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Name	Jessica Kroeze
University	Delft University of Technology (NL)
Department	Interfaculty Reactor Institute, Radiation Chemistry Group
PhD Supervisor	Dr. J.M. Warman / Dr. T.J. Savenije

SUMMARY

Life on earth is powered by the sun. Green plants, algae and cyanobacteria all absorb sunlight to convert it into chemical energy, which drives the machinery that converts carbon dioxide into oxygen. In contrast to fossil fuels like oil and gas, the sun is a nearly inexhaustible energy source. The amount of energy received by the earth from the sun still exceeds the present world energy consumption by many thousand times. This huge amount of energy consists of roughly 5% ultraviolet (which causes sunburn), 43% visible (all colors of the rainbow) and 52% infrared (known from heat lamps) light.

In principle, two different methods for the conversion of solar energy into useful energy exist. Firstly, sunlight can be converted into heat, which can be used for *e.g.* warm water production. Secondly, sunlight can directly be transformed to electricity by means of solar cells. Well-known examples of low-power solar cells are those applied in pocket calculators and watches. Larger scale applications are the solar panels along the A9 highway. The Nuna I & II solar driven racing cars form a futuristic example of the use of solar energy. In general, solar cells have the advantage that no mechanical parts are required, guaranteeing virtually maintenance-free operation during many decades. Disadvantages are formed by the intermittency and seasonality of sunlight.

The commercial solar cells in the above-mentioned applications are based on silicon, an atom that can be found in sand and glass. All these cells belong to the class of *conventional* solar cells. **Chapter 1** gives a brief explanation of how these solar cells work. The scientific research on and production of this type of solar cells has proceeded for many decades. Although these cells are considerably efficient, which means that they are able to convert up to a quarter of the solar energy into current, they possess a large drawback: they are very expensive to produce since they require very pure materials.

This thesis deals with a different class of solar cells. The research on these cells started to develop in the late '80s of the last century. The main feature of this type of cells is that they consist of rather inexpensive basic parts: a thin film of a so-called *wide bandgap* inorganic semiconductor and an organic sunlight-absorbing material. Unfortunately, the efficiency of this type of solar cells is still rather low: around 10% for cells on laboratory scale. This is largely due to the fact that the research on these cells has only recently come into effect, and that the working principle is still far from understood.

Roughly, such a cell works as follows: as mentioned before, the type of solar cell studied in this thesis contains a *wide bandgap semiconductor*. *Wide bandgap* denotes that the energy difference between the *ground state* (without light) and the *excited state* (upon illumination) is high; only under the influence of a package of highly energetic, ultraviolet (UV) light it is possible to transfer a negatively charged particle (an 'electron') to a higher energy level. In such a higher energy level the electron is able to move freely. The negatively charged electrons leave a positively charged place where they were initially situated: these are called holes. Hence, freely moving negative ('minus') and – somewhat less freely moving – positive ('plus') particles are now present in the material. If one would attach metal wires to it, negative and positive poles ('electrodes') are being formed; upon illumination, one would then be able to measure a current!

However, as mentioned earlier, the sun emits only 5% UV light. A semiconductor only would not be sufficient to make an efficient solar cell; it would be much better if also the visible (and infrared) light could be exploited. It is possible however to apply a layer of a visible light absorbing substance ('dye') onto the semiconductor in order to catch the visible light, too. Unfortunately, in an organic dye it is usually more difficult to directly create freely moving electrons and holes under the influence of light. If light is absorbed in such a material, strongly bound plus-minus pairs of electrons and holes are formed; these are called 'excitons'. Excitons can move freely, but do not directly lead to current. If however such an exciton comes in the direct vicinity of the semiconductor, the semiconductor is likely to take up the electron from the exciton. Hence, the semiconductor-dye combination now contains a free electron in the non-organic semiconductor and a hole remaining in the organic dye. Upon attachment of electrodes and illumination with visible light a current can be measured! Because by applying the dye the semiconductor has been made sensitive to visible light, this type of solar cell is called a *dye-sensitized solar cell*. A more detailed description of the processes that take place in these cells is provided in **Chapter 1**.

In order to make solar cells more efficient, first the full working mechanism should be unraveled. There are many ways to study the behavior of excitons, electrons and holes in solar cell materials. The most straightforward way is to attach electrical contacts to the materials and measure the current or voltage, dependent upon for instance the light color, light intensity or morphology of the materials used. However, the use of electrode contact layers may have drawbacks: they could behave non-Ohmic or short-circuits may occur, thereby masking the for the material characteristic behavior of excitons, electrons and holes.

For this thesis a different technique has been applied: the Time-Resolved Microwave Conductivity technique (TRMC). What makes this technique so special is the fact that it enables to measure mobile electrons and holes without the necessity of applying electrodes. The principle of the TRMC method is that as a larger number of mobile charges (electrons and holes) is present in a material, more microwave power is absorbed by this material; in other words, its microwave conductivity is higher. **Chapter 2** is devoted to the theoretical background of this technique and to a description of the separate parts of the TRMC set-up. Furthermore, it is explained which quantitative information can be extracted from TRMC measurements. In addition to TRMC, some other techniques have been applied to study the materials used; these are also briefly discussed. Finally, an overview of the various materials studied throughout this thesis is provided.

Chapter 3 demonstrates how TRMC can be used to determine the charge separation efficiency in a simple double-layer system consisting of the semiconductor titanium dioxide ('TiO₂') and the dye 5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin ('H₂TPPC'). This dye displays a strong resemblance to chlorophyll, the dye that enables leaves to absorb light. An 80 nm thin flat, smooth film of transparent anatase TiO₂, applied by *Electron Beam Evaporation*, was covered with a ca. 60 nm thin layer of H₂TPPC by means of *spin-coating*. The double-layer system was irradiated with 3 ns laser pulses of different (UV and visible) colors. Subsequently, the behavior of the mobile electrons in the TiO₂ was studied in time (so-called 'transients'). If only a single layer of either TiO₂ or the dye is illuminated with visible light, hardly any mobile charges will be observed in these materials. If however the same experiment is carried out with a double-layer of both materials, a much higher microwave conductivity is measured. In addition, it takes one hundred thousand times longer (up to several milliseconds) before the microwave conductivity decays. This constitutes strong evidence for the supposition that during the laser pulse excitons are being formed, which at the TiO₂ interface are separated into mobile electrons in the TiO₂ and holes remaining in the

porphyrin. This assumption was further justified by the observation that the efficiency of this process, to be deduced from the magnitude of the transients, is directly proportional to the amount of light of different colors that is absorbed by the porphyrin. The maximum charge separation efficiency per incident light particle ('photon') found for this system was less than 1%. The most important conclusion that is reached in this chapter, is that excitons in H₂TPPC cannot travel over substantial distances to the semiconductor interface, where charge separation takes place; in other words, the exciton diffusion length in this material is very small. This is disadvantageous for a solar cell, in which ideally each exciton formed should lead to charge separation.

It is often claimed that dyes should be equipped with so-called 'anchoring groups', which ensure favorable interaction with the semiconductor. In **Chapter 4** two nearly identical porphyrins, one with and one without anchoring ('carboxy') groups are compared. The results are virtually indistinguishable: both porphyrins only yield charge separation from the molecules that are in the direct vicinity of the interface with the semiconductor, TiO₂. The charge separation efficiency per incident photon amounts to approximately 1%, and is slightly dependent upon the intensity of the incident light. Again, no appreciable long-distance migration of excitons takes place. Possibly, anchoring groups in a working photovoltaic device (including a liquid electrolyte) ensure a better attachment to the semiconductor; however, they have no marked influence on results obtained with TRMC on simple bilayers of dye and semiconductor.

As mentioned previously, in an ideal solar cell each incident photon leads to an exciton, and each exciton formed leads in turn to charge separation and hence current. The distance an exciton can travel to the semiconductor interface, the exciton diffusion length, should therefore be at least as large as the penetration depth of the light. The magnitude of the exciton diffusion length of a material is determined by the lifetime of the exciton and the so-called exciton diffusion coefficient. If a material possesses a high exciton diffusion coefficient but a short lifetime *or* a long lifetime yet a low exciton diffusion coefficient, then its excitons won't get far. Most dyes have rather limited lifetimes: only several nanoseconds at most. During this short lifetime by far not all excitons will reach the semiconductor interface and lead to charge separation. It has been known, though, that excitons can switch over from a short-lived (called 'singlet') to a well over thousand times longer lived ('triplet') state. Unfortunately, the exciton diffusion coefficient of triplet excitons is usually accordingly smaller, on balance not resulting in an increased exciton diffusion length. In **Chapter 5** it is demonstrated however, that under the influence of heavy metal atoms in the core of dyes (again porphyrins), triplet excitons are formed that combine a long lifetime with a reasonably high exciton diffusion coefficient. For a double-layer system of TiO₂ and a palladium porphyrin ('PdTPPC') an increase in the charge separation yield is still observed longer after the end of the nanosecond laser pulse, resulting from the migration of long-lived triplet excitons to the semiconductor interface. Consequently, the charge separation efficiency per incident photon increases from 1% for the metal free to more than 12% for the palladium porphyrin, which demonstrates that through this effect simple double-layer systems can compete with more complicated types of solar cells based upon nanostructured TiO₂.

The porphyrin studied in **Chapter 6**, a tetraphenyl porphyrin with long (C₈) alkyl chains ('H₂TOPP'), possesses so-called liquid-crystalline properties. This implies that this porphyrin on increasing the temperature above 126 °C not directly turns into a liquid, but will display a sort of intermediate phase (up to 187 °C, the actual melting temperature). Previously, it has been demonstrated that when these disk-shaped materials are heated above 126 °C, and subsequently slowly cooled, they tend to self-organize to stacks of disks. It can

be envisaged that excitons (and free charge carriers) are able to rapidly migrate through such a self-organized stack, which should lead to high charge separation efficiencies. A ca. 50 nm thick film of H₂TOPP was spin-coated onto a flat TiO₂ layer, after which the absorption spectra and the time and wavelength dependence of the charge separation efficiency were measured. All measurements were carried both before as well as after heating of the H₂TOPP/TiO₂ double-layer. Something remarkable was observed: the charge separation efficiency per incident photon in the H₂TOPP/TiO₂ double-layer directly after applying the H₂TOPP is remarkably high: 10%. Similar to the earlier mentioned PdTPPC, long after the end of the nanosecond laser pulse electron injection into the TiO₂ occurs, which points towards diffusion of long-lived triplet states in the still disordered H₂TOPP layer. If now the H₂TOPP/TiO₂ double layer is heated to 130 °C and slowly cooled, the changes in the optical absorption spectrum of the heated-cooled double-layer with respect to the untreated double-layer clearly demonstrate the occurrence of self-organization of the H₂TOPP molecules. However, the charge separation efficiency in the double-layer containing stacked H₂TOPP disks is only 1%! The explanation provided is that the self-organization in the heat-treated H₂TOPP film is such, that the direction of the stacking is parallel to the TiO₂ layer. *Within* such a stack, efficient exciton transport can take place, however, not *between* the separate stacks. Thus, charge separation only occurs in the stack directly adjacent to the TiO₂ layer, resulting in the modest charge separation efficiency of 1%. Therefore, to optimally take advantage of the self-organizing properties of this material, a way of orienting the stacks perpendicularly to the semiconductor layer should be found, in order for efficient exciton transport towards the semiconductor to occur.

A revolutionary approach towards the issue of the restricted exciton diffusion length of many solar cell dyes dates from the early '90s, when for the first time nanostructured TiO₂ was applied. Nanostructured implies that the semiconductor film consists of a porous network of interconnected nanometer-sized particles. The big advantage of nanostructured TiO₂ is the many times larger surface area that is available for charge separation. In order to absorb in a several microns thick nanostructured TiO₂ film all the incident sunlight, only a monolayer of the dye per TiO₂ particle needs to be adsorbed, resulting in the lack of need for large exciton diffusion lengths in the dye. In **Chapter 7**, TRMC has been used in a study of the processes that take place in bare and porphyrin (H₂TPPC) sensitized nanocrystalline TiO₂ films. An important observation was that with laser light intensity, of all colors and independent of the applied dye, the microwave conductivity first increases superlinearly, reaches a maximum and then decreases. This initial superlinear increase is a strong indication for the occurrence of saturation of so-called 'traps' (oxygen vacancies and/or adsorbed species) with increasing light intensity. More evidence for this saturation process was found by measurements of the microwave conductivity in the presence of a continuous UV light source, which makes that the traps become pre-saturated. Now it was found that the microwave conductivity is simply linear with the intensity of the pulsed laser light. Since these observations were identical in either the presence or absence of the dye adsorbed to the TiO₂ particles, the trap states must have an intrinsic origin. If on average more than one electron is present per TiO₂ particle, the microwave conductivity again decreases, most likely due to electrostatic interactions between the electrons.

In **Chapter 8**, a different type of dye has been researched: a polythiophene. Layers of this material of different thicknesses were applied onto a TiO₂ layer, after which the charge separation efficiency was measured using TRMC. The polythiophene/TiO₂ double-layer was illuminated either from the front-side (through the dye) or from the back-side (through the TiO₂). A theory that predicts the relationship between the thickness, the illumination side and

the charge separation efficiency is described and worked out. The experimental results were compared to this model, from which for the polythiophene an exciton diffusion length of 2.6 or 5.3 nm, depending on whether excitons are quenched or reflected at the dye/air interface, was deducted.

The formulas derived in the previous chapter to relate TRMC results to exciton diffusion lengths and electron injection efficiencies are based on solutions to the diffusion equation for the stationary state; this implies that after the laser pulse no changes due to exciton diffusion occur in the system. Due to the latter, they can unfortunately not be applied to the results for PdTPPC triplet excitons described in Chapter 5, since there long after the end of the laser pulse exciton diffusion still takes place. In addition, in the case of triplet exciton diffusion also so-called exciton-exciton annihilation should be taken into account. In order to yet extract more quantitative data from the results of Chapter 5, so-called Monte Carlo simulations have been formulated and performed, the results of which are described in **Chapter 9**. Briefly, several thousands of excitons were created in a fictive dye layer. All excitons were given a predefined lifetime and exciton diffusion coefficient. Furthermore, it was determined beforehand within which mutual distance two excitons annihilate (the ‘annihilation radius’). Subsequently, all excitons were allowed during a very short time step to move. The distance moved in the x, y and z direction is determined by the magnitude of the exciton diffusion coefficient, the length this time step and by a random number between 0 and 1 (to this latter aspect and its resemblance to throwing dice the term Monte Carlo is attributed). After each time step it was checked whether the excitons had still lifetime left, they were within annihilation distance or they had reached the coordinates corresponding to the TiO₂ layer, which was considered equivalent to charge separation due to electron injection. For a series of subsequent time steps the total amount of dissociated excitons was registered, by which a complete transient could be simulated. These simulated transients were compared with the experimental transients. Subsequently, the values for the exciton diffusion coefficient, lifetime, annihilation radius and the electron injection efficiency were adapted such that the best fit to the experimental data was obtained. It was found that the exciton diffusion length in PdTPPC could amount to at least 28 nm. Chapter 9 furthermore provides in a graphic overview of the general influence of these separate parameters, and proofs that the simulations of diffusion of short-lived singlet excitons in the absence of annihilation exactly match the analytically derived predictions.

One of the present shortcomings of dye-sensitized solar cells is the poor overlap between the solar emission spectrum and the absorption spectrum of the dyes used. Much research is therefore devoted towards the design and synthesis of dyes that possess an absorption maximum for red (ca. 700 nm) light, where the sun has its maximum photon flux. Such red-absorbing materials are called *small* or *low bandgap* materials. This *low bandgap* refers to the energy difference between the ‘ground state’ and the ‘excited state’. In fact, two different ways of achieving a low bandgap exist: by lowering of the energy level of the excited state, or by raising the ground state. Both approaches involve some disadvantages: for instance, lowering the excited state may cause a decrease of the driving force for electron injection into the semiconductor. In **Chapter 10**, the behavior of a novel low bandgap material, called ‘PTPTB’, has been studied. If a PTPTB/TiO₂ double-layer is illuminated with laser light, the peak charge separation efficiency is only 0.1%, most probably due to the predicted reduced driving force for electron injection. The same experiments were repeated with a different semiconductor, tin(IV) oxide, ‘SnO₂’. It is known that this semiconductor has a conduction band edge that lies lower in energy than that of TiO₂. In theory, this might result in a larger driving force for electron injection from PTPTB as

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compared to TiO_2 . Indeed, it was found that the charge separation efficiency per incident for a PTPTB/ SnO_2 double-layer amounts to 3%, 30 times higher than that for the PTPTB/ TiO_2 double-layer. Since no evidence for an increased exciton diffusion length for PTPTB applied on SnO_2 was found, it was concluded that the increased driving force for electron injection in SnO_2 results in a higher charge separation efficiency, and that PTPTB combined with SnO_2 forms a promising base for application in photovoltaic devices.