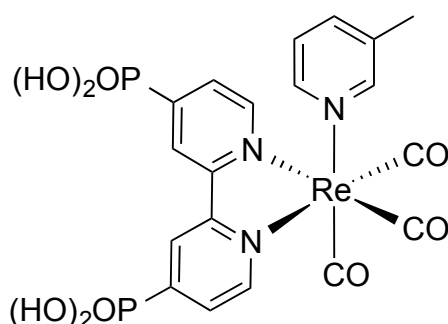
7.2. Future work

In order to make solar-to-fuel conversion technology commercially available, the efficiency and robustness of the systems needs to be improved. Hybrid systems, combining semiconductors and efficient molecular catalysts, are a powerful combination to achieve complex catalytic reactions like the reduction of CO_2 . The Cu_2O multilayer architecture has great potential to be used as the supporting material and even as a light absorber. A comparative study of the kinetics of a system based on Cu_2O with different catalyst layers, might provide insightful information about the catalytic function. In this context, kinetic studies of systems using Pt, MoS_x and molecular electrocatalysts such as the Ni presented in *Chapter 3* appear particularly interesting for the high TOFs of the catalysts. Further studies in this direction can help elucidate the factors determining the suitability of catalysts in photoelectrodes.

Regarding optical interference effects, further analysis and modelling of the phenomena are required in order to assess the amount of new information that can be obtained employing the interference changes. A comparison with other techniques, such as ellipsometry is also needed. Further frequency (wavelength) dependence studies must be performed to establish the origin of the intriguing changes in the refractive index.

Appendix

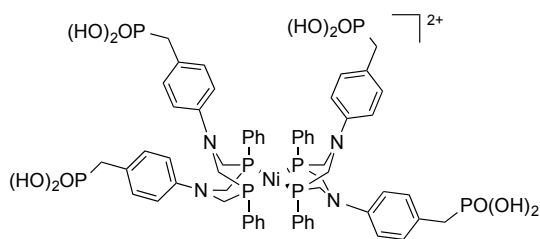
1. [Re(2,2'-bipyridine-4,4'-biphosphonic acid)(CO)₃(3-picoline)] (Re^{Pic})



¹ H NMR (400 MHz, CD ₃ OD)	
2.22 ppm	3 H, s
7.25 ppm	1H, dd
7.75 ppm	1 H , d
8.12 ppm	2 H, q
8.17 ppm	1 H, d
8.25 ppm	1 H, s
8.77 ppm	2 H, d
9.44 ppm	2 H, dd
³¹ P{ ¹ H} NMR (109 MHz, CD ₃ OD)	
6.68 ppm	s

Further details on sample preparation and characterization can be found in the reference: *Improving the photocatalytic reduction of CO₂ to CO through immobilisation of a Molecular Re catalyst on TiO₂.* *Chemistry A European Journal*, 2015, 21, p.3746

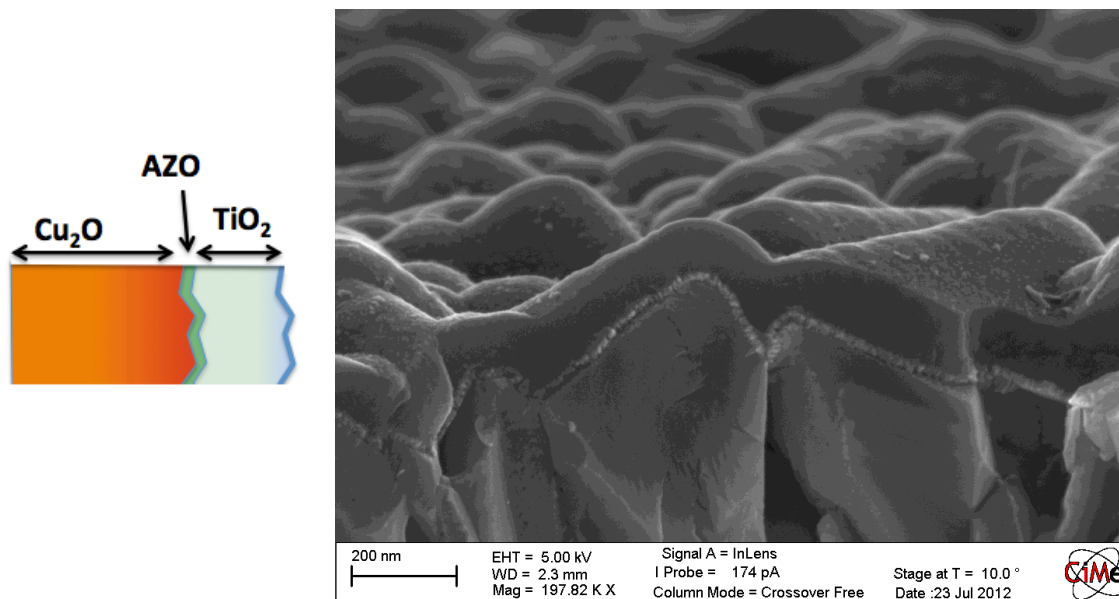
2. $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{PhCH}}_2\text{P}(\text{O})(\text{OH})_2)_2] (\text{NiP})$



^1H NMR (400 MHz, CD_3OD)	
2.97-3.22 ppm	8 H, m
5.6-4.7 ppm	16 H, m
8.23-6.7 ppm	36 H, m
$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_3OD)	
-13.9 ppm	NCH_2P
21 ppm	NCH_2P
25.8 ppm	$\text{PO}(\text{OH})_2$

Further details on sample preparation and characterization can be found in the reference: *Versatile Photocatalytic Systems for H_2 Generation in Water Based on an Efficient DuBois-Type Nickel Catalyst*. Journal of the American Chemical Society, 2014. **136**(1): p. 356-366.

3. Cu_2O (400 nm)/ Al:ZnO (20 nm)/ TiO_2 (100 m)



Cross section SEM of the $\text{Cu}_2\text{O}/\text{Al:ZnO}/\text{TiO}_2$ architecture collected by Prof. Morgan Stefik (University of South Carolina). Image courtesy of Prof. David Tilley (University of Zurich)

Further details on sample preparation and characterization can be found in references: *Highly active oxide photocathode for photoelectrochemical water reduction*. Nat Mater, 2011. **10**(6): p. 456-461 and *Ruthenium Oxide Hydrogen Evolution Catalysis on Composite Cuprous Oxide Water-Splitting Photocathodes*. Advanced Functional Materials, 2014. **24**(3): p. 303-311.

