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# **Electron transfer processes in a dye-TiO<sub>2</sub>/SnO<sub>2</sub>-acceptor assembly**

Towards long lived charge separated states for solar fuels

Master's thesis in Materials Chemistry

Jimmy Björklund



MASTER'S THESIS 2016:NN

# Electron transfer processes in a dye-TiO<sub>2</sub>/SnO<sub>2</sub>-acceptor assembly

Towards long lived charge separated states for solar fuels

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Gothenburg, Sweden 2016

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## Abstract

With increasing demands for carbon neutral fuels, an attractive solution is to develop solar fuel devices. The conversion efficiencies for solar fuel devices are currently low, which in part is due to the challenge of implementing multiple electron transfer (MET) reactions with the catalyst. This thesis has therefore investigated an hybrid organic-inorganic solar fuel assembly, which is capable of MET reactions. The objective of this study has been to prove a conduction band mediated electron transfer process from a semiconductor to an electron acceptor as a proof of principle for this solar fuel assembly. This was achieved by performing photolysis and spectroelectrochemical measurements on both TiO<sub>2</sub> and SnO<sub>2</sub> with hemin and hemin(py)<sub>2</sub> as electron acceptors respectively. In addition, this thesis has also been aimed towards investigating the back electron transfer (electron recombination) which has a detrimental effect on solar fuel assemblies. The electron recombination was investigated on TiO<sub>2</sub>, SnO<sub>2</sub> and on a mixed TiO<sub>2</sub>/SnO<sub>2</sub> semiconductor system. This was studied using single wavelength nanosecond transient absorption spectroscopy. The results showed no clear decrease in the rate of recombination by mixing the semiconductors, but more experiments are required to study this effect. With the electron acceptor hemin(py)<sub>2</sub> absorbed on the dye-sensitized semiconductor films, a significantly slower rate of recombination was observed compared to semiconductor films without an electron acceptor. This was especially apparent in the region between 200 and 1300 microseconds, which could potentially allow for photocatalytical reactions to occur. Incorporation of a catalyst in dye-sensitized semiconductors could thus possibly be advantageous for this type of solar fuel assembly.

Keywords: dye sensitized solar cell, solar fuels, electron recombination, mixed TiO<sub>2</sub>/SnO<sub>2</sub> semiconductor system, conduction band mediated electron transfer, cascade electron transfer



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# 1

## Introduction

### 1.1 Background

With global warming emerging as an increasing risk to humanity and environment alike, the need for drastic measures against carbon dioxide emissions are crucial. One of the most promising carbon neutral energy sources would be to harvest solar energy because of its vast potential. Only the solar energy intercepting earth in one hour alone ( $4.1 * 10^{20} J$ ) would be sufficient to sustain all of earth's energy demands for an entire year. Naturally it is not feasible to believe that we can harvest all that energy. However to merely sustain earth's global energy demands, estimated for the late part of this century, would only equate to a small 0.16 % of earth's area using solar cells of 10 % efficiency. [1]

Despite this vast potential in solar energy, only a very small fraction of our current energy comes from solar energy, both in terms of electricity and fuels. While there at present is a large focus on developing solar energy technologies for generating electricity and heat, the bulk of energy are consumed as fuels [2]. There is thus a strong incentive to develop carbon neutral fuels. An ideal process, already existing in nature is the photosynthesis, which converts carbon dioxide and water into carbohydrates. While very impressive, it is also a slow process [3]. As a consequence, there have been many attempts to create artificial photosynthesis to achieve higher efficiency [4] [5]. In addition more chemical approaches to produce hydrogen, methane and methanol as viable fuels have also been tried.[6]

An altogether different approach of converting carbon dioxide into fuels such as methane or methanol have been tried without harvesting light, but by using an external applied current to drive the reaction [7]. This process however have proven difficult due to the many reaction steps and redox equivalents it takes to complete the process. The process is further impeded by the formation of unstable intermediates, which rapidly reverse to a more stable form by dissipating its energy and electrons to its environment. This process therefore leaves much to be desired both in terms of thermodynamics and kinetics. Typically, in order to create a viable fuel from carbon dioxide, multiple electron transfer (MET) reactions are necessary. As the name implies, multiple electrons are transferred in a near simultaneous step, which reduce the number of unstable intermediates formed, and increase the conversion efficiency.[2]

One particular way of facilitating MET reactions would be to use the principles of a dye sensitized solar cell (DSSC). In addition to a likely increase of the conversion efficiency, the process would also be powered by solar energy from the visible spectra

making it entirely carbon neutral.

### 1.2 Objective

The objective of this master's thesis has been to investigate the electron transfer processes in a hybrid organic- inorganic solar fuel assembly. More specifically, this thesis has been primarily aimed towards proving a conduction band mediated electron transfer from the conduction band of  $\text{TiO}_2$  and  $\text{SnO}_2$  to an electron acceptor, and investigating the rate of back electron transfer (electron recombination) in a mixed  $\text{TiO}_2/\text{SnO}_2$  semiconductor system. By introducing a second semiconductor of lower conduction band energy level to the system, a lower thermodynamic driving force for recombination is proposed to occur. Additionally the electron injection efficiency has often been shown to increase in systems with electron transfer occurring in multiple steps. The methods used to study conduction band mediated electron transfer in this thesis have been spectroelectrochemistry, and photolysis. The rate of recombination has been measured with a nanosecond transient absorption spectroscopy.

A part of this thesis has also been dedicated towards optimization of preparation of  $\text{SnO}_2$  semiconductor paste and making of  $\text{TiO}_2$ ,  $\text{SnO}_2$  and  $\text{TiO}_2/\text{SnO}_2$  semiconductor films. This has included characterization of the semiconductor films using scanning electron microscope (SEM), in terms of nanoparticle size, distribution and also investigating the composition with electron dispersive X-ray spectroscopy (EDX). In addition, the semiconductor films sensitized with a dye or electron acceptor has also been characterized with cyclic voltammetry (CV), UV-vis spectroscopy, spectroelectrochemistry and photolysis.

# 2

## Theory

This part aims to provide a detailed understanding of the physical processes occurring inside solar cell devices for fuel production. This will include some basic quantum mechanics in order to discuss the kinetics of these electron and energy transfer mechanisms. Furthermore the basic design principle for hybrid inorganic-organic assemblies for solar fuel production will also be explained.

### 2.1 Quantum mechanics

Classical mechanics has certain limitations and cannot properly explain the wave particle duality, or light matter interaction. As a result when studying photoinduced reactions, quantum mechanics becomes necessary.

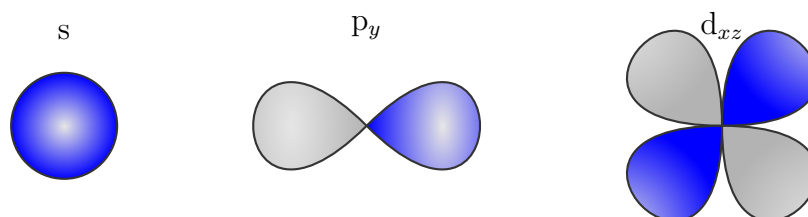
A fundamental cornerstone in quantum mechanics is the Schrödinger equation. This equation models elementary particles from their fundamental energies (potential and kinetic energy) in order to describe their interaction with each other. With a mathematical definition of the interactions of elementary particles inside a system, the wave particle duality is possible to solve. This can be achieved by describing electrons in molecular orbitals with wave functions. By solving the (time independent) Schrödinger equation defined below in equation 2.1, i.e. determining the function  $\varphi$ , these molecular orbitals can be calculated and visualized in three dimensional plots, see figure 2.1[8].

$$\mathcal{H}\varphi = E\varphi \quad (2.1)$$

$\mathcal{H}$  is defined as the Hamilton operator and describes the total energy in the system (see equation 2.2),  $\varphi$  the quantized solution to the Schrödinger equation and proportional to the probability of finding an electron in a certain position by  $|\varphi|^2$ , and  $E$  as the energy of the corresponding molecular orbital.

$$\mathcal{H} = \frac{-\hbar^2}{2} \sum_{n=1}^N \frac{1}{m_n} \nabla_n^2 + V(r_1, r_2, \dots, r_n, t) \quad (2.2)$$

To solve the time independent Schrödinger equation even with several approximations for more than a few particles, requires immense computing capabilities as the problem becomes exponentially more complex with more particles. Thus quantum mechanics is far from ideal when dealing with systems on a macro level. However for investigating the principles of photoinduced electron transfer and light matter interaction, the system can be limited to a small number of particles and the Schrödinger equation can be managed relatively easy.



**Figure 2.1:** Molecular orbitals depicting one s, p and d orbital from left to right.

## 2.2 Light matter interaction

Light is a form of electromagnetic radiation which can interact with charged particles through its oscillating electric field component. Absorption of light may occur only if the magnitude of the electric field component matches the energy between two molecular orbitals to facilitate the transition of an electron to the higher energy level 2.3. [8]

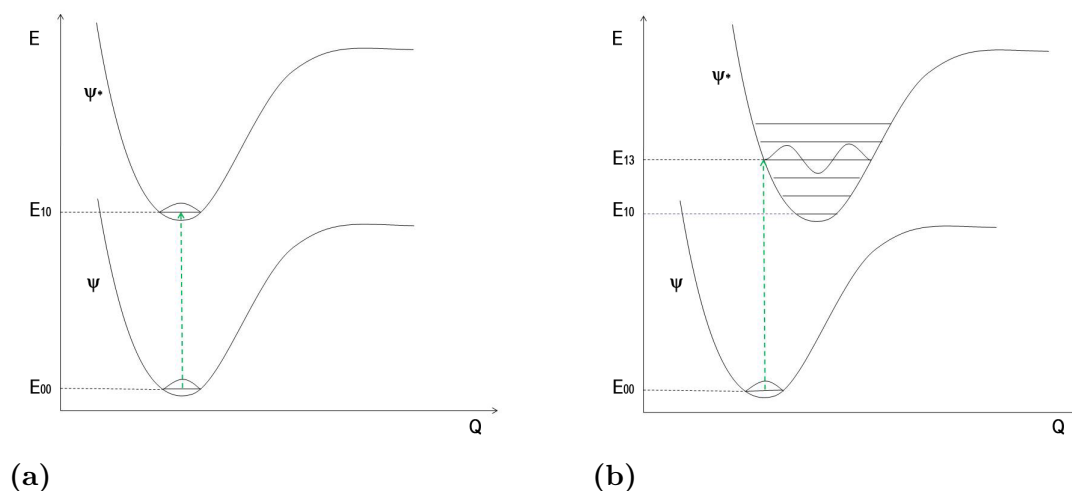
$$E = \frac{hc}{\lambda} \quad (2.3)$$

In order to explain the energy gap between different orbitals, one needs to consider the initial and final state with the Schrödinger equation. A common way of visualizing the energy gap is by a potential surface energy plot, in which the solution to Schrödinger's equation,  $\varphi$ , is plotted against its nuclear coordinates. From this plot, the energy gap can be interpreted as the vertical distance between the initial and final state (Franck Condon principle). By comparing the vertical distance between perfectly matched orbital functions and slightly overlapping orbitals in figure 2.2a and 2.2b respectively, the energy gap can be observed to be larger for the latter. The energy gap is thus dependent on the orbital overlap, which helps explain why some transitions occur more frequently than others.[8] [9]

## 2.3 Deactivation of excited states

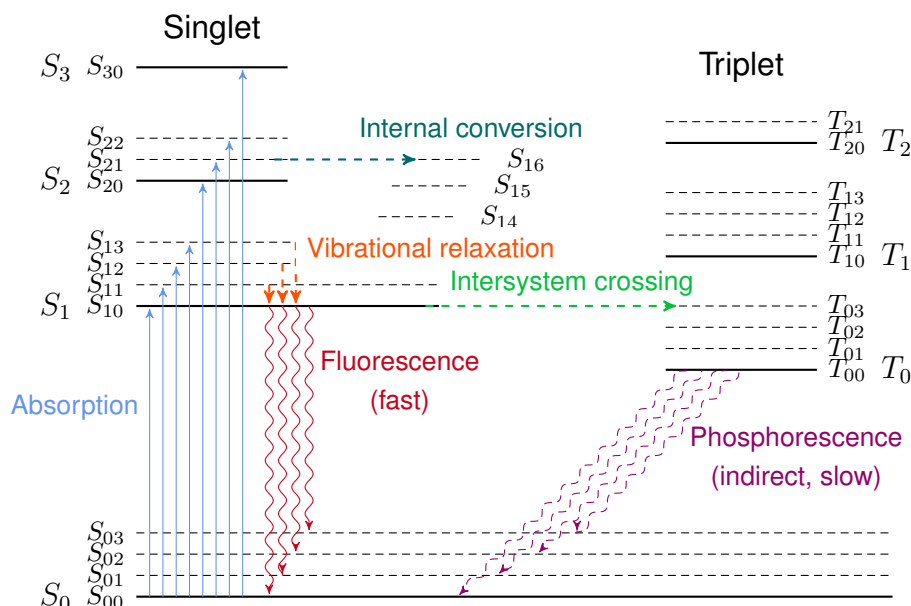
Once an electron has been promoted to an electronically excited state it can dissipate its energy by one of several deactivation pathways, or even a combination of them. Typically the deactivation pathways of these processes are characterized using a Jablonski diagram, see figure 2.3.

In addition to the electronic energy levels, there exist vibrational energy levels which consists of periodic quantized motions of the molecule. The energy gap between vibrational energy states are however relative to the electronic energy levels much smaller.[9] The most fundamental deactivation pathways in an excited molecule



**Figure 2.2:** Potential surface energy plots of two orbitals perfectly overlapping and slightly overlapping in a) and b) respectively. The promotion of an electron from one orbital to another typically occur from the lowest vibrational state due to rapid vibrational relaxation.

are vibrational relaxation, fluorescence, phosphorescence, internal conversion, intersystem crossing and excited state reactions, which are explained in more detail below.

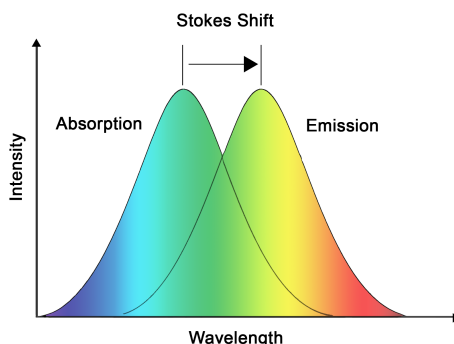


**Figure 2.3:** Jablonski diagram depicting the deactivation pathways inside a molecule. For clarity the spin singlet states ( $S$ ) and the triplet states ( $T$ ) have been separated. In addition, the excited and the vibrational sublevels are drawn by solid and dashed horizontal lines respectively.

### 2.3.1 Vibrational relaxation

The transition between an electronically excited state to the lowest vibrational energy level, is called vibrational relaxation. Since the energy from the excited state is only transferred to a vibrational sublevel in the same orbital, the energy is dissipated as vibrational energy to the surrounding.[8]

The kinetics of vibrational relaxation is rapid and relative to the process of emission (see 2.3.2) much faster. As a consequence of this, emission will as a rule always occur from the lowest vibrational energy level. An additional consequence of rapid vibrational relaxation, is the occurrence of the Stoke's shift, which is the difference between absorption and emission wavelength.[9]



**Figure 2.4:** Illustration of the Stokes shift

### 2.3.2 Fluorescence and phosphorescence

There are two radiative deactivation processes that may occur inside a molecule, which are differentiated by the multiplicity of the energy levels involved in the transition. The transition between two energy levels of the same multiplicity, for example two singlet levels, is known as fluorescence, whereas between different multiplicity is known as phosphorescence. Since the transition between two singlet energy states provide no constraint on the spin, the process is relatively fast. However for phosphorescence, which may occur between a triplet and a singlet state, the spin momentum cannot be conserved in the transition between the two energy levels. This makes it a so called forbidden process, which however only translates into slow kinetics as the spin may be changed by spin-orbit interaction with the nucleus [10]. [8]

### 2.3.3 Internal conversion and intersystem crossing

The energy level in one orbital can potentially match a high vibrational energy level of a lower orbital. If transition between these orbital energy states have the same multiplicity, the process is known as internal conversion. A consequence of internal conversion is the relaxation process after the transition, which occur from a high vibrational energy level to low vibrational state through vibrational relaxation. The process is thus non radiative. Similar to internal conversion, the crossing between energy levels of different multiplicity is also known as intersystem crossing.[9]

### 2.3.4 Excited state reactions

An excited molecule can often as a result of its increased energy react with neighboring molecules. This interaction can in the process of reaction consume the energy from the excited state and result in new molecular species. This process is also known as quenching. While considering which molecules that may or may not interact with an excited species, it often helps to think of it as an entirely new species different from its ground state. This due to the excited state not only has an enhanced reactivity from its higher energy state, but also a changed electron structure which may make certain interactions possible.[9]

### 2.3.5 Lifetime of the excited state and quantum yield

The deactivation pathways of an excited molecule can occur by any of the above mentioned deactivation processes. However to truly understand the behaviour of an excited molecule, the kinetics of these processes must be considered [11].

The expected lifetime of an excited molecule,  $\tau(A^*)$ , can be modelled by a first order kinetic reaction, see equation 2.4.

$$\tau(A^*) = \frac{1}{(k_r + k_{nr} + k_p)} \quad (2.4)$$

$[A^*]$  is the excited state,  $k_r$ , the rate constant of radiative processes,  $k_{nr}$  the rate constant for non radiative processes (not including excited state reactions), and  $k_p$  the rate constant of excited state reactions.

A very useful concept in understanding the efficiency of a specific process is the quantum yield. The quantum yield is defined as the number of excited molecules undergoing a specific process divided by the total amount of excited molecules for a given amount of time, see equation 2.5. [8][9]

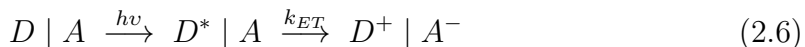
$$\eta_i(A^*) = \frac{k_i}{\sum_i k_i} = k_i \tau_i(A^*) \quad (2.5)$$

## 2.4 Photoinduced electron transfer

The phenomenon photoinduced electron transfer is the transfer process of an electron between a donor and an acceptor in which either exist in an electronically excited state. Photoinduced electron transfer is technically a chemical deactivation process and the desired deactivation pathway of solar fuel devices. This is due to its ability to induce a charge separated state, which is a key function in all solar cell devices.[9][8]

The electron transfer between a donor and an acceptor does not have to be between two different molecules, but can also occur inside one large molecule of two moieties functioning as donor and acceptor. The process of intra-, and intermolecular photoinduced electron transfer are very similar, and only becomes possible when the molecule has been electronically excited with a sufficiently long lifetime for the transfer mechanism to compete with other deactivation pathways. For intermolecular photoinduced electron transfer the lifetime must also be approximate to the

time between collisions of neighboring molecules. The general reaction formula for photoinduced electron transfer can be seen below in equation 2.6. [9]



The possible applications for photoinduced electron transfer are many, for instance it can be used to prevent luminescence and reactivity, or induce chemical changes or even induce luminescence from species that normally do not absorb light at the specific wavelength.[9]

### 2.4.1 Marcus theory

In order to understand and quantify the rate of photoinduced electron transfer, Marcus theory is typically necessary. In Marcus theory, the initial and final state of a reaction are investigated using potential surface energy plots gained from Schrödinger's equation. However for simplicity, the solutions can be approximated to parabolic functions representing the initial donor acceptor complex, and the final charge separated state, see figure 2.5.[12]

In Marcus theory the initial and final state is separated by an intermediate transition state, which in figure 2.5 can be seen as the point of intersection between the two parabolic functions. The energy at the intersection point relative to the initial state determines the activation energy of the reaction, which if positive needs to be supplied for the reaction to occur. In addition to the activation energy, the rate of photoinduced electron transfer is dependent on the reorganisational changes ( $\lambda$ ) of surrounding molecules which must take place to find a new equilibrium, in order to balance the electrostatic force from nuclei distortions and changed polarisation. The rate of photoinduced reaction can be seen below in equation 2.7, where  $\nu_N$  is defined as the average nuclear frequency factor,  $\kappa_{el}$  the electronic transmission coefficient and  $\Delta G^0$  the activation energy.[9] [12]

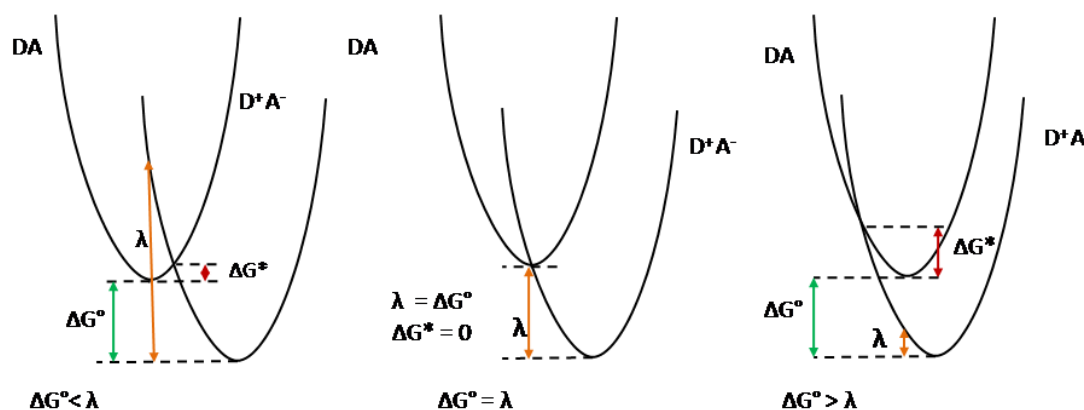
$$k_{et} = \nu_N \kappa_{el} \exp\left(-\frac{(\Delta G^0 + \lambda)^2}{4\lambda RT}\right) \quad (2.7)$$

From the above equation, three different regions can be characterized; the normal-ized region, the activationless region and Marcus inverted region denoted 1 to 3 respectively below.

1. A region of small activation energy, which increase the rate of photoinduced electron transfer with increasing driving forces.
2. A region of negligible activation energy, in which a change in driving force only induce small changes in photoinduced electron transfer rate.
3. A region of strongly exergonic processes, in which the transfer rate is only decreasing with increasing driving force (Marcus inverted region). [9]

## 2.5 Semiconductors

A semiconductor constitutes the middle ground of electrical conductivity of insulators and metals. Unlike the insulator, the semiconductor can conduct electricity



**Figure 2.5:** Schematic representation of the three regions of Marcus theory. From left to right; the normal region, the activationless region and the Marcus inverted region.

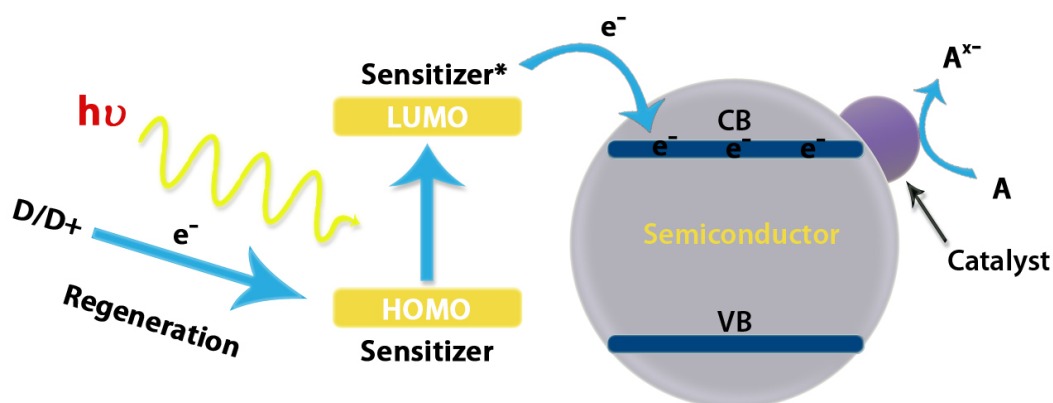
but only under certain conditions. In order to explain this behavior however, one needs to understand the origin of the valence- and conduction band. By considering a single atom, there exist a discrete number of energy levels available for the electrons to occupy. When atoms combine and form a molecule, each atomic orbital transform into a molecular orbital. The same principle can be applied among neighboring molecules if there exist orbital overlap among them. Thus in macroscopic crystalline structures, the discrete energy states become so many that they form continuous bands of energy states. The lower energy band is known as the valence band (VB), which is separated from the higher conduction band (CB) by an energy gap. The energy gap is an important property for electrical conductivity and separates insulators from metals. For metals the energy gap is zero or negligible, and thus allows electrons to be distributed in both the valence band and the conduction band, whereas for insulators the energy gap is large and the electrons are only distributed into the valence band. Metals become electrically conductive as they possess many states filled only part of the time, which allows electrons to readily be accepted by the individual molecules. In contrast, insulators which have few partially filled states, due to being restricted to the valence band alone, can therefore not as easily accept electrons [13] [14]. A semiconductor is an insulator in its ground state, but as the energy gap to the conduction band is relatively small, can be induced to promote electrons to the conduction band with heat or light and thereby become electronically conductive [14]. Electrons promoted to the conduction band by means of heat or light are termed hot electrons, and can be observed by a broad peak in absorbance spectrum at wavelengths between 300 and 1100 nm [15].

## 2.6 Hybrid organic-inorganic assemblies

There are multiple approaches to solar energy conversion by storing energy in chemical bonds. The two most central elements in solar fuel devices consists of capturing

light, and inducing formation and breaking of bonds for energy storage. The properties required for these elements are however different and often difficult to combine. One solution to this problem, is to use the principles of the dye sensitized solar cell (DSSC), which separates the functions of capturing light to the dye-semiconductor interface, and the charge carrier transfer to the semiconductor-electrolyte [16]. By making small adjustments to the design of a DSSC, a device capable of driving a photocatalytic reaction instead of outputting electricity can be made. The hybrid organic-inorganic solar fuel assembly is one design based on the DSSC, and is also the main focus in this thesis, see figure 2.6.

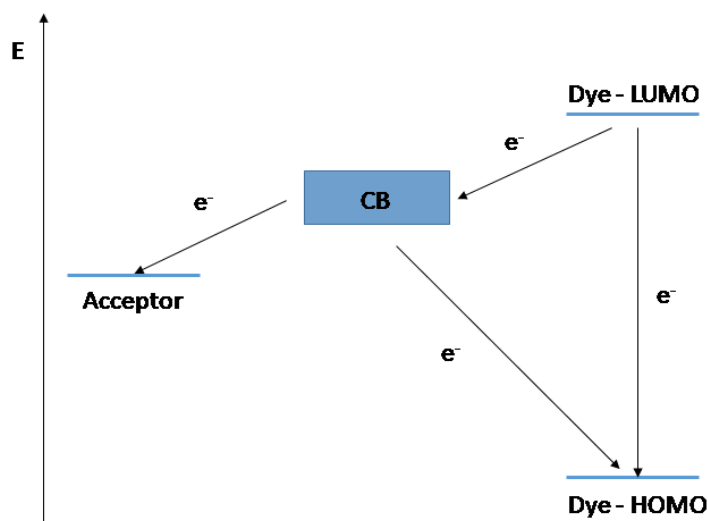
The hybrid organic-inorganic solar fuel assembly, consists of a dye, a semiconductor, a catalyst and a redox couple, not including the chemical reactants and products participating in the catalytic reaction [16]. The  $\text{TiO}_2$  semiconductor has a wide band gap of approximately 3.2 eV [17], which enables band gap excitation with UV light. However since a large portion of the light emitted from the sun occurs in the visible region, a dye can be added to increase the efficiency of the solar fuel assembly. Once the dye has been photoexcited to its lowest unoccupied energy level (LUMO), it can inject the electron into the conduction band of the semiconductor. For the injection to be efficient however, it is important to have a good electronic coupling between the dye and acceptor, in addition to the conduction band being lower in energy level relative to the excited state of the dye. Once the electron has been injected into the conduction band it can travel through the semiconductor to the catalyst, whereupon the catalyst can absorb multiple electrons to reach a highly reduced state. The catalyst will then have the possibility to facilitate multiple electron transfer in a reaction with carbon dioxide and water to form methane or methanol. However in order to balance the charges caused by oxidizing the dye and reducing the carbon dioxide a redox couple or sacrificial donor is also required. As the aim of this thesis is to study electron recombination, no redox couple have been included in the experimental system.[16] [18]



**Figure 2.6:** Schematic illustration of the general principle of a hybrid organic-inorganic assembly for solar fuel production. This image was adapted from [19].

## 2.7 Electron recombination

As described above in the hybrid organic- inorganic assemblies section, light in the visible spectrum can be captured by a photosensitizer to induce an electronically excited state. The electron injection from the excited state of the dye to the conduction band of the semiconductor however occur in competition with other deactivation processes, see section 2.3. One way of achieving a high electron injection efficiency and long life times of charge separated state has been shown by transferring the electrons in many small energy steps, a process also known as cascade electron transfer [18]. In addition to losses induced by poor electron injection, electron transfer is not limited to the forward direction alone, but may also occur in the backwards direction. This electron transfer is commonly referred to as electron recombination, and may for instance occur from the conduction band of the semiconductor to the ground state of the oxidized dye, see figure 2.7. For solar fuel devices, electron recombination impose an efficiency limiting effect, as the backwards electron transfer often competes on approximately the same time scale as electron transfer in the forward direction [20].

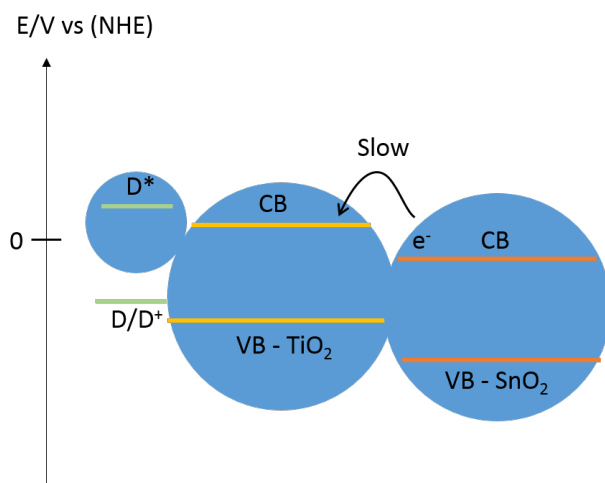


**Figure 2.7:** Schematic representation of photoinduced electron transfer and the recombination process.

The exact efficiency limiting effect is determined by the relative rate difference of the forward and the backwards electron transfer. Since the physics of backwards electron transfer is the same as electron transfer in the forward direction, Marcus theory can be applied in order to predict and minimize the rate of recombination. For instance, if electron transfer occurs in the normal region described by Marcus theory, using a semiconductor of lower conduction band energy level would likely decrease the rate of recombination. Thus the idea of combining two semiconductors to achieve a cascade electron transfer and utilizing a conduction band of low energy could theoretically have a positive effect. Nonetheless, electron transfer processes occurring in the Marcus inverted region have been observed [21] [22] [23]. In addition

any positive effect from using a semiconductor of lower energy will also have to be weighed against the disadvantage of eliminating certain catalysts for multiple electron transfer reactions.

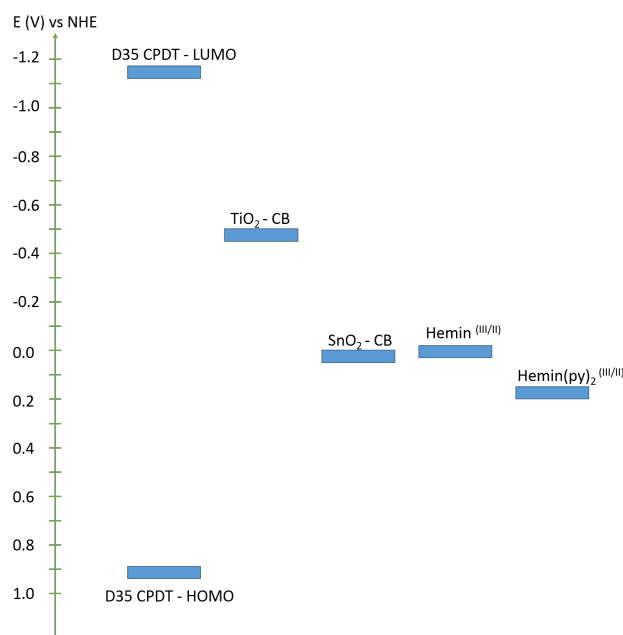
An altogether different approach of minimizing the electron recombination can be achieved by introducing a barrier for backwards electron transfer to induce a long lived charge separated state [20]. In a system with two semiconductors, this can be achieved by physically separating the dye from the semiconductor of lower energy level, see figure 2.8. Thus the electron recombination from the semiconductor of lower energy level must pass through the semiconductor of higher energy, which is thermodynamically not allowed.



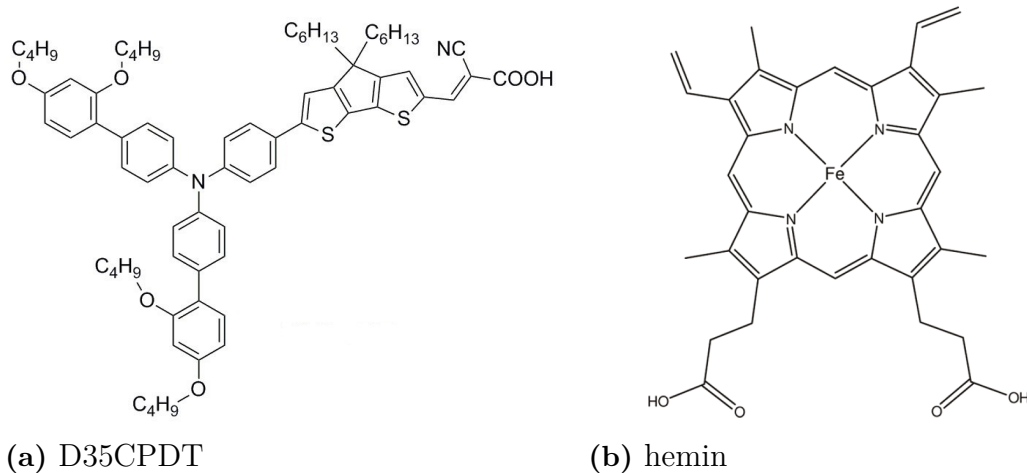
**Figure 2.8:** Schematic representation of a semiconductor system with a physical barrier to prevent electron recombination

## 2.8 System of study

With the main focus of this study being the effect on recombination for different semiconductor systems, the experimental system of study could be reduced to a simple assembly consisting of a dye, a semiconductor and an electron acceptor. For this project, an organic dye named D35CPDT was chosen, due to its known compatibility with the semiconductors in terms of chemical adhesion and energy levels, see figure 2.10a. The choice of electron acceptor was a somewhat more problematic choice for this study, as the relatively high reduction potential of SnO<sub>2</sub>, see figure 2.9 and requirement to adhere to both TiO<sub>2</sub> and SnO<sub>2</sub> excludes many electron acceptors. The electron acceptor Fe-PPIX, also more commonly known as hemin, see figure 2.10b, was ultimately chosen due to its success as an electron acceptor on TiO<sub>2</sub>, and a reduction potential close to SnO<sub>2</sub>, which could allow reduction of hemin on SnO<sub>2</sub> depending on environment. A contributing factor for selecting hemin, was also the possibility of coordinating pyridine to hemin to form hemin(py)<sub>2</sub> with a more positive reduction potential. This coordination would ensure at least one electron acceptor suited for SnO<sub>2</sub>, in addition to the possibility of studying electron recombination with two different electron acceptors.



**Figure 2.9:** Schematic representation of the energy levels for D35CPDT [24],  $\text{TiO}_2$  [20],  $\text{SnO}_2$  [20], hemin [25] and hemin( $\text{py}$ )<sub>2</sub> [26].



**Figure 2.10:** Molecular structure of the dye D35CPDT and hemin illustrated in a) and b) respectively.

### 2.8.1 $\text{TiO}_2$ semiconductors

$\text{TiO}_2$  exist naturally in three different crystalline phases, anatase, rutile and brookite, of which rutile is the most stable and anatase the most chemically active phase. Mesoporous  $\text{TiO}_2$  with an anatase structure has for over two decades yielded the highest efficiency in dye sensitized solar cell devices, and is still the most heavily used semiconductor for research and commercial applications.

### 2.8.2 Solvents and electrolytes

As part of the study of recombination on different semiconductor systems, the effect of solvents have been included as these may influence the energy levels of the solar assembly components and thus impact the efficiency. The solvents investigated are dimethyl sulfoxide (DMSO) and acetonitrile (MeCN), with and without addition of methanol. Methanol is a known electron hole scavenger [27], which theoretically may donate electrons to holes in the conduction band or to the ground state of the excited dye to inhibit recombination.

## 2.9 Measurement techniques

### 2.9.1 UV-vis Spectroscopy

The principles of UV-vis spectroscopy is based on the unique characteristic energy levels of different molecules, which allows absorption at different wavelengths. By using a continuous white light source, and using a prism or diffraction grating, the light can be divided into monochromatic wavelengths [28]. The monochromatic light can then be further divided into two separate beams, with one of them working as a reference. Then, by directing one beam through the sample, and measuring the intensity of this beam relative to the reference, information about the absorption can be gained. The exact absorbed amount can be calculated from Lambert Beer's Law, see equation 2.8 below.

$$A = \log(I/I_0) = \sum_i \epsilon(\lambda) l c_i \quad (2.8)$$

A is defined as the absorbance, and I and  $I_0$  as the intensity of sample and reference respectively. Epsilon,  $\epsilon$ , as the extinction coefficient, l as the optical path length, and c as the concentration of a specific unit.

One application of UV-vis spectroscopy is performing repeated measurements at different times in order to gain information about possible chemical reactions taking place. By plotting the spectra in the same graphs, the relative difference of the peak intensities can be observed and used to indicate if a chemical species have been consumed or produced. In addition, the presence of wavelengths with constant absorption over time (isosbestic point), may also provide information about the chemical reactions. A typical example of an isosbestic point is in a system where a reactant and a product have the same extinction coefficient,  $\epsilon(\lambda)$ , at that specific wavelength. The disappearance of an isosbestic point could then indicate that there no longer is only one reactant and product in the system. [29]

### 2.9.2 Steady state photolysis

Steady state photolysis is a technique combining an external light source with UV-vis spectroscopy. The addition of an external light source can be used to investigate a specimen's interaction with light, to either prevent or induce chemical reactions. [29]

### 2.9.3 Nanosecond-transient absorption spectroscopy

The idea of nanosecond transient absorption spectroscopy (TAS) is to study excited state decay or excited state reactions occurring on the micro to nanosecond timescale. This instrument is an important tool to study the electron recombination processes in photosynthetic systems, which typically occur on these timescales.

The principle of transient absorption spectroscopy is based on repeated light absorption measurements performed on a single sample, where a change in absorption corresponds to a changed electronic structure of a chemical species (Lambert Beer's law). Thus, by exposing the sample to a laser pulse and studying the induced absorption changes, information about photoinduced electron transfer processes can be obtained. [9]

The instrument functions by generating a pulsed laser light in an oscillator which pass through an optical parametric oscillator (OPO) to achieve the appropriate wavelength, see figure 2.12. The wavelength should be consistent with the energy required for ground state excitations of the molecule to be investigated. This beam is also called the pump beam. Perpendicular to this beam, a white light source is used to measure the absorbance of the sample, typically in the range of 400 - 1100 nm depending on the molecule investigated. The intensity of the beam can be measured by a charge coupled device (CCD) camera. From the measured intensity it is possible to calculate the differential absorption  $\Delta A$  from equation 2.9. The signal of the differential absorption can be either negative or positive depending on what energy transfer process occur, see figure 2.11. [9] [11]

The three most general processes include ground-state-bleaching, excited state absorption and product absorption, which are described in more detail below. For a quantitative analysis of the kinetics of energy transfer processes occurring in photosynthetic systems, like recombination, a photodiode can be used as a detector instead of a CCD camera. The output signal then, unlike the CCD camera, only show the decay of absorption over time at a specific wavelength, see figure 2.11. From this curve it is possible to extract the life time of electrons in the excited state, thereby enabling a quantitative estimate of the rate of recombination.[9] [11]

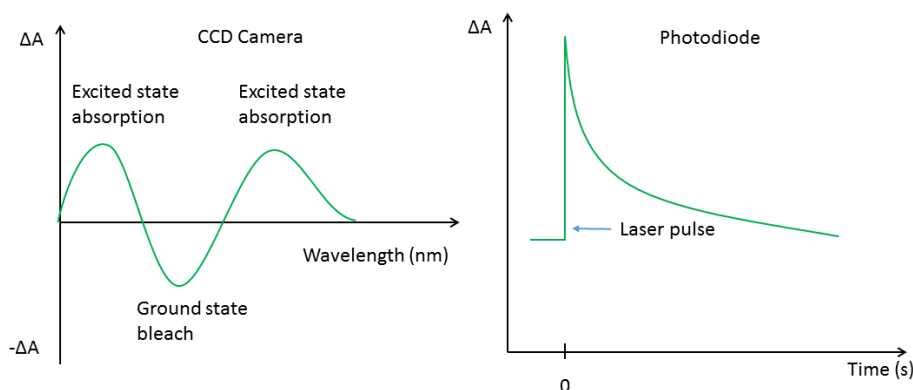
$$\Delta A = A_{\text{After pump beam}} - A_{\text{Before pump beam}} \quad (2.9)$$

#### 2.9.3.1 Ground-state bleach

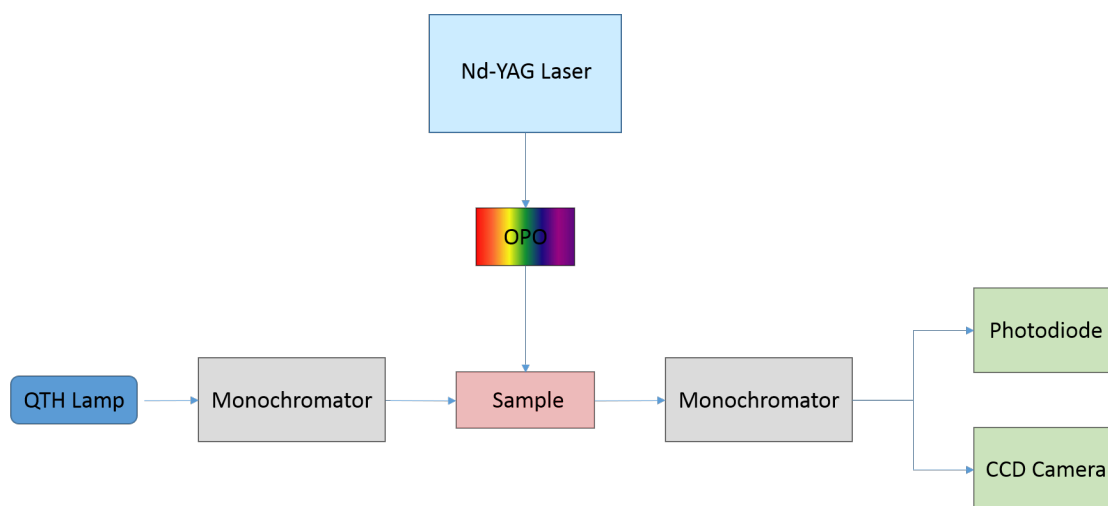
As some electrons excited with the pump beam remain in their excited state, the chances of exciting electrons from the ground state is statistically lower. This results in a negative  $\Delta A$  at the specific wavelength where ground state absorption is located. [11]

#### 2.9.3.2 Excited state absorption

After exciting electrons with the pump beam, there exists a chance of exciting those electrons even further to a higher electron state with the probe beam. The higher the level of the electron state, the closer the energy levels are spaced, and the more



**Figure 2.11:** A general result obtained by a CCD camera and photodiode respectively



**Figure 2.12:** Schematic illustration of nanosecond transient absorption spectroscopy.

likely an excitation is to occur. As more light is absorbed during the probe beam a positive  $\Delta A$  is observed.[11]

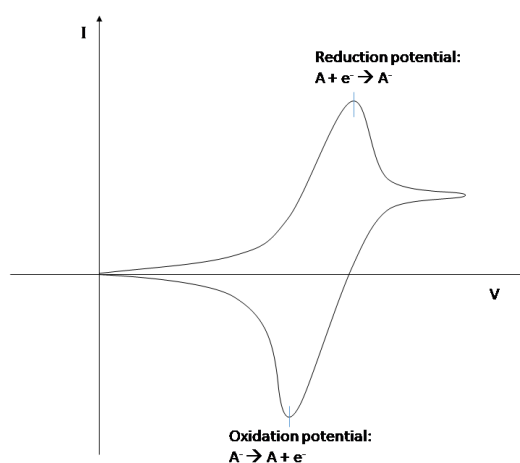
### 2.9.3.3 Product absorption

Upon excitation of electrons, reactions may occur resulting in a short lived transition state, or a longer lived molecular state. There are several examples of this process, like formation of a triplet state, isomerized state and of particular interest for photosynthetic systems, also charge separated states. With the formation of new molecular species, new ground state absorption peaks will be created with a positive

$\Delta A$  at those wavelengths. However as reactants are also consumed, the effect will be a negative  $\Delta A$  at the ground state absorption peak of the reactant.[11]

### 2.9.4 Cyclic voltammetry

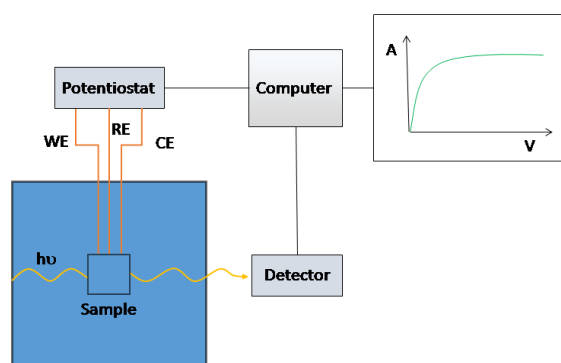
Cyclic voltammetry is commonly used to determine the formal potential of molecules, which by Nernst equation can be calculated to yield the redox potential. Typically a three electrode system is used in the measurements, consisting of a reference electrode, working electrode and counter electrode. By varying the potential of the working electrode and measuring the current flow between the working electrode and the counter electrode, a current-potential curve of a reversible redox reaction can be obtained. From this curve the oxidation and reduction potential can be extracted, see figure below. [14]



**Figure 2.13:** Illustrates a simple curve gained by cyclic voltammetry

### 2.9.5 Spectroelectrochemistry

Spectroelectrochemistry is the combination of electrochemistry with a spectroscopic instrument. By using electrochemistry to apply an electric field between the working electrode (sample) and the counter electrode, the chemical state of the sample can be controlled. By setting the potential of the applied field to the oxidation potential and waiting enough time, the sample will be in its oxidized form, which can be measured with a spectroscopic technique. In this master's thesis, the spectroscopic technique UV-vis spectroscopy was performed in order to obtain the oxidation and reduction potential of the dye and electron acceptors.[14]



**Figure 2.14:** Schematic illustration of spectroelectrochemistry.

### 2.9.6 Scanning electron microscopy

Scanning electron microscopy (SEM) is an instrument used to produce an image of a sample. Unlike a conventional microscope, SEM uses electrons instead of photons to provide information about the sample. An image of the sample is typically produced by either back scattered electrons (BSE) or secondary electrons (SE). Back scattered electrons are electrons elastically scattered from the sample which originate from the primary electron beam. Back scattered electrons help to provide topological contrast and information about chemical composition. The secondary electrons are created from inelastic scattering with the specimen, which cause loosely bound electrons to be ejected. As a result, these electrons have much lower energy and can thus only provide information from near the surface of the specimen. Secondary electrons contribute to some topological contrast and a particularly good focus of surface details like edges and corners.[30]

### 2.9.7 Energy dispersive X-ray spectroscopy

A common addition to SEM is the Energy dispersive X-ray spectroscopy (EDX). This technique provides elemental analysis, by collecting the characteristic X-rays generated by bombarding the sample with electrons.

# 3

## Methods

### 3.1 Chemicals

- Ferriprotoporphyrin IX chloride (hemin) (97% Sigma-Aldrich)
- Dimethyl sulfoxide (DMSO) (>99.9% Sigma-Aldrich)
- Acetonitrile (MeCN) (>99.9% Sigma-Aldrich)
- Ethanol (99,7%, Solveco)
- Methanol (MeOH) (>99% Sigma-Aldrich)
- Titanium dioxide paste (18NR-T, Dyesol)
- Tin(IV) oxide colloidal dispersion (15% in water, Alfa Aesar)
- Tin(IV) oxide colloidal (SN15CG, Nyacol)
- Pyridine (99,5% Sigma-Aldrich)
- Polyethylene glycol (PEG) (Mn=20 000, Sigma-Aldrich)
- Polyethylene glycol (PEG) (Mn=12 000, Alfa Aesar)
- Polyethylene oxide (PEO) (Mn=100 000, Alfa Aesar)
- Isopropanol (>99 % Sigma-Aldrich)
- RBS<sup>TM</sup> 25 solution concentrate (Sigma-Aldrich)
- Tetrabutylammonium hexafluorophosphate (TBAPF6) (98% Sigma-Aldrich)
- Dyenamo red (D35CPDT) (Dyenamo)

### 3.2 Equipment

- Ultra 55 FEG SEM
- Two different Varian Cary 50 Bio UV-vis spectrophotometer
- Xenon-lamp
- Continuum Surelite laser
- Surelite OPO
- QTH lamp
- 2 monochromators
- Photodiode detector
- Conductive glass (Solaronix TCO22-15)
- Non conductive glass (tedpella INC)
- Optical cover glass

### 3.3 Preparation of semiconductor pastes

The  $\text{TiO}_2$  paste was a commercially available paste ready to use without any modifications. The  $\text{SnO}_2$  paste was prepared by mixing 2 g of a colloidal dispersion of  $\text{SnO}_2$  nanoparticles and 0.15 g polyethylene glycol (20 000 g/mol). The mix was then stirred for one hour before adding 0.4 ml ethanol and stirring an additional 15 minutes. The mix was then left over night, after which it was stirred for 15 minutes and added 0.2 ml milli-q water. Due to difficulties with the  $\text{SnO}_2$  paste to adhere homogeneously to the glass substrate after sensitizing with a dye or electron acceptor, several methods to create a new  $\text{SnO}_2$  paste were also tried. However, due to time constraints, no successful paste could be synthesized and the original  $\text{SnO}_2$  paste described above had to be used for all experiments. The failed attempts of synthesis of  $\text{SnO}_2$  have been included briefly below.

#### 3.3.1 Failed synthesis of $\text{SnO}_2$ paste

A hydrothermal method was adapted from [31], but modified to work with our pressure vessel. First, 1 ml acetic acid was added to 30 ml 15 wt%  $\text{SnO}_2$  colloidal dispersion. Upon adding the acetic acid, the solution turned translucent. The solution was then stirred over night and transferred to the pressure vessel with a teflon lining and put in an oil bath of silicone oil at 200 °C for circa 72 hours. The solution was then allowed to cool, and ultrasonicated for 5 min before approximately 2,5 wt% polyethylene oxide (PEO) (100 000 g/mol) and polyethylene glycole (PEG) (12 000 g/mol) were added. The paste was stirred over night and stepwise added small amounts of polymers to reach a sufficiently high viscosity (approximately 5 wt%).

A second method based on synthesis of 20 nm  $\text{SnO}_2$  nanoparticles without heat treatment was also attempted [32]. This method basically consisted of mixing a 15 wt%  $\text{SnO}_2$  colloidal dispersion of  $\text{SnO}_2$  with acetic acid with a volume ratio of 37 to 1 and adding PEG (20 000 g/mol) to attain the necessary viscosity.

#### 3.3.2 Mixed semiconductor films

The mixed semiconductor films were created by mixing 0.513 g  $\text{TiO}_2$  paste with 0.092 g  $\text{SnO}_2$  paste and a few drops isopropanol. The mixed paste was then ultrasonicated for 30 min, stirred at 5 min and ultrasonicated an additional 30 min before applied onto glass by the process described in the section below.

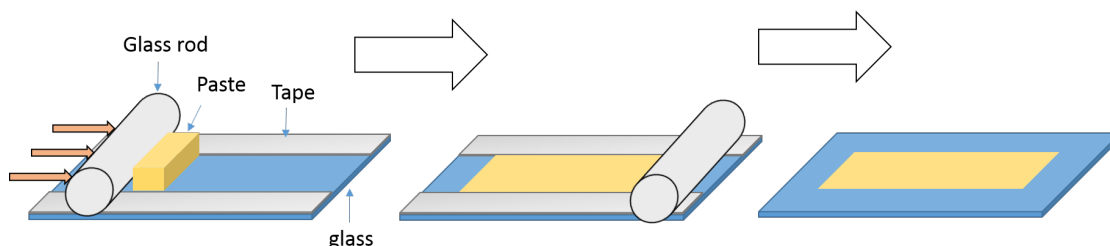
### 3.4 Preparation of semiconductor films

Thin films of  $\text{TiO}_2$ ,  $\text{SnO}_2$  and  $\text{TiO}_2/\text{SnO}_2$  were prepared on either a conductive or non-conductive optically transparent glass depending on the experiment. Conductive FTO glass was used for spectroelectrochemistry, CV and SEM, whereas for UV-vis spectroscopy, photolysis, and TAS a cheaper non conductive glass was sufficient. The semiconductor pastes were applied to the glass by doctor-blading, see figure 3.1. Basically the paste was pressed out on the optically transparent glass

**Table 3.1:** Time and temperature program in oven for  $\text{TiO}_2$ ,  $\text{SnO}_2$  and  $\text{TiO}_2/\text{SnO}_2$  semiconductor films.

| Temp ( $^{\circ}\text{C}$ ) | Duration |
|-----------------------------|----------|
| 150                         | 10 min   |
| 200                         | 10 min   |
| 250                         | 15 min   |
| 300                         | 15 min   |
| 350                         | 15 min   |
| 400                         | 15 min   |
| 450                         | 30 min   |

by a glass rod, elevated by the thickness of scotch tape ( $\approx 6\ \mu\text{m}$ ) placed on both sides of the film. The films were then heated on a hotplate at  $125^{\circ}\text{C}$  for 10 min and sintered in an oven using the temperature program in table 3.1. Pre-heating on the hot plate was performed in order to let the paste dry off some solvent, and to adhere better to the surface. Typically the samples were left in the oven over night after a completed temperature program to allow for a slow cool down.



**Figure 3.1:** Schematic illustration of the doctor-blading technique.

In order to adhere the dye and the electron acceptor to the films, solutions were used to dip the films in for a set amount of time or until a specific absorption was reached. The concentrations of the solutions used were 0.3 mM D35CPDT in EtOH and 0.3mM hemin in DMSO. For the electron acceptor hemin(py)<sub>2</sub>, the semiconductor film was first dipped into the hemin solution, and then dipped into pure pyridine for 30 min to achieve coordination [33].

## 3.5 Experimental procedure

### 3.5.1 Transient absorption spectroscopy

Transient absorption spectroscopy measurements were performed with a semiconductor film together with a solvent and 0.1 M TBAPF<sub>6</sub> as electrolyte. The solvent was purged with argon gas for 30 minutes to remove oxygen, before wetted against the semiconductor film with an optical cover glass. In general, three samples were measured on all experimental systems, unless otherwise noted.

#### 3.5.2 Steady state photolysis

All measurements with steady state photolysis were performed in a cuvette with a solvent, either acetonitrile or DMSO. In addition to the solvent, a few drops of methanol was added as an electron hole scavenger, and also 0.1 M TBAPF<sub>6</sub> as electrolyte. Prior to measurements, the cuvettes were sealed with parafilm and purged with argon gas for 30 minutes, to remove any oxygen. In order to avoid heating the sample unnecessarily, the xenon lamp was used with a water filter and a U-340 filter, which was set to allow wavelengths corresponding to energies of band gap excitation for TiO<sub>2</sub> and SnO<sub>2</sub> (260-400 nm).

#### 3.5.3 Spectroelectrochemistry and cyclic voltammetry

The spectroelectrochemistry and cyclic voltammetry experiments were performed with films on conductive FTO glass. Similar to the preparation for the steady state photolysis experiments, the samples were put in a cuvette with DMSO or acetonitrile and 0.1 M TBAPF<sub>6</sub> as working electrolyte. The samples were also sealed with parafilm, and purged with argon gas for 30 minutes to remove any oxygen in the cuvette. The electrodes used for the measurements were a Ag/Ag<sup>+</sup> reference electrode and a glassy carbon as counter electrode.

#### 3.5.4 UV-vis spectroscopy

The UV-vis spectroscopy measurements were always performed with a solvent purged with argon gas for a minimum of 15 minutes.

#### 3.5.5 Data analysis

##### 3.5.5.1 Excited state decay fitting

The electron recombination was investigated by the decay signal on a wavelength corresponding to the oxidized dye. This was done as the pump beam was tuned to excite dye molecules, which cause photoinduced electron transfer and formation of oxidized dye molecules that through recombination revert to their neutral state. In this thesis, the decay of the oxidized dye molecules was modeled with a biexponential function, as electron transfer in theory is described by an exponential process (see equation 2.7). Furthermore, as the system was not a homogenous solution or a perfect monolayer, different recombination rates may occur within the sample making two exponential functions necessary in the fitting. All the fitting of the transient absorption spectroscopy results were performed with OriginPro 2015 with equation 3.1.

$$I(t) = I_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (3.1)$$

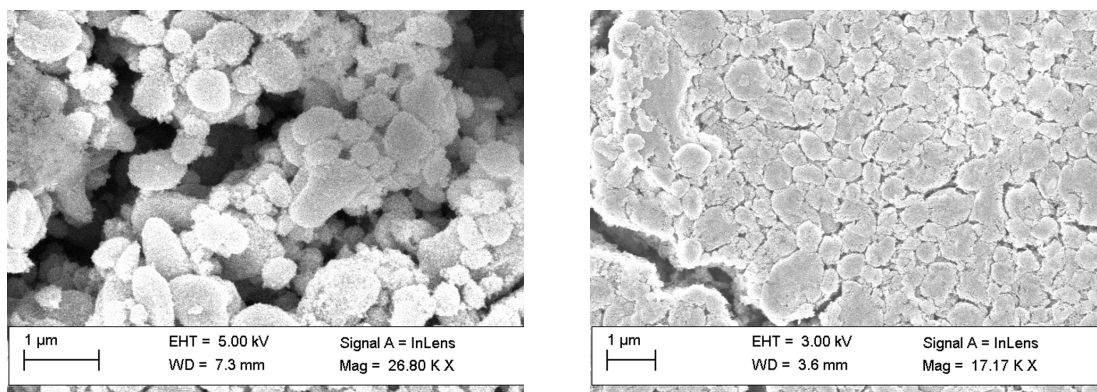
The above function models the intensity (I) as a function of time (t), where A<sub>i</sub> is the intensity of the exponential decay function and τ<sub>i</sub> a constant describing the decay.

# 4

## Results

### 4.1 Materials Characterization

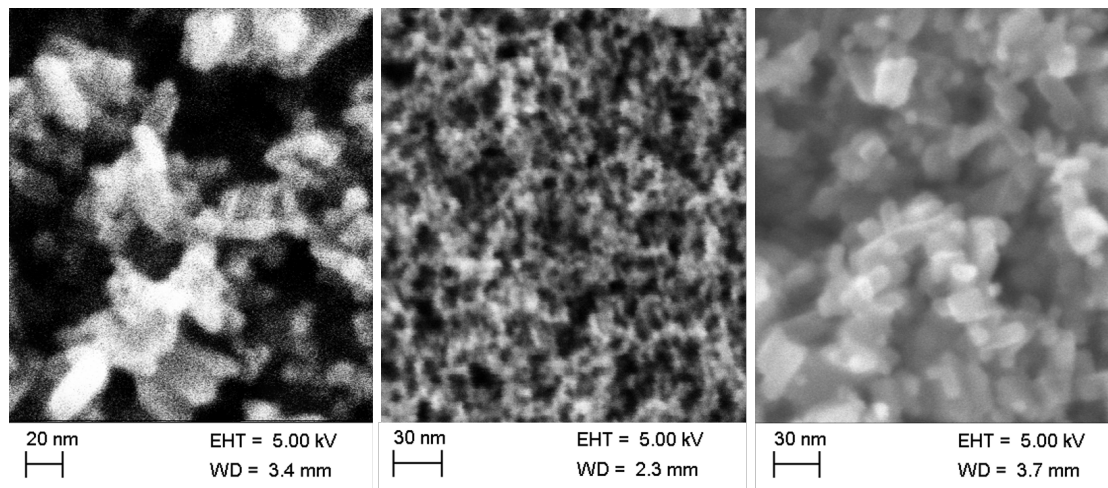
The characterization of the nanoparticle size and size distribution of semiconductor films were performed with SEM and can be observed below in figure 4.1 and 4.2. The failed synthesis methods of  $\text{SnO}_2$  semiconductor films can be seen in figure 4.1, where the size of the nanoparticles can be estimated to be in the range of hundreds of nanometers to micrometer size for both the hydrothermal method and the other method based on mixing. The SEM images of the  $\text{TiO}_2$ ,  $\text{SnO}_2$  and mixed  $\text{TiO}_2/\text{SnO}_2$  which were actually used for experiments are displayed in figure 4.2. The nanoparticles for these semiconductor films all have a good narrow size distribution, with estimated average nanoparticle size in the range of 10-30 nm, with a relatively similar roundish shape. In addition, EDX was performed on the mixed semiconductor film to estimate the amount of  $\text{TiO}_2$  and  $\text{SnO}_2$ . The atomic % are summarized in table 4.1 below.



**Figure 4.1:** SEM images produced with secondary electrons of semiconductor films made from  $\text{SnO}_2$  paste created by the hydrothermal method, and the method based on mixing, depicted from left to right respectively. The size of the nanoparticles can be estimated in the range hundreds of nanometers to micrometers.

#### 4.1.1 Spectroscopic and electrochemical properties of Hemin

The reduction potential of hemin on  $\text{TiO}_2$  was initially investigated on a  $\text{TiO}_2$  film in a DMSO solvent with 0.1 M  $\text{TBAPF}_6$  as electrolyte. However, due to complica-



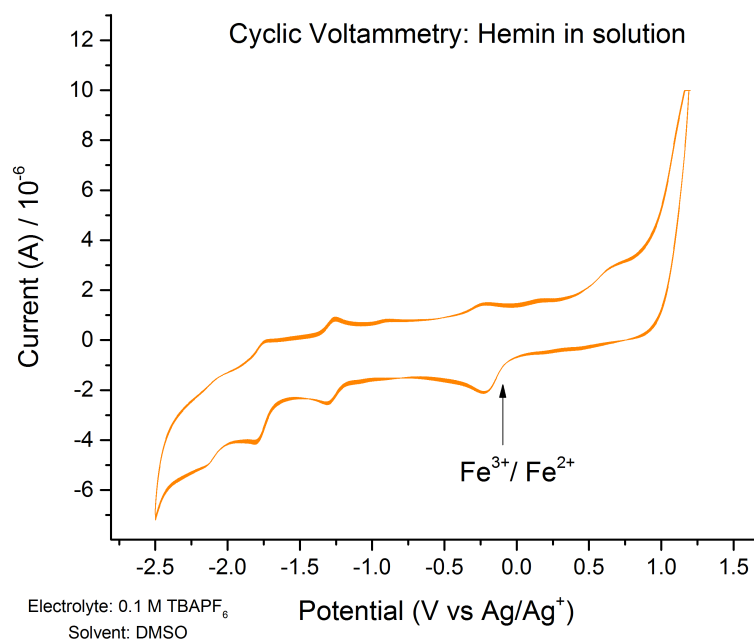
**Figure 4.2:** SEM images produced with secondary electrons of  $\text{TiO}_2$ ,  $\text{SnO}_2$  and mixed  $\text{TiO}_2/\text{SnO}_2$  semiconductor films depicted from left to right respectively. The sizes of the nanoparticles are all estimated in the range of 10-30 nm.

**Table 4.1:** Summary of elemental analysis performed with EDX at three different points. The results are reported in atomic %.

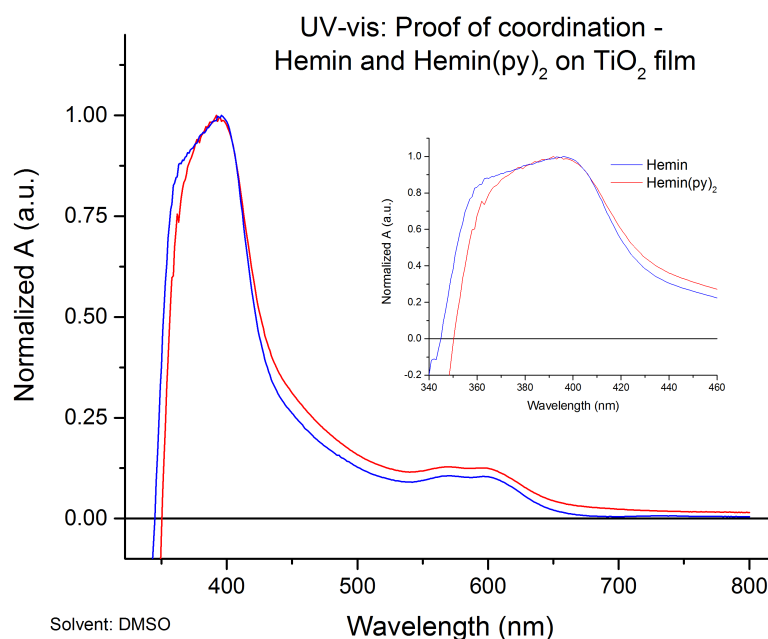
|            | O       | Ti      | Sn     |
|------------|---------|---------|--------|
| Spectrum 1 | 69.71 % | 27.67 % | 2.62 % |
| Spectrum 2 | 71.07 % | 26.55 % | 2.38 % |
| Spectrum 3 | 70.48 % | 27.00 % | 2.52 % |

tions with measuring the reduction potential of hemin on  $\text{TiO}_2$ , no clear reduction peak could be deduced and cyclic voltammetry measurements were performed in solution instead. The cyclic voltammetry measurement of hemin in DMSO and 0.1M  $\text{TBAPF}_6$  seen in figure 4.3 is a previously unpublished result performed by my supervisor Valeria Saavedra.

The formation of  $\text{hemin}(\text{py})_2$  from hemin and pyridine was analyzed using UV-vis spectroscopy in a solution of DMSO with 0.1M  $\text{TBAPF}_6$  as electrolyte. The small red shift in absorption for hemin treated with pyridine seen in figure 4.4 is an indication of formation of  $\text{hemin}(\text{py})_2$  [25].



**Figure 4.3:** Cyclic voltammetry experiment performed on hemin in a solution of 0.1M TBAPF<sub>2</sub> and DMSO, purged with argon gas. CE = platina, RE = Ag/Ag<sup>+</sup>. The reduction potential of Fe<sup>3+</sup> / Fe<sup>2+</sup> was estimated to -0.2 V vs Ag/Ag<sup>+</sup>.

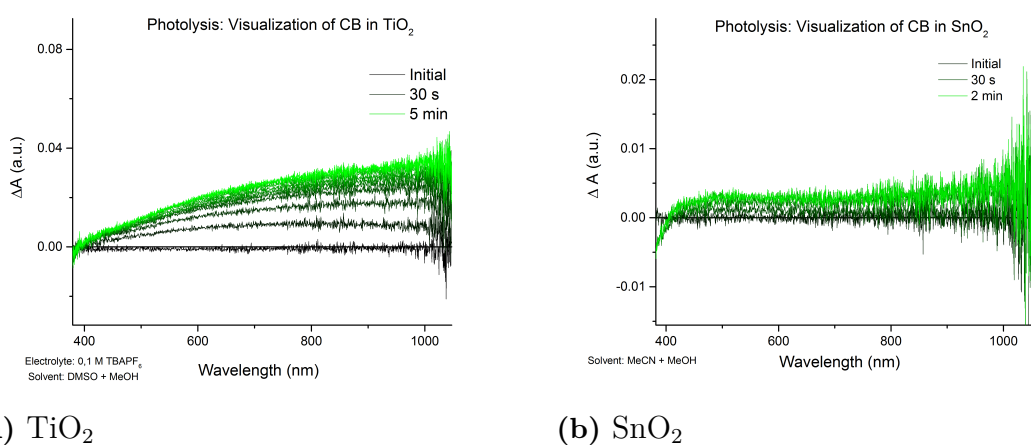


**Figure 4.4:** UV-vis spectroscopy measurement performed on hemin and hemin treated with pyridine in DMSO. A small redshift in absorbance for hemin treated with pyridine can be observed, which indicates a coordination of pyridine to hemin.

## 4.2 Conduction band mediated electron transfer

### 4.2.1 Photo induced band gap excitation in semiconductors

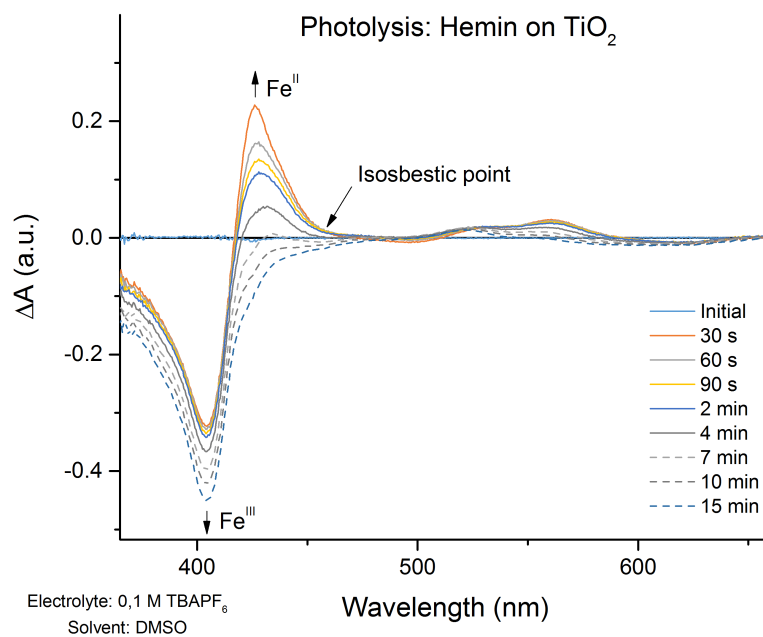
To make sure the photolysis instrument is capable of photoinduced band gap excitation in both  $\text{TiO}_2$  and  $\text{SnO}_2$ , photolysis experiments were performed on the semiconductors to visualize absorption from the conduction band. The broad, monotonically increasing absorption seen between 400-1100 nm in figure 4.5a and 4.5b is consistent with an increasing amount of electrons promoted to the conduction band [15].



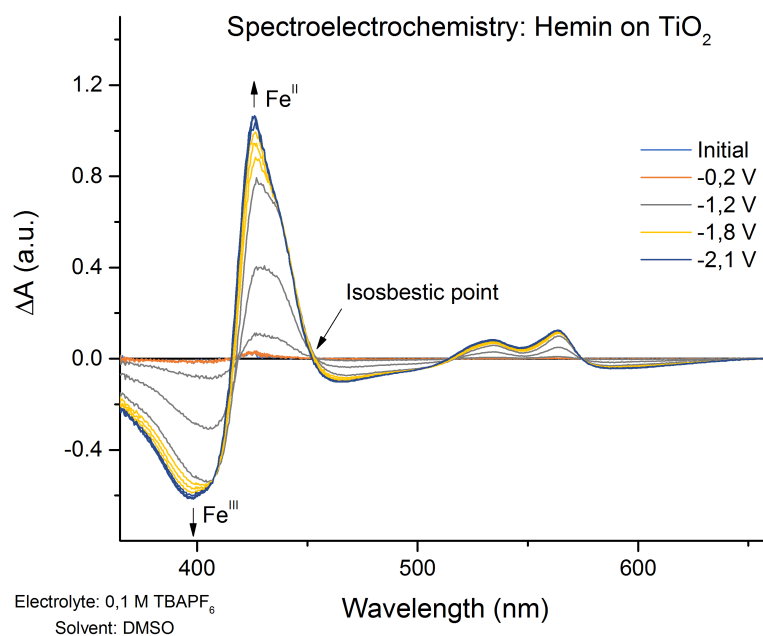
**Figure 4.5:** Photolysis experiment of  $\text{TiO}_2$  and  $\text{SnO}_2$  displaying broad absorption from the conduction band between 400 and 1100 nm.

### 4.2.2 Conduction band mediated transfer between semiconductor and electron acceptor

A second step towards a proof of principle for conduction band mediated electron transfer is to induce band gap excitation in the semiconductor coupled to a reduction of an electron acceptor. This experiment has been performed with two different methods for band gap excitation; electric field and photo-excitation, using spectroelectrochemistry and steady state photolysis respectively. The photolysis experiment and spectroelectrochemistry results for hemin on  $\text{TiO}_2$  is displayed in figure 4.6 and 4.7. In these figures, a close resemblance of the two peaks located at approximately 403 and 425 nm can be seen between the two experiments. In the photolysis experiment however the peak at approximately 425 nm initially increases rapidly, but starts a decrease after 30 seconds, unlike in the spectroelectrochemistry experiment where the corresponding peak increase monotonically throughout the experiment (6 minutes). Furthermore, the isosbestic point located at 450 nm only remains in the spectroelectrochemistry experiment, whereas in the photolysis experiment the isosbestic point disappears in less than 2 minutes.

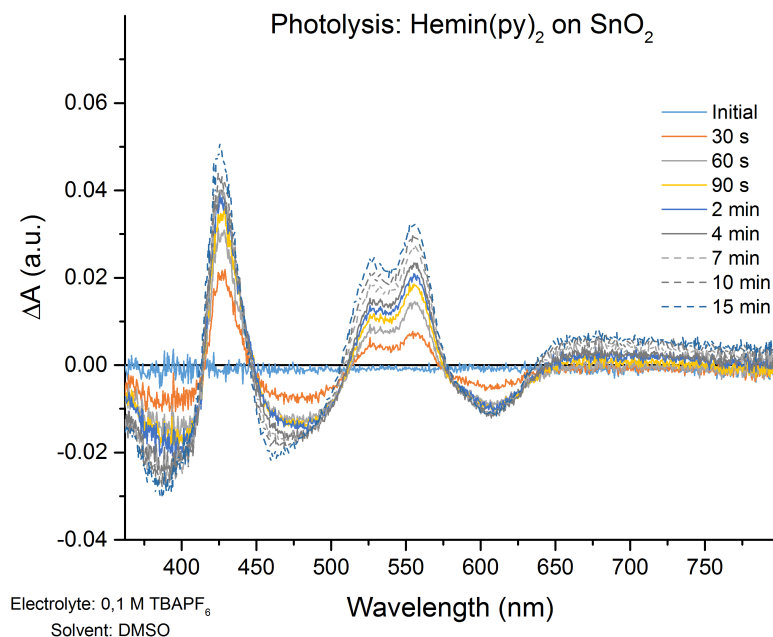


**Figure 4.6:** Photolysis measurement depicting photo-induced reduction of hemin on  $\text{TiO}_2$ .



**Figure 4.7:** Spectroelectrochemistry measurement depicting reduction peaks of hemin on  $\text{TiO}_2$  induced by stepwise increase in electric field potential (V).

The same experiments were also performed on the  $\text{SnO}_2$  semiconductor with  $\text{hemin}(\text{py})_2$  as electron acceptor. The peaks located at 385 nm and 425 nm in the photolysis experiment (figure 4.8) are also observed in the spectroelectrochemistry experiment (figure 4.9) at approximately the same wavelengths. These peaks are also corresponding well with the two peaks observed in the experiments with hemin on  $\text{TiO}_2$ . The peak located at approximately 385 nm shows a monotonic decrease, and the peak at 425 nm a monotonic increase in both the photolysis and spectroelectrochemistry experiment. In addition, the isosbestic point also remain throughout the entire duration of the experiments.

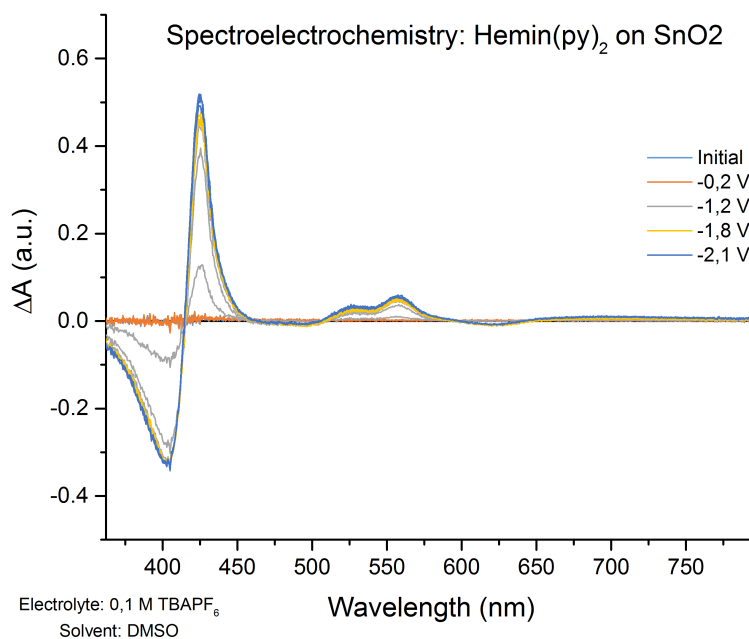


**Figure 4.8:** Photolysis measurement depicting photo-induced reduction of  $\text{hemin}(\text{py})_2$  on  $\text{SnO}_2$ .

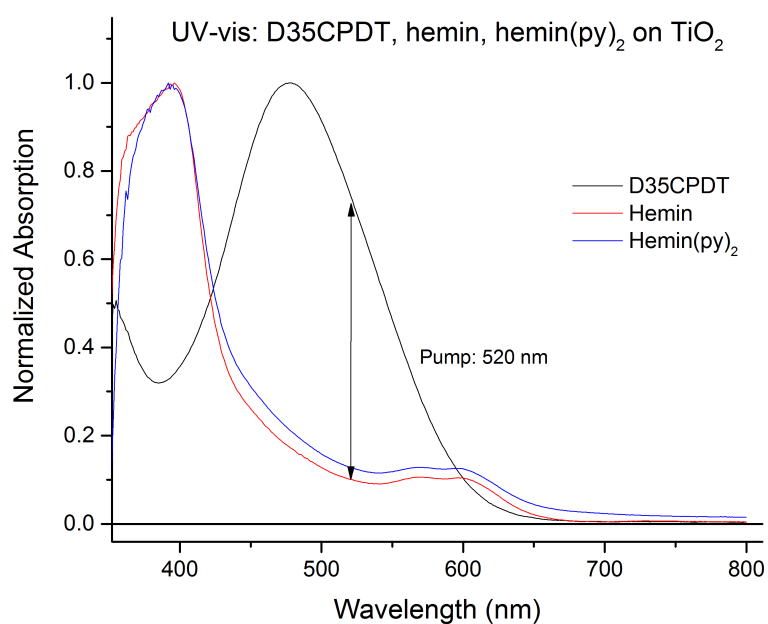
## 4.3 Recombination study of semiconductor systems

### 4.3.1 Excitation wavelength

The pump wavelength was selected with an approximate optimal ratio of the dye absorption to the other components i.e. the electron acceptor. This was achieved by performing UV-vis spectra on D35CPDT and hemin on  $\text{TiO}_2$  and selecting the highest absorption of D35CPDT to the lowest absorption of hemin, see figure 4.10. The same experiment with the  $\text{SnO}_2$  films was however not performed, as the effect of using a different semiconductor film likely only induce very small shifts in the absorption spectra.



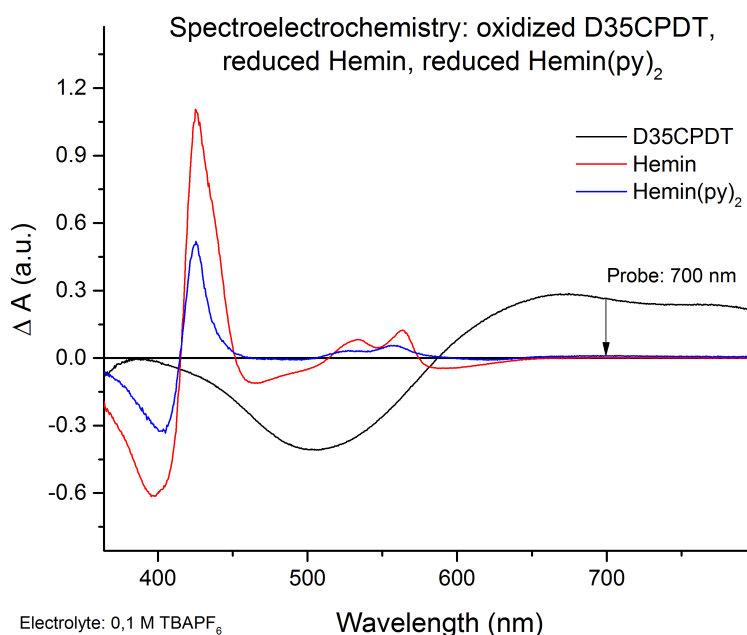
**Figure 4.9:** Spectroelectrochemistry measurement depicting reduction peaks of hemin(py)<sub>2</sub> on SnO<sub>2</sub> induced by a stepwise increase in electric field potential (V).



**Figure 4.10:** UV-vis spectra of D35CPDT, hemin and hemin(py)<sub>2</sub> on TiO<sub>2</sub>. The selected pump wavelength is indicated in the spectra by the black arrow at 520 nm.

### 4.3.2 Probe wavelength

The probe wavelength was selected to achieve minimal overlap between the dye and the electron acceptor in order to avoid absorption not coupled to the recombination process. This was possible by performing and comparing the UV-vis spectra of the dye in its oxidized state and the electron acceptors in their reduced state. Due to time restraints, the measurements could not be performed on the same semiconductor and solvent. The UV-vis spectrum of the oxidized D35CPDT was achieved on  $\text{TiO}_2$  in acetonitrile, the reduced hemin on  $\text{TiO}_2$  in DMSO, and the reduced hemin( $\text{py}$ )<sub>2</sub> on  $\text{SnO}_2$  in DMSO. The results of these spectra can be seen in figure 4.11.



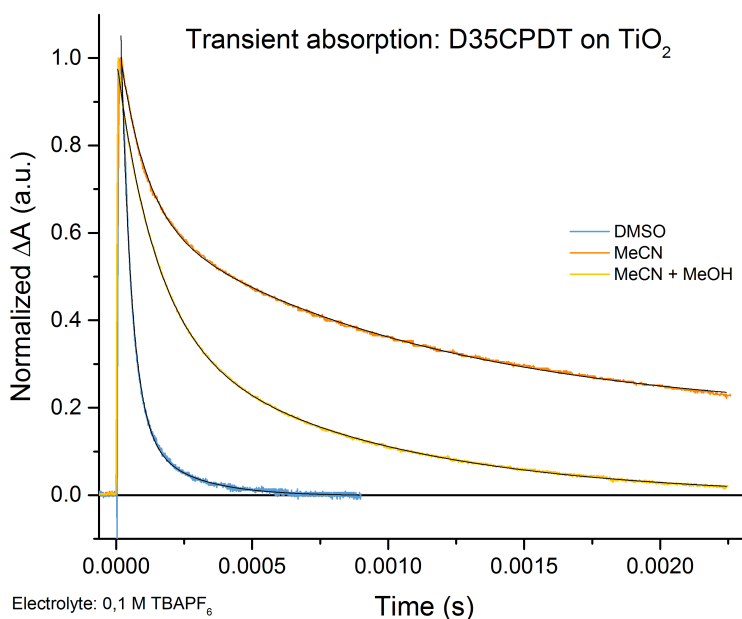
**Figure 4.11:** UV-vis spectra of the oxidized dye D35CPDT, and the reduced electron acceptors hemin and hemin( $\text{py}$ )<sub>2</sub>. The chosen probe wavelength is indicated by a black arrow at 700 nm.

### 4.3.3 Quantification of photoinduced electron transfer rate using transient absorption spectroscopy

#### 4.3.3.1 The effect of solvents on electron recombination

Transient absorption spectroscopy measurements were performed with different solvents including both acetonitrile and DMSO, with and without addition of methanol. The results performed with D35CPDT on  $\text{TiO}_2$  is displayed in figure 4.12. The slowest decay of the oxidized dye or rate of recombination, was observed for acetonitrile without methanol, followed by acetonitrile with methanol, and lastly DMSO with a significantly faster rate of recombination than both other solvents. The result

for DMSO with methanol however was not included in figure 4.12 as it displayed a negative absorption which could not be explained. As a consequence the transient absorption measurements with different semiconductor systems were performed in acetonitrile with methanol, to avoid an unknown process occurring in the sample.

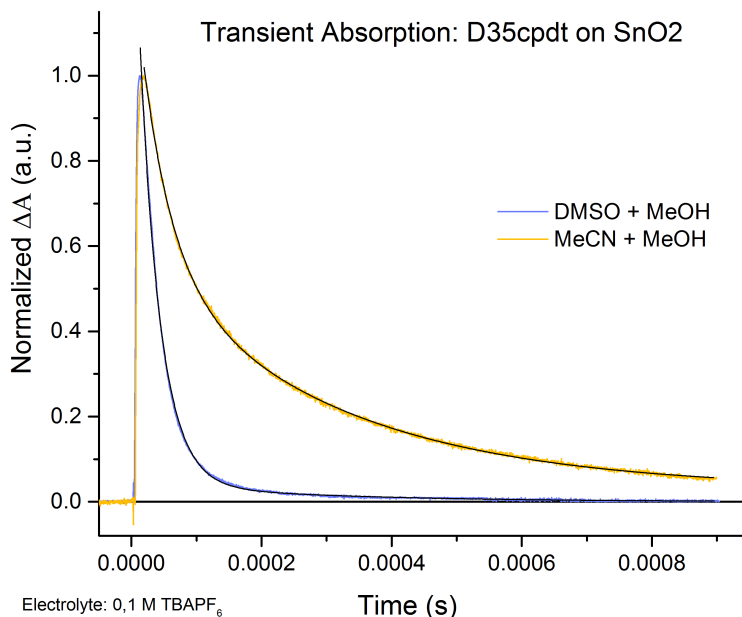


**Figure 4.12:** Transient absorption measurements of D35CPDT on  $\text{TiO}_2$  films in acetonitrile and DMSO with and without methanol.

The solvent's effect on the rate of recombination was also investigated on the  $\text{SnO}_2$  semiconductor with DMSO and acetonitrile with methanol. The rate of recombination displayed in figure 4.13 for DMSO with methanol was significantly faster than the recombination rate for acetonitrile with methanol. In addition, the rate of recombination compared between  $\text{TiO}_2$  and  $\text{SnO}_2$  in figure 4.12 and 4.13 is much faster for  $\text{SnO}_2$ .

#### 4.3.3.2 The effect of semiconductor systems on electron recombination

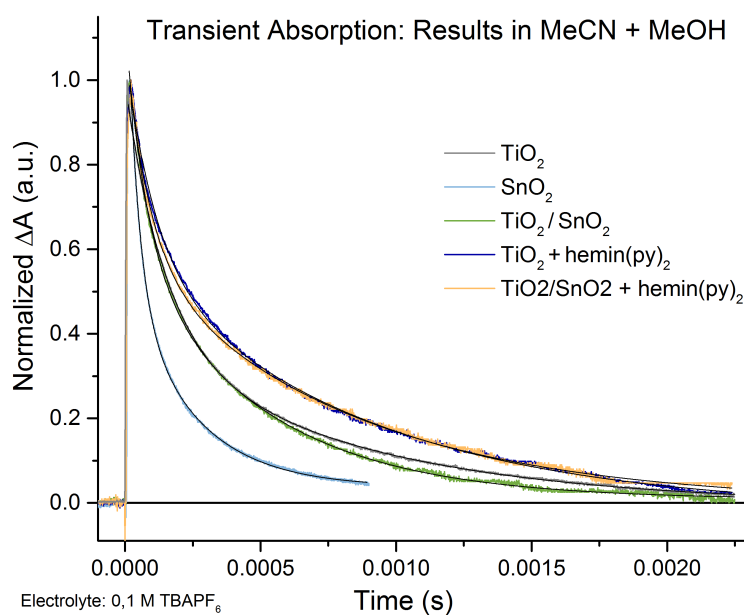
Different semiconductor systems were investigated with transient absorption spectroscopy in acetonitrile with methanol. The results are displayed in figure 4.14 below. The slowest decay, is observed for the  $\text{SnO}_2$  semiconductor, followed by the mixed  $\text{TiO}_2/\text{SnO}_2$  and  $\text{TiO}_2$ . In addition the semiconductors with  $\text{hemin}(\text{py})_2$  adhered to the surface, show a slower recombination than all other systems. The rate constants obtained from fitting all the transient absorption measurements are summarized in table 4.2.



**Figure 4.13:** Transient absorption measurements of D35CPDT on SnO<sub>2</sub> films in DMSO and acetonitrile with methanol added to both solutions.

**Table 4.2:** Table of rate constants obtained from curve fitting with a biexponential function. The parameters A1 and A2 have for convenience been converted into % to easier describe the amount of recombination occurring with each individual recombination processes.

| Sample                                                                | Solvent   | A1 (%) | A2 (%) | K1 (10 <sup>-4</sup> ) | K2 (10 <sup>-4</sup> ) | Ktot (10 <sup>-4</sup> ) |
|-----------------------------------------------------------------------|-----------|--------|--------|------------------------|------------------------|--------------------------|
| D35CPDT - TiO <sub>2</sub>                                            | DMSO      | 87     | 13     | 2.3                    | 0.5                    | 3.0                      |
| D35CPDT - TiO <sub>2</sub>                                            | DMSO/MeOH | 83     | 17     | 3.2                    | 1.4                    | 5.7                      |
| D35CPDT - SnO <sub>2</sub>                                            | DMSO/MeOH | 96     | 4      | 3.6                    | 0.5                    | 5.7                      |
| D35CPDT - TiO <sub>2</sub>                                            | MeCN      | 50     | 50     | 1.2                    | 0.1                    | 0.6                      |
| D35CPDT - TiO <sub>2</sub>                                            | MeCN/MeOH | 60     | 40     | 0.8                    | 0.1                    | 0.6                      |
| D35CPDT - SnO <sub>2</sub>                                            | MeCN/MeOH | 60     | 40     | 2.3                    | 0.4                    | 2.0                      |
| D35CPDT - TiO <sub>2</sub> /SnO <sub>2</sub>                          | MeCN/MeOH | 49     | 51     | 1.4                    | 0.2                    | 0.9                      |
| D35CPDT - TiO <sub>2</sub> - Hemin(py) <sub>2</sub>                   | MeCN/MeOH | 54     | 46     | 1.0                    | 0.1                    | 0.6                      |
| D35CPDT - TiO <sub>2</sub> /SnO <sub>2</sub> - Hemin(py) <sub>2</sub> | MeCN/MeOH | 46     | 54     | 0.8                    | 0.1                    | 0.6                      |



**Figure 4.14:** Transient absorption measurements of D35CPDT on different semiconductor systems with and without an electron acceptor. The slightly stepwise decay observed for the green and orange curve, is an artifact attributed to poor settings of the oscilloscope.



# 5

## Discussion

### 5.1 Conduction band mediated electron transfer

The photolysis experiment on  $\text{TiO}_2$  and  $\text{SnO}_2$ , seen in figure 4.5a and 4.5b, display a broad absorption from 400 - 1100 nm which is consistent with electrons being promoted from the valence band to the conduction band[15]. This photolysis experiment, thus proves that band gap excitations can occur with the xenon lamp, and the filters (transmittance between 260-400 nm).

The conduction band mediated electron transfer was investigated using photolysis and spectroelectrochemistry as two complementary methods to each other. In figure 4.6 the photolysis experiment of hemin on  $\text{TiO}_2$  show clear peaks at 403 and 425 nm, which are consistent with literature data of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  respectively [26]. A similar spectrum is also obtained for spectroelectrochemistry, see figure 4.7, in which the  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  are located at approximately the same wavelengths. However, one significant difference between the two methods is the disappearance of the isosbestic point at 450 nm after approximately 2 minutes in the photolysis experiment. This is contrary to the spectroelectrochemistry experiment where the isosbestic point remain through the entire duration of the experiment (6 minutes). The disappearance of the isosbestic point in combination with a decrease in  $\text{Fe}^{2+}$  observed in the photolysis experiment suggests a formation of  $\text{Fe}^+$ . The explanation as to why this only occurs in the photolysis experiment is unclear, however the process by which the reduction of hemin occur is fundamentally different for the photolysis and spectroelectrochemistry experiments. In photolysis, no external electrons are supplied and the reduction can thus only occur by electrons supplied from the conduction band of the semiconductor. The spectroelectrochemistry method however, uses a counter electrode to supply and transport the electrons through an external current to the working electrode which generates an excess of electrons in the sample.

Although spectroelectrochemistry is a complementary method to photolysis as it promote electrons in the conduction band differently, the results gained from analyzing porous semiconductor films may be difficult to interpret. According to some literature [34], the porous semiconductor could allow molecules to diffuse through the porous semiconductor film, and accept electrons directly from the working electrode without necessarily utilizing the conduction band in the semiconductor. However, as the absorption peak for  $\text{Fe}^{2+}$  in the photolysis experiment, is consistent with both literature, and spectroelectrochemistry and significantly larger than the auto reduction performed on of hemin under dark conditions (see figure A.1), there is strong indication of an induced conduction band mediated electron transfer process

for hemin on  $\text{TiO}_2$ .

In figure 4.8 and 4.9, the photolysis and spectroelectrochemistry results for hemin(py)<sub>2</sub> and  $\text{SnO}_2$  can be observed. There is a close resemblance between these results and the results of hemin on  $\text{TiO}_2$ . This is not too surprising as the coordination of pyridine to hemin and a slightly different semiconductor should theoretically only induce a small shift in absorption wavelength due to a changed electronegativity [35]. It is therefore relatively easy to identify the absorption peaks for  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  which can be approximated to 385 nm and 425 nm respectively for the photolysis spectra. With a monotonically increasing absorption peak of  $\text{Fe}^{2+}$  in both photolysis and spectroelectrochemistry, and no disappearing isosbestic points, formation of  $\text{Fe}^+$  seems unlikely. With the same argument as previously, the reduction peaks corresponding well with both methods and literature seems to indicate a conduction band mediated electron transfer process.

## 5.2 The effect of solvents on recombination

As a small part of this thesis, the effect of solvents on the electron recombination was investigated. The results observed in figure 4.12, display a clear difference in recombination rate for the different solvents. In DMSO the rate of recombination is significantly faster than acetonitrile, which is observed both with and without addition of methanol on  $\text{TiO}_2$  and  $\text{SnO}_2$  (see figure 4.13). Another interesting observation of the study of solvents, is the effect of methanol, which was initially added due to its known ability to donate electrons (hole scavenger). Methanol was theorized to decrease the rate of recombination, as the donated electrons fill up the holes in the system and thereby making recombination difficult. However, the effect of adding methanol, displays the opposite behaviour and recombination occur faster. Without investigating the mechanism for recombination, it is difficult to draw any conclusions as to why this occurs.

## 5.3 The effect of semiconductor assemblies on recombination

Due to the strong effect on electron recombination by using different solvents, the semiconductor assemblies have been evaluated in the same solvent. In the measurements performed in the solvent acetonitrile with methanol, see figure 4.14 and table 4.2, several interesting observations can be made. Firstly, the  $\text{SnO}_2$  recombination is observed to be faster than for  $\text{TiO}_2$ , despite its lower thermodynamical driving force. This behaviour is also supported in literature [36] and could potentially be explained by a relatively lower electron injection efficiency, and faster electron mobility [37]. It is however, worth mentioning that a high electron mobility may only have a negative impact on the recombination rate in a system lacking an electron acceptor, as once electrons transferred to the electron acceptor cannot easily recombine.

Another interesting observation is the rate of recombination for the mixed  $\text{TiO}_2/\text{SnO}_2$

semiconductor system, which is slower than  $\text{SnO}_2$  and similar to or possibly faster than  $\text{TiO}_2$ . By using the EDX results in table 4.1, the composition of the semiconductor film, can be estimated to approximately 90 atomic%  $\text{TiO}_2$  and 10 atomic%  $\text{SnO}_2$ . The close correlation between the concentration of  $\text{TiO}_2$  and the electron recombination rate observed in figure 4.14, seems to suggest a very small or negligible contribution of using  $\text{TiO}_2$  in combination with  $\text{SnO}_2$  for this system and concentration. It should be stressed however, that since no experiments have been performed with different concentrations, no general conclusions concerning the effect of mixing  $\text{TiO}_2$  and  $\text{SnO}_2$  can be made. One explanation for the measurement could be that electrons are not efficiently transferred between the  $\text{TiO}_2$  and  $\text{SnO}_2$ , thus forming an average of two independent recombination processes. This explanation, however seems unlikely as the recombination occurs over a relatively long time interval, and electron transfer between the semiconductors should be possible. An alternative explanation could be that the effect of cascade electron transfer only show a very small incremental effect on the electron injection efficiency compared to direct electron transfer. Regardless, these theories are impossible to confirm without more experimental data on different concentrations. However, one observation that can be made is that, long lived charge separated states induced by a physical barrier, see figure 2.8 do not seem to form in a significant concentration.

The results of  $\text{TiO}_2$  and the mixed  $\text{TiO}_2/\text{SnO}_2$  semiconductor system with the electron acceptor  $\text{hemin}(\text{py})_2$ , display a considerably slower recombination than the recombination observed without an electron acceptor. This behaviour can relatively easily be explained by considering the electron transfer from the electron acceptor to the dye as very slow, and thereby decreasing the rate of recombination. The effect of slower recombination however, is most prominent in the mid region of figure 4.14 (between 200-1300 microseconds) and after approximately 2 milliseconds approaches the same concentration as the other semiconductor systems. This can also be observed from the coefficients in table 4.2 where a lower value of  $A_1$  is obtained for both measurements performed with  $\text{hemin}(\text{py})_2$ . As the comparably lower rate of recombination for systems with  $\text{hemin}(\text{py})_2$  is time dependent, the advantage of using an electron acceptor distributed throughout the semiconductor film is also dependent on the catalytic rate of reaction in the solar fuel device. If the bulk of the catalytic reaction is achieved in the late region of figure 4.14 (for instance 2 milliseconds or later), the advantage may be small, whereas if most of the reaction occurs in the mid region (between 200-1300 microseconds) the effect may a significant improvement. One possible way of implementing these results obtained from studying the electron acceptors, could be to use catalysts incorporated in the semiconductor film to minimize the recombination.



# 6

## Conclusion

This thesis have successfully shown proof of conduction band mediated electron transfer for hemin on  $\text{TiO}_2$  and hemin(py) $_2$  on  $\text{SnO}_2$  through experiments with steady state photolysis and spectroelectrochemistry. A decreased rate of recombination with mixed  $\text{TiO}_2/\text{SnO}_2$  semiconductors, was not observed in transient absorption measurements, but further experiments on different concentrations are necessary in order to conclude a general effect from cascade electron transfer. In addition, the transient absorption measurements performed on  $\text{TiO}_2$  and mixed  $\text{TiO}_2/\text{SnO}_2$  with hemin(py) $_2$  in acetonitrile with methanol displayed a longer lived charge separated state. This effect was especially apparent in the range of 200 to 1300 microseconds, and could potentially have significant implications for designing future solar fuel devices.

### 6.1 Future work

This thesis was mainly been aimed towards investigating the fundamental behaviour of mixed  $\text{TiO}_2/\text{SnO}_2$  semiconductor films with regards to electron recombination. However, one interesting aspect that was only briefly discussed was long lived charged separated states created by a physical barrier, see figure 2.8. This idea could be interesting to try out with screen printing or similar methods for strategic placement of the components of the solar fuel assembly. A requirement for this would be to create a  $\text{SnO}_2$  paste of appropriate nanoparticle size and viscosity. Additionally, a study on the effect of concentrations in mixed  $\text{TiO}_2/\text{SnO}_2$  semiconductors could be interesting to investigate to determine if a cascade electron transfer mechanism could be an improvement for solar fuel devices.



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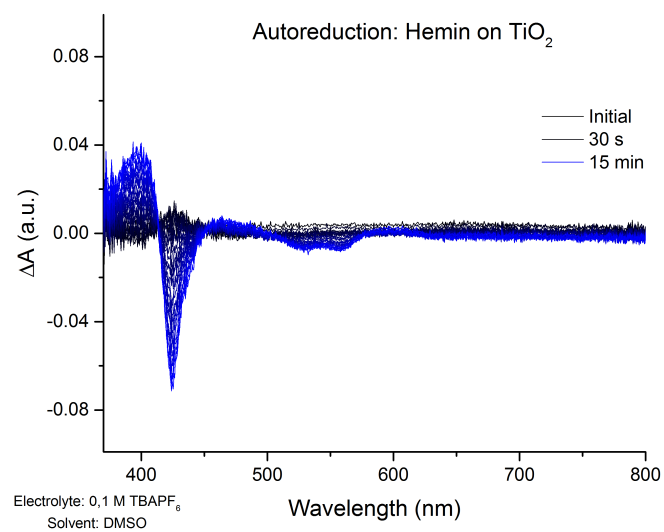
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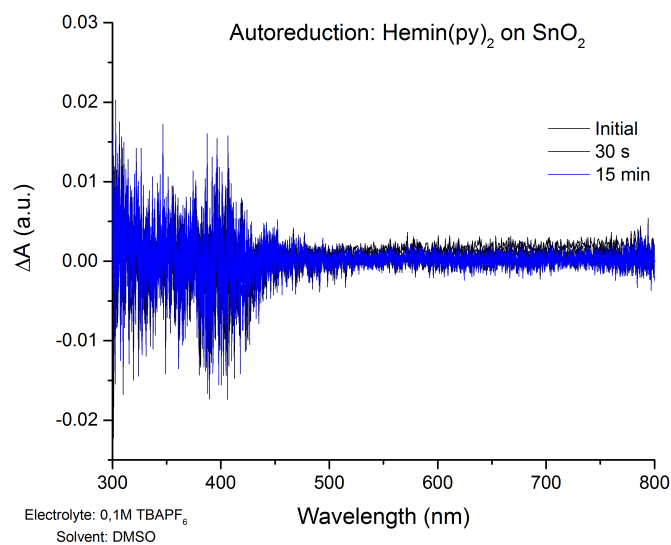


# A

## Appendix 1

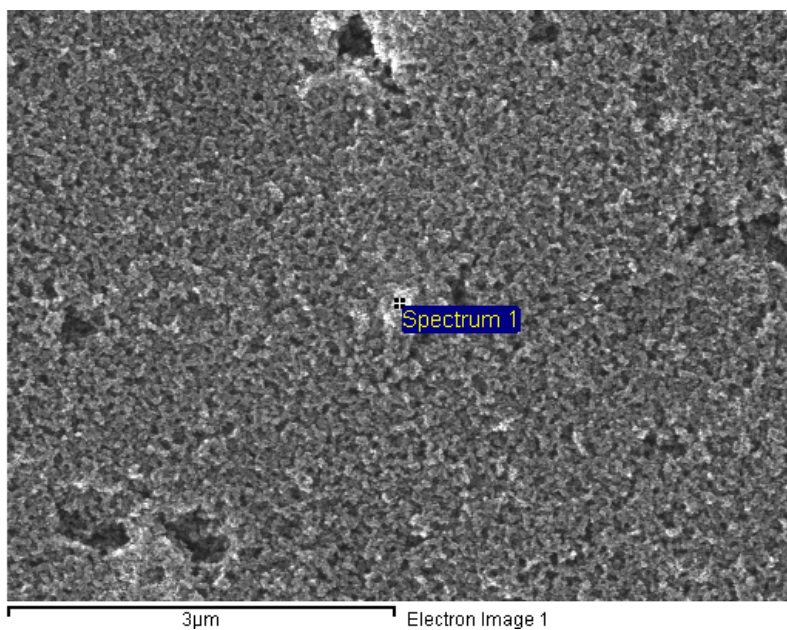


**Figure A.1:** Autoreduction of hemin on  $\text{TiO}_2$  performed in DMSO with 0,1M  $\text{TBAPF}_6$  in a dark room.

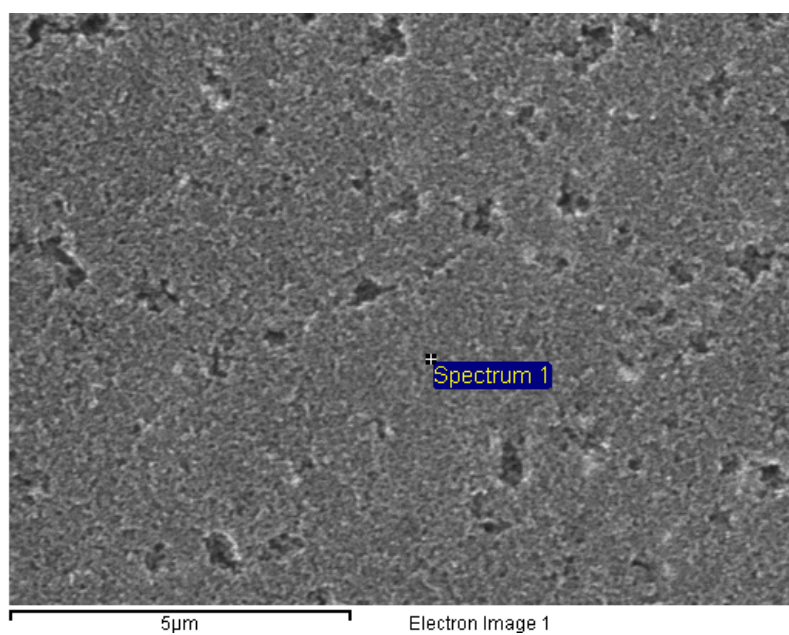


**Figure A.2:** Autoreduction of hemin(py)<sub>2</sub> on TiO<sub>2</sub> performed in DMSO with 0,1M TBAPF<sub>6</sub> in a dark room.

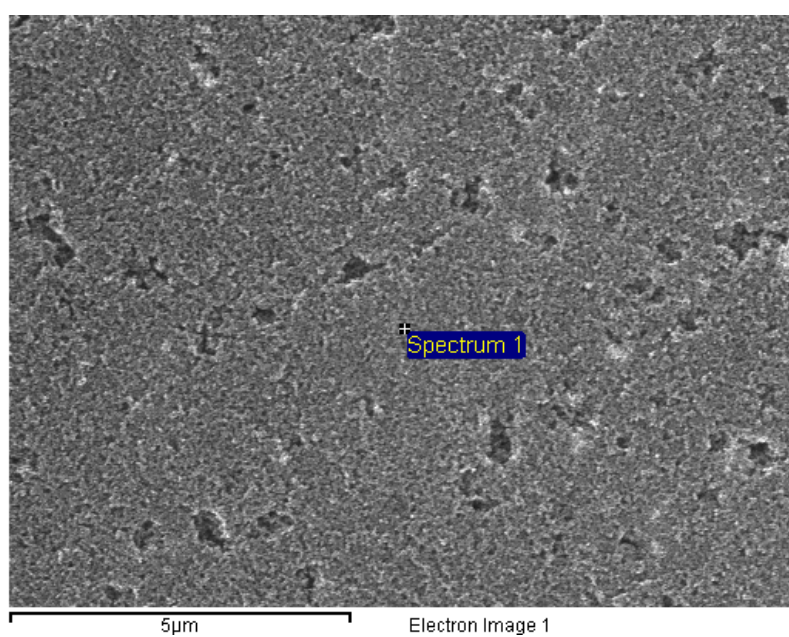
## A.1 EDX locations on SnO<sub>2</sub>/TiO<sub>2</sub> film



**Figure A.3:** SEM image of the location of spectrum 1.



**Figure A.4:** SEM image of the location of spectrum 2.



**Figure A.5:** SEM image of the location of spectrum 3.