Hybrid solar cells of titanium dioxide sensitized with organic semiconductors
Stellingen

behorende bij het proefschrift

"Hybrid solar cells of titanium dioxide sensitized with organic semiconductors"

Carolien Zilverentant, 2 december 2003

1. In zonnecellen bestaande uit een combinatie van polymeer en nanogestructureerd titaandioxide moet een optimum gezocht worden tussen infiltratiediepte, exciton diffusielengte en poriegrootte. (*Hoofdstuk 6 van dit proefschrift*)


5. Het AM 1.5 spectrum is niet maatgevend voor de efficiëntie van een zonnecel, omdat geen rekening wordt gehouden met invloeden van tijd, plaats en seizoen op het zonnespectrum.

6. Met de huidige opslagmethoden is de ontwikkeling van een waterstofeconomie niet mogelijk.
7. In tegenstelling tot de mens is een batterij gewenster zonder geheugen.


9. De ontwikkeling van moderne technologieën laat een omgekeerde evenredigheid van vermenigvuldigingsfactoren zien: als voor microtechnologie mega-investeringen nodig zijn, verlangt nanotechnologie giga-investeringen.

10. In het streven naar kennis is de moderne mens verworden van een "homo universalis" tot een 'homo multimedialis'.

11. De tweehonderd meter sprint naar de trein zou een olympische sport moeten worden.

12. De beste manier om iets te doen is het niet te laten.

Deze stellingen worden verdedigbaar geacht en zijn als zodanig goedgekeurd door de promotor Prof. dr. J. Schoonman.
Propositions

belonging to the Ph.D. thesis

"Hybrid solar cells of titanium dioxide sensitized with organic semiconductors"

Carolien Zilverentant, 2 December 2003

1. In a solar cell, comprised of a combination of polymer and nanostructured titanium dioxide, an optimum has to be found between infiltration depth, exciton diffusion length, and pore size. (*Chapter 6 of this thesis*).


3. Fujitsunka et al. unjustly estimate the degree of polymerisation of UV-irradiated 2,2'-bithiophene and 2,2':5',2''-terthiophene to be higher than a few units. (*Fujitsuka, M.; Sato, T.; Segawa, H.; Shimidzu, T. Chem.Lett. 1995, 99-100*).

4. Investigation of thin oxide films with ion beam analysis should be based on experiments, not on simulation programs. (*Kling, A ; da Silva; M.F. ; Soares, J.C. ; Freitas, P.P. ; Baptista, D.L ; Zawislak, F.C. Nucl. Instr. and Meth. in Phys. Res. B. 2000, 61-163, 539-552*).

5. The AM 1.5 spectrum does not represent the practical efficiency of a solar cell, because the influences of time, place, and season on the solar spectrum are not taken into account.

6. With the current storage methods the development of a hydrogen economy is not possible.
7. In contrast to humans, a battery with a memory is undesired.

8. The health effects of a disaster with poisonous compounds does not always fulfil the Adagium of Paracelsus ("the dose determines the poisonousness"). (Firework disaster Enschede: Measurements of elements in blood and urine; health impact assessment, RIVM rapport 630930003, 2001).

9. The development of modern technologies shows an inverse proportionality of prefixes: if mega-investments are necessary for micro-technology, giga-investments are demanded for nano-technology.

10. In striving for knowledge, modern man has degenerated from "homo universalis" to "homo multimedialis".

11. The two hundred meters sprint to the train should become an Olympic sport.

12. The best way to do something is not to leave it.

These propositions are considered defendable and have been approved as such by the supervisor Prof. dr. J. Schoonman.
Hybrid solar cells of titanium dioxide sensitized with organic semiconductors

Carolien Huisman-Zilverentant
Hybrid solar cells of titanium dioxide sensitized with organic semiconductors

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
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voorzitter van het College voor Promoties,
in het openbaar te verdedigen

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Caroline Lydia ZILVERENTANT

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1

Introduction

In this introductory chapter the use of solar energy, the working mechanism of solar cells, recent developments, and characterization methods are discussed. It concludes with a brief outline of the contents of this Ph.D. thesis.
1.1 Introduction

The environmental problems caused by the use of fossil fuels and the abundance of solar irradiation on earth, make solar cells a promising, sustainable energy source. Already in 1839 E. Bequerel discovered that silver halide-coated Pt inside an electrolyte shows a current under illumination. He introduced this as the photovoltaic effect. Adam and Day described the same effect in 1877 for selenium and by 1914 Se solar cells converted sunlight into electricity with about 1% efficiency. Russell Ohl (Bell Laboratories) discovered in 1939 for the first time that silicon exhibited a light-induced current. Soon after, the first single-crystalline and polycrystalline silicon (Si) cells were synthesized. In the period 1940–1955 the importance of semiconductor p-n junctions and the role of acceptor and donor impurities were clarified and controlled in the production process step-by-step. The first “efficient” silicon solar cell was made in 1954 and research activities have increased steadily ever since. To date, commercial Si solar cell panels (Fig. 1.1) reach an efficiency of about 15% (laboratory value: 22%), but the high production cost is the major bottleneck for their implementation on large scale. Organic or hybrid solar cells use cheap wide-band gap oxide semiconductors, like titanium dioxide, as a base material, which is sensitized by a visible light-absorbing species, either organic or inorganic in nature. While the high resistance and small exciton diffusion lengths of organic compounds result in low efficiencies for bi-layer cells, nanoscale blends of the organic and inorganic compounds are promising alternatives.

Fig. 1.1. A commercial silicon solar panel.
1.2 Renewable energy

Mankind is using increasing amounts of energy. Limited resources and environmental pollution, caused by the combustion of fossil fuels (like oil, natural gas and coal), call for sustainable alternatives to produce energy. The energy consumption in 1999 is distributed over various energy sources as shown in Figure 1.2.

**World Energy Consumption 1999**

- 23% natural gas
- 40% petrol
- 7% hydroelectric
- 7% nuclear
- 1% renewable
- 22% coal

**Fig. 1.2. World energy consumption distribution for 1999.**

Although to date the use of renewable energy sources is limited, direct conversion of sunlight into electricity is a promising option. Since the solar energy reaching the earth is more than sufficient to power all human activities, solar cells offer a way towards utilisation of renewable energy. The yearly amount of solar energy reaching the earth is about \(5 \times 10^{20}\) J. Installing solar cells with an efficiency of 10% on a tenth of the surface of the Sahara desert could provide the world energy demand. National and international politics aim for an increase of the percentage renewable energy towards 10-20% in the coming 20 years, as a result of the Kyoto agreement. Besides solar energy, wind, water (tidal and hydroelectric), geothermal, and biomass are sustainable energy sources.
1.3 Solar cells

Solar energy can be used in two ways, i.e., in the form of heat and in the form of electrical energy. In the first form, solar radiation can be used for urban heating. Solar collectors are used to heat water, which simply consist of an absorbing (black) panel on the roof of a house in which water flows through tubes. The water is heated and stored in a thermally isolated tank. In this way, water can easily reach a temperature of 80°C. The conversion into electricity is done using photovoltaic cells, which are the subject of this Ph.D. thesis.

1.3.1 Types of solar cells

Solar cells can be divided into several categories. In Table 1.1 the main categories and their efficiencies are shown. Cells without a commercial efficiency denoted are in the development stage. The number given for each category is the highest efficiency reached so far.

Although commercial Si-based solar cells exhibit quite a high efficiency, they have a number of serious drawbacks. Because of the low doping concentrations (ppm level) needed for efficient p-n junctions (see paragraph 1.3.2), extremely high-purity silicon is required. Currently, the solar panel industry relies on scrap material from the chip industry, which is a bulk user of silicon. If, in time, additional silicon excavation and purification is necessary, the price of silicon will rise even further. Next to the production of very pure silicon, encapsulation to prevent oxidation in air is necessary and expensive. All these factors lead to a price of solar electricity higher than that of electricity based on fossil fuels. Other types of high purity semiconductor solar cells with even higher efficiencies, like GaAs, are even more expensive and sometimes contain hazardous and/or rare elements. These types of cells are mostly used in space applications. The highest theoretical efficiency for single crystalline silicon solar cells is 31%, due to spectral mismatch and recombination losses. Stacks of different solar cell materials could increase this efficiency even further (i.e., tandem or multi-junction cells).
1.3.2 Semiconductors
Semiconductors consist of molecules or atoms of which the energy levels overlap in such a way, that two energy bands are created: a valence band (VB) and a conduction band (CB). At 0K the VB is completely filled with electrons and the CB is completely empty. At higher temperatures some electrons are excited from the VB to the CB, due to thermal motion. The distribution of electrons over the bands can be calculated at any temperature using the Fermi-Dirac equation. For pure semiconductors there are no energy levels in between these bands and this forbidden energy area for electrons is referred to as the band gap. The Fermi-level ($E_F$) is the electrochemical potential of the electrons. All energy levels below $E_F$ are filled with electrons, while those above $E_F$ are empty. A schematic picture is shown in Fig. 1.3.

Table 1.1. Solar cell categories and efficiencies.

<table>
<thead>
<tr>
<th>Solar cell type</th>
<th>Efficiency of commercial cells</th>
<th>Efficiency in laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single crystalline Si</td>
<td>13 –16 %</td>
<td>24.7 %</td>
</tr>
<tr>
<td>Polycrystalline Si</td>
<td>12 – 15%</td>
<td>19.8 %</td>
</tr>
<tr>
<td>Amorphous Si</td>
<td>4 – 7%</td>
<td>10.1 %</td>
</tr>
<tr>
<td>III/V GaAs, (Ga)InP</td>
<td>21%</td>
<td>25.1%†</td>
</tr>
<tr>
<td>II/VI CdTe, ZnSe, CdS</td>
<td>5%</td>
<td>16.5%</td>
</tr>
<tr>
<td>I/III/VI CuInS₂, Cu(In,Ga)Se₂ *</td>
<td>12%</td>
<td>19%</td>
</tr>
<tr>
<td>Dye-sensitized organic</td>
<td>7%</td>
<td>12%</td>
</tr>
<tr>
<td>Bi-layer organic heterojunction</td>
<td></td>
<td>1%</td>
</tr>
<tr>
<td>Solid state nanostructured heterojunction</td>
<td></td>
<td>3%</td>
</tr>
</tbody>
</table>

† For crystalline GaAs. For multicrystalline GaAs and crystalline InP these numbers are 23.3% and 21.9% respectively. For a GaInP/GaAs multi-junction cell an efficiency of 30.3% is reported.  
* In combination with ZnO and CdS.
In metals overlapping bands are formed and no bandgap is present. The electrons are free to move and form an electron gas, leading to a high conductivity of heat and charge.

![Diagram showing energy levels and bandgap](image)

*Fig. 1.3. Overlap of energy levels leads to formation of bands.*
*Picture taken from ref.8.*

Insulators have a very high bandgap. It cannot be crossed by electrons that are excited thermally or through absorption of photons. These compounds hardly exhibit any conduction of heat and charge. In semiconductors, only few electrons can cross the band gap at moderate temperatures and, therefore, conductivity is limited. Conductivity can be increased by the increase of temperature and the introduction of levels in the band gap (i.e., doping). The first method will not be discussed here. Addition of dopants may change the properties of a semiconductor (Fig. 1.4). If, for example, phosphorus (P) atoms are added to silicon in low concentration (ppm level), additional electrons are present in the CB because P has one valence electron more than Si. In this way an n-type semiconductor is formed. On the other hand, if, for example, boron (B) is used as a dopant, extra holes are created, because B has one valence electron less than Si and a p-type semiconductor is obtained. In both cases the conductivity is increased substantially. In a more physical description these donors (like P) and acceptors (like B) are present as defect levels close to the bottom of the CB and the top of the VB respectively. By thermal motion these levels are readily accessible.
1.3.3 Working mechanism of solar cells
If a p- and an n-type material are connected, electrons and holes recombine at the interface and charge is built-up (no free charges present). The positively charged donors (P⁺) and negatively charged acceptors (B⁻) remain in the lattice and a depletion layer is formed. At a certain thickness of the depletion layer, the growth stops, because electrons from the n-side and holes from the p-side cannot recombine anymore, due to the large electrical field. In this so-called p-n junction an internal electrical field is now present.

![Diagram of semiconductor bands with doping](image)

**Fig. 1.4.** A: Doping of a semiconductor lattice with electron donors or acceptors. B: Electron distribution for undoped (intrinsic) and doped semiconductors at room temperature (Fermi-Dirac approach). Picture B is taken from ref.8.

This is schematically shown in Fig. 1.5. In physical terms, the Fermi-levels of both sides have to equalize upon contact, thereby creating a flow of electrons from the n-type to the p-type semiconductor. While the edges of the bands are pinned due to the large amount of surface states, band bending occurs between the interface and the bulk of the semiconductors. This is associated with surface charging. The band gap of silicon is 1.1 eV, which means that photons of visible light can excite electrons from the VB into the CB. Due to the internal electric field holes will drift to the p-type side and electrons to
the n-type side, if they are created in the depletion layer or close enough to reach it by diffusion. The electrons migrate into an external circuit where they can perform work and are recombined with the holes if the circuit is closed.

![Diagram showing depletion layer formation and charge recombination](image)

**Fig. 1.5. Formation of a depletion layer upon contact between an n- and a p-type doped semiconductor (A) and working mechanism of a silicon solar cell (B).**

Research on Si-based solar cells is directed towards higher efficiencies, upscaling of production, and development of amorphous and thin-film devices. A different approach to realize cheap solar cells is the use of organic chromophores. In these so-called organic or hybrid solar cells, a wide band gap semiconductor, mostly an oxide like titanium dioxide or zinc oxide, is combined with a light-absorbing dye, which injects electrons into the conduction band of the metal oxide upon excitation with visible light (Fig. 1.6). To close the current circuit and to regenerate the oxidized dye molecule, an electron has to be provided to the system. The principle of combining a visible-light absorbing species with a wide band gap semiconductor is called
“sensitization”. Most organic dyes can be treated both as semiconductors with narrow bands and as molecular compounds. If regarded as molecular compounds, excitation takes place between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO).

![Diagram of a hybrid solar cell](image)

**Fig.1.6. Working principle of a hybrid solar cell.** Photons are absorbed by the dye and an electron will be excited to the LUMO level. This electron can be injected into the CB of the TiO$_2$. The electron can be collected and perform work in the external circuit. It is transported back to regenerate the dye and to close the circuit.

There are several demands for dyes to be suitable for use in hybrid solar cells:

1. The HOMO-LUMO energy difference must be small enough to absorb visible light.
2. The absorption spectrum must have a large overlap with the solar spectrum to absorb as much visible light as possible.
3. The extinction coefficient (also called absorption coefficient) must be as high as possible to absorb sufficient light, while using only a thin film of dye.
4. The HOMO level must be higher in energy than the CB of the n-type semiconductor used.

5. For use with n-type semiconductors it should be a p-doped material in order to form a p-n junction where electrons and holes are drifting to opposite sites as a result of the built-in electrical field, thus preventing recombination. This requirement is only valid for solid-state devices.

6. The difference between the CB edge of the n-type semiconductor and the HOMO level of the dye must be as large as possible, as it determines the open circuit voltage of the solar cell (see paragraph 1.3.6).

7. Preferably, the dye is cheap, non-toxic, and exhibiting flexible properties (for example solubility). Furthermore, it must be stable under illumination and oxidation/reduction cycling.

8. The dye must be able to conduct the (bound) electron-hole pairs, formed upon illumination, to the interface and inject it into the CB of the n-type semiconductor. In most organic compounds this electron-hole pair is present as a neutral cluster (exciton). The exciton should be able to diffuse as far as possible before it recombines, to utilize a large part of the organic film. Photons absorbed further away from the interface than the exciton diffusion length will not reach the interface and will not contribute to the photocurrent.

While in this thesis emphasis will be placed on organic dyes, also inorganic compounds can be used as sensitizers for wide-band gap semiconductors, like CuInS$_2$ and CdSe$^{+u}$. Most organic dyes are p-type semiconductors, but some can also be n-type (for example perylene derivatives). This leads to the possibility to fabricate all-organic solar cells, for example, for deposition on flexible substrates.

There is a large range of organic molecules that can be used to design dye-sensitized solar cells among which are metal complexes, like porphyrines and phthalocyanines, and semiconducting polymers like polyphenylene vinylenes and polythiophenes. A few examples of organic dyes are shown in Fig. 1.7.
Organic compounds are in general versatile (adding of side groups enables control over properties like light absorption and solubility), flexible, and easy to process. Albeit laborious fabrication, their price usually drops if made in larger quantities. For the moment most dyes that are used in solar cells suffer from insufficient stability, limited charge-carrier mobilities, little spectral overlap, unwanted doping by oxygen, and low purity. Much effort is directed to solve these problems and to design new compounds that increase the stability and efficiency of hybrid solar cells.

![Poly[2-methoxy-5-(3,7-dimethyloctyloxy)para-phenylene vinylene] (MDMO-PPV)](image)

![Poly(3-octylthiophene) (P3OT)](image)

Zinc phthalocyanine (ZnPc)

![Perylene tetracarboxy diimide (n-type semiconductor)](image)

*Fig. 1.7. Examples of organic chromophores*
Bi-layer ("flat film") solar cells made of wide band-gap (oxide) semiconductors in combination with organic compounds have a low efficiency (mostly less than 1%). This is caused by the fact that organic materials tend to have a high resistivity, which leads to ohmic losses. The organic films must be thick enough to absorb enough light, but only a very narrow region near the interface between organic dye and inorganic semiconductor is found to be active, as excitons can only move a limited distance before they recombine. If the internal electrical field does not separate them fast enough they will be lost. The exciton diffusion length is in the order of 5 to 20 nm for most organic compounds.

A different approach is to apply a different morphology. In 1991 the first hybrid solar cell with high efficiency (8%) has been reported by O'Regan and Grätzel. In this so-called Grätzel-type or dye-sensitized cell, anatase TiO₂ is used in nanocrystalline form to which organic dye molecules (a ruthenium complex) are covalently attached with monolayer coverage (Fig. 1.8). The use of nanostructured TiO₂ (nc-TiO₂) overcomes the problem of high resistance, since only a monolayer of dye is used. At the same time the increased surface area ensures enough dye absorption to absorb all the light. A drawback of this device is, however, the need of a liquid electrolyte for regeneration of the oxidized dye molecules after electron injection. This leads to the risk of leakage or even explosion, which is not desired for commercial devices. The electrolyte also suffers from degradation problems. Nowadays, a laboratory efficiency of 12% is reached, but commercial application of this kind of cells is still in the initial stage.

1.3.4 Recent developments
Much effort is being directed towards the development of similar nanostructured heterojunctions that can function without a liquid electrolyte. An ion-conducting polymer or a transparent material that can transport holes to the back contact can replace the liquid. Another possibility is to use dyes that combine both functions and do not only absorb light and inject electrons, but can also transport holes. In Fig. 1.9 a schematic picture of such a nanostructured heterojunction is shown.
Although organic substances exhibit in general much lower hole mobilities than inorganic compounds, semi-conducting polymers have shown to approach these high values and are suitable for utilization in these cells\textsuperscript{29}. For more details see §5.1.

**Fig. 1.8.** Schematic principle of a dye-sensitized solar cell. The working principle is similar to the cell depicted in Fig 1.6, the main difference being the liquid electrolyte (mostly an I/I\textsubscript{3} redoxcouple in an organic solvent) that reduces the dye molecules back to neutral. Injection of electrons from dye to TiO\textsubscript{2} is extremely fast (femtosecond time scale), while recombination rates are low, thus proving that an electrical field due to a p-n junction is not needed in this case.

To realize efficient solar cells several requirements have to be fulfilled. First of all intimate contact between the compounds on a nanoscale range is necessary. The intermixing properties should be on the scale of the exciton diffusion length, for efficient charge collection to take place. Selective contacts are needed to extract the electrons and holes at opposite sites of the device. To provide a pathway for both electrons and holes, it is important to achieve percolation, as well as good electrical contact in both the inorganic and the organic phase. If TiO\textsubscript{2} is employed it is preferred to have the anatase crystal structure, as this has been shown to exhibit the best characteristics for solar cells\textsuperscript{30}. Nanosized particles of TiO\textsubscript{2} are commercially available in a
variety of sizes and thin films of these nanoparticles can be deposited using, amongst others, spin casting, dip coating, and doctor blading (for more details about nanoporous TiO₂ and fabrication methods of films thereof, see §2.5). Afterwards, usually a high-temperature step is needed to obtain good-quality films, in which the particles form an interconnected nanostructured porous network. If the sensitizer is applied after formation of the TiO₂ network, interpenetration has shown to be a problem, because most organic dyes are quite bulky. Filling the voids of the TiO₂ before sintering is in most cases impossible in view of the limited high-temperature stability of most dyes. Creating a network of both compounds in one-step would be an elegant solution, but a further constraint is imposed by the fact that most synthesis routes for nanosized TiO₂ particles are performed in solution using aggressive chemicals.

Fig. 1.9. Schematic drawing of a nanostructured heterojunction solar cell. A composite of metal oxide and organic dye is deposited onto a substrate (usually glass coated with a transparent conducting oxide (TCO)). Selective contacts are needed, to prevent short-circuiting.

Besides TiO₂, other materials have been employed in bulk heterojunctions recently. The combination of buckminsterfullerene (C₆₀ and derivates) and semiconductor polymers has led to cells with efficiencies of over 2.5% in the past years. Both compounds are spincoated from the same solvent and a
blend of interconnected islands is formed. Recently, a mix of CdSe nanorods and poly(3-hexylthiophene) was reported to have an efficiency of 1.7%\(^o\). Many groups are working on new combinations of compounds and device morphology and increasing progress in conversion efficiencies is to be expected in the coming years\(^o\).

1.3.5 Limiting factors for solar cell performance

Much research to date is focussed on improving solar cell systems. Either by synthesis of new compounds, by altering device structures or by adjusting properties, researchers are trying to overcome problems that limit solar cell performance nowadays. The following limiting factors are recognised:

1. Recombination of excitons or electron-hole pairs. This can happen spontaneously or can be caused by traps (amongst others formed by defects) or recombination centres.

2. Ohmic losses. Organic compounds tend to have a high resistance and this is more serious if thicker films are needed. This problem can be detected from I-V curves that show a limited forward current and from the slope of the curve at 0V. The occurrence of high resistances can be caused by a low conductivity for holes/electrons/excitons or by bad contact between the elements of the cell (for example electrodes or between nanosized particles). Sometimes heat treatments, doping or buffer layers (for example: LiF or PEDOT-PSS) can help.

3. Unwanted doping. For most organic substances water and oxygen are acceptors. Often this doping leads to higher conductivities, but it can also cause inhibition of the photocurrent (see Chapter 5) or degradation. Avoiding this doping is hard and calls for more complicated preparation and measuring techniques.

4. Limited exciton diffusion length. Excitons generated further away from the interface with the n-type semiconductor will recombine. Improvement is sought in more ordered structures, that are either imposed by molecular alterations (for example: side chains, more stacking, liquid crystals) or by advanced deposition techniques (for example: forming crystalline films, aligning dipole moments).
5. Low stability. The influence of oxygen was already mentioned, but also prolonged illumination (either with or without oxygen present) can sometimes lead to degradation. Especially semiconducting polymers are subject to bond breaking, eventually leading to lower performances. In other systems defects can form during operation or elements of the system can react or diffuse.

1.3.6. Electrical measurements

Solar cell characteristics

Several techniques can be employed to investigate the properties of solar cells. One of the most commonly used methods is to measure current-voltage (I-V) curves for the complete cells. In Fig. 1.10 an example of typical I-V curves are shown.

![I-V curve diagram](image)

*Fig. 1.10. I-V curves for a typical photovoltaic device, recorded in dark and under illumination.*

In the dark the I-V plot shows a diode-type behaviour, which stems from the rectifying nature of the depletion layer near the p-n junction. When illuminated, again a diode-type curve is obtained, but shifted both on the current and on the voltage scale. This photovoltaic effect is characterized by the axis-intercepts, which are called short circuit current, $I_{sc}$, and open circuit voltage, $V_{oc}$. The maximum power point can be found by determination of
the intercept of the largest possible rectangle that can be fitted inside the curve. The fill factor, \( FF \), is a measure for the "squareness" of the curve and is calculated with equation 1.1.

\[
FF = \frac{V_{mp} I_{mp}}{V_{oc} I_{sc}} \quad \text{(Eq. 1.1)}
\]

In which \( V_{mp} \) and \( I_{mp} \) are the voltage and the current at the maximum power point respectively. The \( FF \) is a number between 0 and 1. The power conversion efficiency, \( \eta \), is used as a tool to compare different solar cells and is defined as the percentage of the solar irradiation that is converted into power. It is calculated using equation 1.2.

\[
\eta = \frac{V_{oc} I_{sc} FF}{P_{in}} \quad \text{(Eq. 1.2)}
\]

In which \( P_{in} \) is the incoming power of the light source used. If under illumination the I-V curve of an investigated sample crosses the origin, no photovoltaic effect is present. However, if it shows higher currents than in the dark under forward and/or reverse bias voltages, the sample is said to exhibit photoconductivity.

To make a correct comparison of the characteristics of different cells possible, all measurements should be carried out under the same circumstances, using the same spectral distribution and intensity of the light source, as well as at the same temperature. For this reason international standard test conditions are defined. Cells should be measured at 25°C under a light that is calibrated to the solar spectrum. This so-called AM 1.5 global spectrum is defined to have a radiant intensity of 1000 W/m² and a spectral distribution comparable to the added direct and diffuse spectrum of the sun in the earth atmosphere at an incoming angle of 48.2°. Calibrated solar spectra are available using (commercial) solar simulators. In literature I-V curves are often plotted on a log-log scale, as to be able to compare curves recorded in dark and under illumination.

Another important tool to investigate solar cells is to measure the so-called "photo-action spectrum". A wavelength dependent scan of the photocurrent
is collected, usually without any bias voltage present. The curve that is obtained is compared to the absorption spectrum of the dye and, furthermore, the photocurrent can be related to the number of incoming photons per wavelength. This leads to a number called the Incident Photon to Current conversion Efficiency (IPCE also called External Quantum Efficiency; EQE), which is a measure of the conversion effectiveness of the cell in the part of the solar spectrum where absorption takes place. For good solar cells, this IPCE should be close to 100% over a broad range of wavelengths. If the photocurrent is related to the number of absorbed photons instead of to the number of incoming photons, the Absorbed Photon to Current conversion Efficiency (APCE also called Internal Quantum Efficiency; IQE) results, which is higher than the IPCE in most cases. To calculate the APCE, the absorption spectrum of the cell should be known. In Fig. 4.3 IPCE and APCE spectra of thin films of zinc phthalocyanine on TiO₂ are shown, together with the accompanying photo-action and absorption spectrum.

Mott-Schottky analysis

Mott-Schottky analysis is an impedance-based technique, which can be used to find the donor density and flat-band potential of a system in which at least one double layer (behaving as a flat-plate capacitor) is present. While making a potential scan a small extra voltage modulation in the form of a sine-form ac potential is applied to the system and the current modulation is monitored. From this the impedance can be calculated.

In a solid-state system, like a bi-layer hybrid solar cell without liquid electrolyte, an equivalent circuit can in most cases be depicted like in Fig. 1.11.

The impedance of the system (Z) is the complex resistance and can be separated into a real (Z') and a complex part (Z'') like:

\[ Z = Z' + iZ'' \]  

(Eq. 1.3)

in which \( i^2 = -1 \). For a resistor the imagery part is zero (Z''=0) and the real part equals the resistance (Z'=R). For a flat plate capacitor the following equations apply:
\[ Z = \frac{1}{i\omega C} \quad Z' = 0; \quad Z'' = -\frac{1}{\omega C} \quad \text{(Eq. 1.4)} \]

in which \( \omega \) is the angular frequency (2\( \pi f \), with \( f \) the frequency in Hz) and \( C \) is the capacitance. For the equivalent circuit in Fig. 1.11 the impedance is:

\[ Z = R_s + \left[ \frac{1}{R_p} + i\omega C \right]^{-1} \quad \text{(Eq. 1.5)} \]

A plot of the complex part of \( Z \) as a function of the real part (Nyquist plot) shows a semicircle, cutting the \( Z' \) axes at \( R_s + R_p \) for \( \omega = 0 \) and at \( R_p \) for \( \omega = \infty \). A plot of the same data, now with \( \log(Z') \) and \( \log(Z'') \) as a function of \( \log(f) \) is called a Bode plot (see for an example Fig. 2.8) and shows a straight line for \( \log(Z'') \) with a slope of \(-1\) and a curved line for \( \log(Z') \) that becomes horizontal for high frequencies. At that frequency the capacitor cannot follow the alternating voltage anymore and behaves like a resistor. For the limit of \( \omega \to \infty \) we can neglect \( 1/R_p \) and the impedance of the reduced equivalent circuit becomes:
\[ Z(\infty) = R_s - i \frac{1}{\omega C} \]  
(Eq. 1.6)

Now, from the imaginary part of the impedance, the capacitance can be easily determined.

If no frequency (within apparatus limitations) can be found, where \(1/R_p\) can be neglected, another approach can be followed. From the Nyquist or Bode plot \(R_s\) should be determined and this value should be subtracted from the impedance data.

The impedance of the system becomes:

\[ Z = \left[ \frac{1}{R_p} + i\omega C \right]^{-1} \]  
(Eq. 1.7)

The admittance is the inverse of the impedance and reads as:

\[ Y = \frac{1}{Z} = \frac{1}{Z' + iZ''} = \frac{Z' - iZ''}{(Z')^2 + (Z'')^2} \]  
(Eq. 1.8)

which again can be separated into a real and an imaginary part, like:

\[ Y' = \frac{Z'}{(Z')^2 + (Z'')^2}, \quad Y'' = \frac{-Z''}{(Z')^2 + (Z'')^2} \]  
(Eq. 1.9)

For our system the admittance is now:

\[ Y = \frac{1}{R_p} + i\omega C \]  
(Eq. 1.10)

From the imaginary part of the admittance the capacitance can now be calculated.

At a certain frequency a scan of the capacitance as a function of bias voltage can be made. The Mott-Schottky equation reads:

\[ \frac{1}{C^2} = \left( \frac{2}{e\varepsilon_0\varepsilon_r N_o A^2} \right) \left( \varphi - \varphi_p - \frac{kT}{e} \right) \]  
(Eq. 1.11)

in which \(e\) is the elemental charge, \(k\) is the Boltzmann constant, \(T\) the temperature, \(\varepsilon_0\) the permittivity of vacuum, \(\varepsilon_r\) the dielectric constant of the semiconductor, \(N_o\) the donor density of the semiconductor, \(A\) the contact...
surface with the semiconductor, $\varphi$ the applied potential on the semiconductor, and $\varphi_b$ the flat-band potential. If $1/C^2$ is plotted as a function of the bias voltage $\varphi$, the so-called Mott-Schottky curve yields a straight line. If the dielectric constant of the investigated semiconductor is known, the donor density is easily found. From the intercept with the $\varphi$-axis the flat-band potential can be determined.

For Schottky junctions (metal-semiconductor interface) this method is straightforward. For p-n junctions the product of dielectric constant and donor density of both semiconductors contributes to the curve. The Mott-Schottky plot now yields two linear regions. At the flat band potential no depletion layer is present and by changing the applied potential a depletion layer starts to form at both sides of the p-n junction. The slope of this part of the plot is determined by both materials, although, it is dominated by the lower doped material. At a certain potential one of both materials is in complete depletion and acts as a dielectric medium, only shielding the electrical field a bit for the other material. The depletion increases in the other material and the slope of the curve is only determined by $\varepsilon N_o$ of that semiconductor. In Chapter 2 these measurements are used to study the donor density of TiO$_2$ thin films synthesized using different deposition techniques. For nanostructured systems, the assumption that a flat-plate capacitor is present is invalid and a Mott-Schottky analysis is in most cases not possible.

For more complicated systems (for example exhibiting frequency dependent elements) a more elaborate study has to be performed to find the equivalent circuit. Most of the time, a full impedance analysis has to be performed, including fitting of impedance spectra and varying certain parameters. Using related techniques like DLTS (Deep Level Transient Spectroscopy) and IMPS (Intensity Modulated Photo Spectroscopy) more detailed information about the system can be obtained, like the location of trap levels and kinetics.
Kelvin probe

The Kelvin probe is a non-contact, capacitor-based technique to measure the difference in workfunction between two materials\(^{39}\). Being non-destructive and very sensitive, it is widely used in semiconductor surface measurements\(^{40-48}\), including monolayer coverage by organic molecules\(^{49-55}\). It consists of a piezo-driven gold grid, vibrating at resonance at a short distance (1-2 mm) from the sample surface (Fig. 1.12).

![Diagram of Kelvin probe](image)

**Figure 1.12. Principle of the Kelvin probe.**

In general, a difference in workfunction, i.e., the distance between Fermi-level and vacuum-level exists, between the gold and the sample, leading to a contact-potential difference (Fig. 1.12). This is compensated by a variable bias voltage. The charge on the as-created flat-plate capacitor can be written as:

\[
Q = C \times V_{total} = C \times (V_{CPD} + V_{comp}) = \frac{\varepsilon_0 \varepsilon_r A}{d} \times (V_{CPD} + V_{comp})
\]  

(Eq. 1.12)

In which \(Q\) is the charge, \(C\) the capacitance, \(V_{total}\) the total voltage, \(V_{CPD}\) the contact potential difference, \(V_{comp}\) the compensating voltage, \(\varepsilon_0\) the dielectric permittivity of vacuum, \(\varepsilon_r\) the relative dielectric constant of the material, \(A\) the area of the capacitor, and \(d\) the distance between the plates. Due to the vibration of the grid the capacitance is a sine-function of the distance between the surfaces – being compensated by an opposite voltage source.
The workfunction of the probe being known, the Fermi-level of the sample can now be calculated. Changes in the compensating voltage during illumination must be due to either a change in electronegativity (i.e., dipoles) or band bending (i.e., surface charging). In Fig. 1.13 an energy diagram with all the relevant parameters is shown.

Fig. 1.13. Energy diagram during Kelvin-probe measurements of a p-type semiconductor. The workfunction ($\phi$) is defined as the difference between the Fermi level ($E_F$) and the vacuum level ($E_{\text{vac}}$). The difference in work function between a reference metal ($\phi_M$) and a p-type semiconductor ($\phi_N$) leads to a contact-potential difference ($V_{\text{CPD}}$) from which the Fermi-energy of the semiconductor can be deduced, if the work function of the reference metal is known. The valence- and conduction bands (VB, CB) are bent, due to local surface charging, the energy being pinned at the surface. The difference in energy between the bulk and the surface is referred to as the band bending ($V_{\text{bb}}$) and can be deduced from the difference in Kelvin-probe signal in the dark and after saturation with light. The electronegativity ($\chi$) is the difference between the surface potential and the vacuum level.
For the measurements a Besocke Delta Phi commercial set-up is used, containing a 2-mm diameter vibrating gold-grid. The resonance frequency is \(-170\) Hz. The contact potential difference can be visualised on an oscilloscope and is canceled by the compensating voltage. This compensating voltage is recorded by a Keithley 2001 digital multimeter and transferred to a PC using a GPIB output with an interval of 1s. The sample is grounded and electrical interference is avoided. Measurements can be carried out in ambient atmosphere, in vacuum or in a selected gas. Stabilisation of the dark-signal takes normally up to two hours per sample and with sufficient grounding of the set-up, the noise-signal can be as low as 10 mV. The workfunction of the gold-grid is taken as 5.34 \pm 0.09 V\(^a\).

In paragraph 3.2 Kelvin-probe measurements are used to investigate zinc phthalocyanine films on TiO\(_2\). Using different wavelengths to irradiate samples yields information on sub-bandgap features. This Surface Photovoltage Spectroscopy (SPS) technique is also used to study injection processes in solar cells\(^a\).

1.3.7 Characterization techniques

XRD

X-ray diffraction (XRD) can be used for structural and phase analysis, as well as for stress and texture measurements. It can detect the crystalline phases of powders, crystals, and thin-film samples with high resolution and good signal-to-noise ratio. The angle of the incoming X-ray beam as well as the angle of the detector is scanned over a range of different angles and the number of diffracted X-rays is plotted as a function of the angle. The diffracted beams follow Bragg’s law:

\[
  n \lambda = 2d \sin \theta \tag{Eq. 1.13}
\]

where \(n\) is the diffraction order; \(\lambda\) is the wavelength of the X-rays; \(d\) is the distance between two lattice planes and \(\theta\) is the Bragg angle between the surface and the X-ray beam where a maximum in the diffracted intensity
occurs. The angle between the diffracted and incoming beam is $2\theta$. The principle of diffraction is shown in Figure 1.14.

![Diagram of Bragg's diffraction law]

*Fig. 1.14. A schematic representation of Bragg's diffraction law*

The X-rays are reflected from a plane with the angle of reflection equal to the angle of incidence. A part of the X-rays is transmitted to be subsequently reflected by succeeding planes. A plot of the intensities as a function of $2\theta$ is analysed and the location of the peaks is characteristic for different crystal planes. Using a database, the spectra can be matched to a known crystal structure. The range $2\theta = 10^\circ$ to $90^\circ$ is sufficient to cover the most useful part of the spectrum for most materials. Thin films can be investigated by grazing incidence diffraction, where the incident beam strikes the sample at a fixed angle of about 1-4 degrees and the path length of the X-rays through the samples is much longer than in the case of $\theta$-$2\theta$ scanning, yielding more intensity of the diffracted X-ray beam.

**Electron Microscopy and Energy Dispersive X-ray Diffraction**

Scanning Electron Microscopy (SEM) is one of the most used tools in materials research. It provides information about morphology, phase distribution, compositional differences, crystal orientation, and the presence
of defects. A schematic presentation of an Electron Microscope is shown in Figure 1.15.

A beam of accelerated electrons is focussed onto a sample by electromagnetic fields. These electrons interact with atoms in the sample, which eventually yields a two-dimensional grey-scale image. A wide range of magnifications from 10 to 100,000 is covered\(^4\). Most semiconductor samples have a low conductivity and the electrons of the beam will charge the surface. Therefore, before analysis of the samples, a layer of gold is sputtered on top to provide electrical conductivity. Sputter coating is a technique to deposit thin films of various elements on substrates using an argon plasma. Accelerated Ar-ions hit an electrode made of the desired element, evaporating part of it, which is deposited on the sample. For the measurements discussed here, gold is sputtered using an Edwards Sputter Coater S 150B with a current of 20 mA and a pressure around 7 mbar of argon. The samples are fixed on the holder by carbon stickers. SEM pictures have been obtained using a Joel JSM 5800 LV electron microscope.

Transmission Electron Microscopy (TEM) is a related technique in which electrons, transmitted through the sample, are being studied. The resolution of this technique is much higher (down to the atomic level), but sample preparation is more laborious, while only very thin samples in the form of powder or of a thin film can be used. Atomic Force Microscopy (AFM) does not use electron beams, but yields information on surface morphologies by running a very small and sharp needle over the sample. The needle touches the surface and follows its height profile (contact and tapping mode). If it moves above the sample at a fixed height, it maps the Coulomb forces between the sample surface and the needle (non-contact mode).

The composition of the sample can be analysed using Energy Dispersive X-ray diffraction (EDX). This technique consists of a detector that is used to measure X-rays from the sample induced by the electron beam from the SEM. A Si (Li) semiconductor detector analyses the characteristic X-rays emitted from the sample. The energy of the detected X-rays relates to the elements present in the sample and the intensity of the peaks is proportional
to the amount of the element present. With the EDX technique qualitative analysis (identification of elements) as well as quantitative analysis can be performed. The measurements in this report were carried out using an Oxford Link-Isis EDX.

![Schematic representation of a Scanning Electron Microscope.](image)

**Fig. 1.15. Schematic representation of a Scanning Electron Microscope.**

**Film thickness**

Film thicknesses of thin films can be determined in two ways. For most materials it is convenient to scratch the surface or to etch a trench to create a sharp transition from substrate to film. With a surface profilometer, consisting of a very sharp and small needle that follows the surface, a step can be visualized from which the film thickness can be calculated. In Fig. 1.16 an example of such a step profiler spectrum is shown.

For hard materials, like TiO₂, neither scratching nor selective etching is possible without damaging the underlying substrate. In this case we can make use of the interference of visible light with films with a thickness in the order of this wavelength. By measuring the reflection (%R) as a function of wavelength it is possible to calculate the thickness of the film. The reflection can be measured with a spectrophotometer. The principle of measuring the reflection is based on Bragg's law (see the part about XRD). Interference of thin films with visible light yields maxima and minima in the reflection
spectrum. To calculate the thickness of the films from the reflection data the following formula is used:

$$a = p \frac{\lambda_1 \lambda_2}{\lambda_1 - \lambda_2} \frac{1}{2n_d}$$

(Eq. 1.14)

where $\lambda_1$ and $\lambda_2$ represent wavelengths where the reflection has a maximum or a minimum, $n_d$ is the refraction index, $p$ is the number of waves (between two adjacent maxima $p=1$), and $a$ is the thickness of the film. From the reflectance spectra it is now possible to calculate the thickness of the sample. The reflection spectra of the samples are measured in the wavelength interval 200-900 nm with a CARY 1 UV-VIS spectrophotometer. The same information can also be found in transmission spectra. In Fig. 1.17 an example of such a reflection spectrum is shown.

**Fig. 1.16.** Surface profile of a zinc phthalocyanine film on TCO, scratched with a sharp needle. The film thickness can be determined to be around 350 nm.

**Fig. 1.17.** Reflection spectrum of a thin TiO$_2$ film.
Introduction

It is also possible to determine film thicknesses from cross-section pictures with the SEM. This requires uniform samples, a perpendicular cut of the sample, and SEM equipment with a resolution high enough to observe the cross-section in detail.

UV-VIS spectroscopy

From absorption spectra information can be obtained about the electronic structure of compounds. The spectrum represents a fingerprint of the compound in which charge transfer and electronic/vibrational excitations can be recognized. Peak shifts upon changes in temperature, chemical surrounding, and structure can be a tool to investigate overlap between molecules and effects of chemical alterations. A comparison between the absorption spectrum and the photoaction spectrum is important to recognize which part of the solar spectrum is used effectively in the solar cell. From the absorption spectrum of a semiconductor it is also possible to determine the bandgap. The basis of all spectroscopic parameters is the law of Lambert-Beer:

\[ \log \frac{I}{I_0} = -\alpha [J] l = -a \]  

(Eq. 1.15)

in which \( I \) is the light intensity after passage through a sample with a length \( l \), \( I_o \) is the intensity of the incoming light, \( \alpha \) is the molar absorption coefficient (extinction coefficient) of an absorbing species \( J \) with a molar concentration of \([J]\) and \( a \) is the absorbance (also called Optical Density O.D.) of the sample. The sample can either be present in solution, in powdered form, or in a thin film. In the last two cases no molar concentration term is present in the equation. The value \( I/I_o \) is referred to as transmittance \( T \) and is commonly expressed as a percentage. This transmittance is measured with a detector behind the sample. The reflection \( R \) and absorption \( A \) are also percentage numbers and add up to 100% with \( T \). Often the reflection of thin film samples is neglected and the absorption is calculated using:

\[ A=100\% - T \]  

(Eq. 1.16)

For powders also the reflection should be measured to calculate the absorption. From the absorbance as a function of sample length, the slope is equal to the extinction coefficient (see equation 1.13).
Raman spectroscopy

Raman spectroscopy is related to infrared (IR) spectroscopy and yields information on the excitation of vibrational energy levels. The difference between the two techniques is related to their respective selection rules. In IR spectroscopy vibration excitation is visible if the dipole moment of the molecule is changed, while in Raman spectroscopy the polarizability of the molecule (i.e., the "shape") must change. The set-up used in this study is home-built and uses a 532 nm excitation laser. Spectra can be obtained between 50 and 1400 relative cm⁻¹. Raman spectroscopy is a powerful technique because it is fast, easy to use, and capable of recording fingerprint spectra of molecules. Crystal structures can also be studied due to the fact that also phonons (lattice vibrations) are Raman active. In Chapter 6 Raman spectroscopy is used to investigate the crystal structure of TiO₂ thin films.

Luminescence spectroscopy

Luminescence is a powerful tool to investigate optical and electronic processes in solar cell materials. Photoluminescence (PL) spectroscopy can yield information about the energy of electronic and vibrational levels, about trap levels (if they are luminescent), and the nature of excitons inside organic materials. It also presents a fingerprint of the studied compounds. From measurements at different temperatures, information can be obtained about the relative importance of different processes. For hybrid solar cells PL spectroscopy is used often to study the separate and combined compounds for the p-n junction. If the PL of the organic compound decreases upon addition of the metal oxide, this means that a competing process is occurring, i.e., injection of electrons from the organic to the inorganic compound. This quenching effect is used as a first assessment of the quality of the solar cell, but requires a quantitative and reliable measurement of the PL. In Chapter 7 PL spectroscopy is used extensively to study different thiophene oligomers. Some more information on the background of spectroscopic processes is given below.
Introduction

In principle, every compound, except metals, can show luminescence in some way. In Fig. 1.18 an energy diagram is shown following the Born-Oppenheimer approximation, which is valid for most organic and inorganic substances. This approximation states that the electronic and nuclear motions can be separated, because nuclei have a much higher mass than electrons and therefore move on a far slower timescale. Electronic energy diagrams can now be displayed as a function of internuclear distance. Upon laser excitation, several processes can occur. Usually the minimum of the first excited state (most of the time a singlet, denoted here as \( S_1 \)) is not exactly above the minimum of the ground state (\( S_0 \)). According to the Franck-Condon principle, transition takes place between vibrational levels that have maximum overlap of their wave functions. Thus, the electron will be excited to a higher vibrational level in the first excited singlet state (\( S_1 \)) band upon absorption of a photon. Subsequently, vibration relaxation to the lowest vibrational level takes place rapidly. From there the electron can relax to the ground state, converting its energy into heat (radiation-less decay) or light (fluorescence, F). It can also move to another singlet state via internal conversion or to a triplet state (T) via intersystem crossing (ISC). From a triplet state phosphorescence (P) can be observed, if the electron falls back from the lowest vibrational level to the ground state. While triplet-singlet transitions are forbidden due to the spin selection rule, phosphorescence is mostly very weak. Fluorescence and phosphorescence are also referred to as luminescence in a combined term. Next to excitation with light, also other mechanisms that can produce radiative emission exist. Current can lead to electroluminescence, for example, but these kinds of processes are outside the scope of this introduction and here only photoluminescence will be addressed. In some cases, the excitation energy can be transferred to a neighbouring atom/molecule/ion. This process is called energy transfer.

From the figure it is also clear that there is an energy difference between the absorption (following the excitation) and fluorescence as a result of the vibration relaxation. This so-called Stokes-shift can be observed as the difference between the maximum of the absorption spectrum and the fluorescence spectrum, provided that the same transition is being considered.
Fig. 1.18. Energy diagram, showing the ground state and two excited states with their vibrational levels and optical processes. Symbols are explained in the text. The configuration coordinate is related to the internuclear separation.

Other spectroscopic techniques include transient absorption and photoinduced absorption (PIA), which yield information about lifetimes of excited species and kinetics of processes inside solar cells.

1.4 Outline of this thesis

In this Ph.D. thesis hybrid solar cells, based on sensitisation of titanium dioxide, are investigated. The research is focussed on the bottlenecks for the functioning of solar cells. First, the main compounds are introduced and several of their properties are discussed. In Chapter 2 TiO₂ will play the leading part, whereas in Chapters 3 and 5 the sensitizing organic dyes are in the spotlight. In Chapter 3 bi-layer devices of TiO₂ and zinc phthalocyanine are investigated in detail. Doping with oxygen and the resulting effect on the photovoltaic activity of the cells is discussed in Chapter 4. In Chapter 6 the focus is shifted to nanostructured systems and a new method to deposit films
of nanostructured TiO$_2$ is introduced, sensitized with the semiconducting polymer poly(3-octylthiophene). One of the key issues in this chapter is the question as to which extend the polymer can penetrate a nc-TiO$_2$ film. In Chapter 7 the formation of a nanostructured heterojunction using yet another approach is described. First, the pores of an nc-TiO$_2$ film are filled with small thiophene oligomers, which are subsequently polymerized under UV-illumination. The techniques employed in this chapter are mostly spectroscopic of nature. In Chapter 8, finally, a recently developed technique to obtain highly ordered porous TiO$_2$ to form solar cells with poly(3-octylthiophene) is presented. The TiO$_2$ photonic crystals used in this chapter are under intense study to date for their interesting optical properties. We are, however, merely interested in their inherent high ordering and have successfully made inverse TiO$_2$ opals with small pores that can be used in solar cells.
References

(2) Solar Cells and Their Application; Partain, L.D. Editor, John Wiley and Sons. 1995.


2

Titanium Dioxide

In this chapter the focus is on titanium dioxide ($\text{TiO}_2$), which forms the basis of all solar cells that will be discussed throughout this thesis. $\text{TiO}_2$ is a suitable material to use in solar cells because of its stability, low price, and ease of fabrication. It is a wide-bandgap semiconductor with a convenient position of the conduction and valence band energies. Because $\text{TiO}_2$ is easy to deposit with various morphologies, crystal structures, and thicknesses it is especially useful for laboratory devices. In § 2.1 background information on the properties of $\text{TiO}_2$ will be given, while in § 2.2- § 2.4 three ways to deposit thin, dense films of $\text{TiO}_2$ will be discussed in detail. Finally, in § 2.5 techniques to prepare nanoporous films of $\text{TiO}_2$ are described.
2.1 Introduction

Titanium dioxide

Titanium dioxide \((\text{TiO}_2)\) belongs to the family of transition metal oxides, to which for example also \(\text{ZnO}\) and \(\text{FeO}\) belong. It is commercially available in three crystal structures: anatase, rutile, and brookite. In addition, five other polymorphs can be made synthetically, but the first two mentioned have the most interesting properties. Anatase is formed by chemical reactions at temperatures below 500° C. Rutile can be obtained by heating other polymorphs to high temperatures (700-1000°C) and is the thermodynamically stable structure at all temperatures. Anatase and rutile have a different arrangement of the oxide ions. The anatase structure is cubic-close packed while the structure of rutile is based on a slightly distorted hexagonal-close packing of oxide ions. These structures are shown in Figure 2.1.

\(\text{TiO}_2\) was produced from the mineral \(\text{FeTiO}_3\) (ilmenite) for the first time in 1791. In the beginning of the 20th century industrial production started, replacing toxic lead oxides as pigments for white paint. At present the annual production of \(\text{TiO}_2\) exceeds 4 million tons. It is used as a white pigment in paints (51% of total production), plastic (19%), paper (17%), toothpaste, chewing gum, and as a UV-absorber in sun cream and other cosmetic products (together 3%). Ilmenite is especially abundant in Australia, the USA, India, and South-Africa. Rutile and anatase can also be found as minerals. Titanium dioxide pigment may be manufactured by either the sulfate or the chlorine process. In the sulfate process ilmenite is transformed into iron- and titanium sulfates by adding sulphuric acid. The \(\text{TiSO}_4\) is extracted and calcined to form \(\text{TiO}_2\). This process yields a substantial amount of waste iron sulfides and a poor quality \(\text{TiO}_2\). Therefore, to date the chlorine process has become the dominant method. This process uses rutile, which is either used as excavated or is produced in a crude quality from ilmenite using the Becher process. The Becher process reduces the iron oxide in the ilmenite to metallic iron and then re-oxidises it to iron oxide separating out the titanium dioxide as synthetic rutile of about 91 to
93 percent purity. The process involves a high temperature furnace to heat the ilmenite with coal and sulfur. The slurry of reduced ilmenite (which consists of a mixture of iron and titanium dioxide in water) is oxidised with air and can be separated in settling ponds. The iron oxide (that represented at least 40 per cent of the ilmenite) is returned to the mine site as waste and landfilling. The rutile is reacted with chlorine to produce titanium tetrachloride, which is purified and reoxidized, yielding very pure TiO₂. The chlorine gas is recycled.

Fig. 2.1. Unit cell of TiO₂ polymorphs: anatase (A) and rutile (B).
The space group of anatase is I₄/amd and the dimensions of the unit cell are: a=3.784 nm and c=9.515 nm. The space group of rutile is P₄/mmm and the dimensions of the unit cell are: a=4.593 nm and c=2.959 nm.

TiO₂ has received a great deal of attention due to its chemical stability, non-toxicity, low cost, and other advantageous properties. As a result of its high refractive index it is used as anti-reflection coating in silicon solar cells. And because of its hardness and high coating quality it also finds application as corrosion protector. In batteries, the anatase form is used as anode material in which lithium ions can intercalate reversibly. For solar cell applications the anatase structure is preferred over the rutile structure, as anatase exhibits a
higher electron mobility, a lower dielectric constant, a lower density, and a lower deposition temperature. The bandgap of anatase is slightly larger than that of rutile, but both only absorb in the UV part of the solar spectrum. In Table 2.1 selected properties of anatase and rutile TiO₂ are summarized.

<table>
<thead>
<tr>
<th></th>
<th>Anatase</th>
<th>Rutile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap (eV)⁷</td>
<td>3.26</td>
<td>3.05</td>
</tr>
<tr>
<td>Density (kg/m³)⁸</td>
<td>3.84×10³</td>
<td>4.26×10³</td>
</tr>
<tr>
<td>Dielectric constant⁹</td>
<td>55</td>
<td>170 E//c; 86 E//a*</td>
</tr>
<tr>
<td>Refractive index⁷</td>
<td>2.49-2.55</td>
<td>2.61-2.90</td>
</tr>
</tbody>
</table>

* E//c: electrical field parallel to c-axis of unit cell. E//a: electrical field parallel to a-axis.

Due to oxygen vacancies TiO₂ is an n-type semiconductor. These vacancies are formed according to the following reaction:

\[
\text{TiO}_2
\]

\[
\text{O}_o^* \rightarrow \text{V}_o^{**} + 2\text{e}^- + \frac{1}{2} \text{O}_2(\text{g})
\]  \text{(R 2.1)}

in which the Kröger-Vink defect notation is used. In words, this says that inside TiO₂ a positive (2+) charged oxide ion vacancy (V_o^{**}) is formed upon release of two electrons and molecular oxygen. This reaction can, for example, be induced by heating (in a oxygen poor environment).

**Zinc oxide**

Zinc oxide (ZnO) is, like titanium dioxide, a wide-bandgap semiconductor and belongs to the family of amphoteric metal oxides (meaning that it can both react with acids and bases). ZnO adopts a wurtzite-type structure consisting of a hexagonal-close packing, where each zinc atom is coordinated by four oxide ions forming a distorted tetrahedron. In a similar manner each oxide ion is surrounded by a distorted tetrahedron of zinc ions, but the orientation of this tetrahedron is antiparallel to that surrounding the Zn atom⁹. This structure is show in Figure 2.2⁹.
ZnO has found practical applications in rubber products, printing ink, and electrical circuits. It is also used, like TiO₂, as a white pigment in paints, cosmetics, and pharmaceutical products\(^*\). Other properties are presented in Table 2.2.

![Schematic representation of the ZnO wurtzite structure.](image)

**Fig. 2.2. Schematic representation of the ZnO wurtzite structure.**

**Table 2.2. Properties of ZnO\(^*\).**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap (eV)</td>
<td>3.3</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.008-2.029</td>
</tr>
<tr>
<td>Resistivity (Ωcm) (^*)</td>
<td>0.1</td>
</tr>
<tr>
<td>Density (kg/m(^3))</td>
<td>5.61x10(^3)</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>1.7-2.5</td>
</tr>
</tbody>
</table>

\(^*\)Depends strongly on doping level

Zinc oxide absorbs in the UV region, has a high transparency in the visible region of the solar spectrum, and a high reflectance in the infrared (IR). It is an n-type material with a high electrical conductivity due to the presence of oxide ion vacancies and interstitial excess zinc atoms\(^*\).

Because of its reasonable chemical stability, good electrical conduction, wide band gap, and high transparency zinc oxide is one of the promising new candidates in opto-electronic applications like solar cells, heat-mirror coatings, photothermal conversion systems, gas sensors, ultrasonic
oscillators, acoustic wave, and photoluminescent devices. In §2.4, it is investigated whether thin films of ZnO and aluminium doped ZnO films can be deposited using Spray Pyrolysis Deposition.

2.2 Chemical Vapour Deposition

Chemical Vapour Deposition (CVD) is a technique for the deposition of thin films and powders from gas-phase precursors (compounds that can form the desired product by a chemical reaction). It is an extremely versatile process that can be used to process almost any compound including:

- Elements
- Metals and alloys
- Carbides
- Sulfides
- Nitrides
- Borides
- Oxides
- Composites
- Intermetallic compounds

CVD is widely used and has proven to be a reliable, reasonably cheap, and easy production method with which large substrate areas can be coated in short times. In industry a continuous process is employed to produce ceramic and semiconductor films.

There are various CVD processes such as: Atmospheric-Pressure Chemical Vapour Deposition (APCVD), Low-Pressure Chemical Vapour Deposition (LPCVD), Metal-Organic Chemical Vapour Deposition (MOCVD), Plasma-Assisted Chemical Vapour Deposition (PACVD), Plasma-Enhanced Chemical Vapour Deposition (PECVD), Laser Chemical Vapour Deposition (LCVD), Photochemical Vapour Deposition (PCVD), Chemical Vapour Infiltration (CVI), and Chemical Beam Epitaxy (CBE). In this thesis, we will use a Low-Pressure Metal-Organic Vapour Deposition (LPMO-CVD) technique to deposit thin films of TiO$_2$. There are also different ways to induce the chemical reaction that leads to the formation of the desired
product. These include: Resistive Heating, e.g., by using tube furnaces (can be subdivided into hot-wall and cold-wall reactor types), Radiant Heating, e.g., by using halogen lamps, Radio Frequency Heating, e.g., by using induction heating, and Light Excitation (UV/visible/laser).

Derivatives of CVD include Atomic Layer Deposition (ALD, also called Atomic Layer Epitaxy, ALE), which involves a pulsed input of precursors and the possibility of a monolayer-by-monolayer growth”.

Suitable precursors for CVD should be volatile, but at the same time stable enough to arrive intact at the reactor. They should decompose or react inside the reactor to give the desired product at a moderate temperature and may not lead to pollution of the film with undesired elements (for example carbon in case of organic precursors). They are preferably cheap and non-toxic and the by-products of the reaction should be non-flammable, non-toxic, and non-corrosive or should be chemically converted afterwards. Typical precursor materials fall into a number of categories such as:

- Halides - TiCl₄, TaCl₅, WF₆
- Hydrides - SiH₄, GeH₄, AlH₃(NMe₂)₂, NH₃
- Metal Alkyls - AlMe₃, Ti(CH₃Bu)₄
- Metal Alkoxides - Ti(OC₅H₃)₄
- Metal Dialylamides - Ti(NMe₂)₄
- Metal Diketonates - Cu(acac)₂
- Metal Carbonyls - Ni(CO)₄

The principle of CVD is to grow thin films on substrates from the gas-phase. Precursor gasses (often diluted in carrier gases) are delivered into a reaction chamber. As they pass over or come into contact with a heated substrate, they react or decompose forming a solid phase, which is deposited onto the substrate. The substrate temperature is critical and can influence the chemical reaction.

The principle of the CVD process is schematically shown Fig. 2.3. The process can be considered to consists of different steps:
1. Transport of reactants to the deposition zone.
2. Reactions in the gas phase. Mostly undesired (homogeneous nucleation), but sometimes necessary to form reactive compounds.
3. Diffusion of the reactants from the gas stream through a stagnant boundary layer to the substrate surface.
5. Chemical reaction between adsorbed molecules/atoms or between adsorbed molecules/atoms with molecules/atoms in the gas-phase. This reaction can be monomolecular (decomposition) or involve more molecules/atoms.
7. Diffusion of gaseous by-products through the stagnant boundary layer to the bulk stream.
8. Transport of gasses to the exhaust of the reactor.

One of these steps will be slowest and, therefore, be the rate-limiting step (also referred to as rate-determining step). In general, three cases are distinguished, which yield three regions in the Arrhenius plot (Fig. 2.4). Here an example for SnO$_2$ is shown. In this plot the growth-rate of the CVD film (on a log-scale) is plotted as a function of the reciprocal temperature. From the slope of the curve the activation energy of the CVD process can be calculated.

Fig. 2.3. Schematic representation of the CVD process.
Fig. 2.4. Arrhenius plot for the growth of SnO₂ films with CVD.

I. Thermodynamic limited regime. In this case step 1 or 8 is rate determining. The temperature is so high, that reaction will immediately take place when precursor molecules enter the reactor. Homogeneous nucleation will occur and powderous products will be formed. Therefore, less precursor is available for reaction on the substrate and the growth rate is inversely proportional with temperature.

II. Diffusion-limited regime. Step 3 or 7 is rate limiting. All precursor molecules that arrive at the substrate surface will immediately react. This leads to instable growth and rough films. The growth rate is almost independent of temperature.

III. Reaction-limited regime. Step 4, 5 or 6 (i.e., the surface processes) is rate limiting. Diffusion is faster than reaction and the films will grow in a controlled way, yielding a flat and dense structure and the initial surface roughness will decrease. The growth rate is highly dependent on temperature.
A CVD apparatus, in general, consists of several basic components:

1. Gas delivery system – For the supply of precursors to the reactor chamber.
2. Reactor – Chamber in which deposition takes place
3. Energy source – To provide the energy that is required to decompose the precursors or to have the precursor react.
4. Vacuum system – To keep the reactor at low pressure. If desired.
5. Exhaust system – System for removal of volatile by-products from the reaction chamber.
6. Exhaust treatment systems (also referred to as scrubber system) – In some instances, exhaust gasses may not be suitable for release into the atmosphere and may require treatment or conversion to safe/harmless compounds.
7. Process control equipment – Gauges, controls etc. to monitor process parameters such as pressure, temperature and time. Alarms and safety devices are also included in this category if they are present.

In this study an LPMO-CVD reactor is used to deposit thin films of TiO₂. In Fig. 2.5 a schematic drawing of the set-up is depicted, showing the various elements of the apparatus. Titanium tetraisopropoxide (TTIP) is used as a liquid precursor.

In Table 2.3 the reaction conditions are displayed, which are used in the experiments to deposit thin films of TiO₂. The deposition temperature is varied to study the crystal structure, the rate-limitations of the reaction, and the properties of the resulting TiO₂. As substrate material TCO (transparent conducting oxide) is used, which consists of a glass substrate (2.3 mm thick) with a conducting, transparent film (400 nm) of fluor doped tin dioxide (SnO₂:F) on top.

In literature the CVD process of anatase TiO₂ is described in detail, with most depositions performed at temperatures of 300-450 °C\(^{16,17}\). However, to be able to deposit TiO₂ films on top of (nanostructured) organic films for hybrid
solar cells, a lower deposition temperature is necessary in order to prevent decomposition or evaporation of the organic phase. Some reports have shown that amorphous TiO₂ is formed already at 150°C from metal-organic precursors. With an annealing step afterwards this could be transformed into anatase, provided that the organic phase is completely confined and is able to withstand this temperature. To grow smooth films, the reaction should preferably be reaction-limited.

![Diagram](image)

**Fig. 2.5.** Scheme of the LPMO-CVD set-up. A bye-pass (combination of valves) is used to facilitate the flow of nitrogen gas before the carrier flow is led through the precursor vessel. The reflux cooler is set at a slightly lower temperature than the precursor solution to obtain a saturated vapour.

**Table 2.3.** Deposition conditions for LPMO-CVD of thin film TiO₂.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature reactor</td>
<td>100-350 °C</td>
</tr>
<tr>
<td>Temperature TTIP</td>
<td>85 °C</td>
</tr>
<tr>
<td>Temperature reflux</td>
<td>65 °C</td>
</tr>
<tr>
<td>Pressure in reactor</td>
<td>20 Torr</td>
</tr>
<tr>
<td>Bulk nitrogen flow</td>
<td>500 sccm</td>
</tr>
<tr>
<td>Carrier nitrogen flow</td>
<td>50 sccm</td>
</tr>
<tr>
<td>Temperature of lines</td>
<td>80 °C</td>
</tr>
</tbody>
</table>

*1 Torr = 133,3224 Pa

* sccm stands for standard cubic centimetres per minute, i.e., ml/min under standard conditions (temperature, pressure).
CVD experiments are performed at different temperatures and the crystal structure of the TiO₂ films are studied with XRD. In Fig. 2.6 XRD spectra are shown for TiO₂ films on TCO, deposited at different temperatures. From the figure, it is apparent that at temperatures below 250°C no anatase TiO₂ is formed. Annealing the samples after deposition in air at 450°C for 2hrs does not crystallize the samples. At 250°C the TiO₂ films are still amorphous, but annealing in air at 450°C for 2 h does now yield the anatase structure. At 300°C and beyond, anatase TiO₂ is formed directly during the CVD process. Other precursors, or the addition of oxygen might lower the crystallisation threshold of the CVD reaction. On soda-lime glass, it is not possible to obtain anatase TiO₂ at any temperature, which is due to the sodium ions that diffuse into the TiO₂ during deposition. Hence, this kind of glass is not applicable, as sodium ions from the glass will prevent crystallisation and will contaminate the films.

![XRD plots of TiO₂ films on TCO, grown at 140°C, 200°C, 250°C, 250°C (annealed at 450°C for 2 hours in air), and 300°C. Spectra are vertically offset for clarity. The * denotes the peaks from the TCO substrate, the # denotes the anatase peaks.](image-url)
From SEM measurements (not shown) the films look smooth and homogeneous. In Fig. 2.7 the Arrhenius plot of the TiO$_2$ growth rate between 150°C and 300°C is shown. The film thicknesses were determined using the interference patterns in the reflection spectra as described in §1.3.7. The growth rate can be calculated from the film thickness and the deposition time. The slope of this curve can be related to the activation energy for the CVD process, which is calculated to be 78 kJ/mol for this curve. The literature value is 150.6 kJ/mol. The discrepancy between the experimentally obtained value and the literature value is probably due to the errors of the reflection method to determine the film thickness. The error in this method is estimated to be easily 100 nm, which has a large influence on the calculated growth rate for thin films. Clearly, this method to determine film thicknesses is not ideal. Using cross-section measurements (SEM) would be a more reliable method, but for thin films a high resolution is a prerequisite, which is not available in our department. It is indeed shown, that for these temperatures the CVD process is in the reaction-limited regime.

![Arrhenius plot](image)

*Fig. 2.7. Arrhenius plot of the CVD of TiO$_2$. In the inset linear fit parameters are shown.*

Electrical measurements are performed to investigate the properties of the CVD-deposited TiO$_2$ films. The electrode materials are TCO and mercury. I-V plots in the dark of the TiO$_2$ films show a diodic behaviour (inset Fig. 2.8)
with good rectifying characteristics. Bode plots of the impedance at different bias potentials are shown in Fig. 2.8. For the largest part the curves overlap, showing that no drastic changes in the TiO$_x$ take place if a bias voltage is applied.

Fig. 2.8. Bode plots of the real and imaginary part of the impedance of a TiO$_x$ film (around 100 nm thickness) deposited at 300°C. Inset: I-V curve of the same sample. As a front-contact a circular mercury droplet with a diameter of 2 mm is applied. In the forward direction the mercury droplet is positively charged.

As mentioned in §1.3.6 this Bode plots can be used to determine the frequency at which the Mott-Schottky method can be applied to determine the donor density. In the case of TiO$_x$, the donor density obtained is a value for the concentration of oxide ion vacancies (V$_{ox}^-$) in the film, as they are the dominant electron donors in this system. From the Bode plot we can conclude that only at very high frequencies (> 200 kHz) straightforward Mott-Schottky analysis is allowed. This frequency is in fact around the maximum that can be applied in Mott-Schottky measurements, due to the apparatus limitations of the Frequency Response Analyser (Solartron 1255)
used in this study. The resistance of the TiO₂ is apparently quite high. In Fig. 2.9 a Mott-Schottky plot of this sample is shown, measured at 100 kHz.

![Graph of Mott-Schottky plot](image)

**Fig. 2.9.** Mott-Schottky plot of a TiO₂ film (thickness 100 nm) on TCO, deposited with CVD at 300°C. The modulating frequency is 100 kHz and the scan is started at 1V. As a front-contact a circular mercury droplet with a diameter of 2 mm is applied. In the forward direction the mercury droplet is positively charged.

A hysteresis is observed when scanning to and from -1V. This is not uncommon in Mott-Schottky plots and is probably related to storing of charges in the first half of the potential scan, which are released at a slow rate in the second half. This assumption would lead to a deviation in the value of the flat-band potential for the second half of the scan. At voltages between 0.2 and 1V a second slope is seen, which originates from the TCO substrate. The donor density of this TCO film is about $10^9$ cm⁻³.

If TiO₂ films are annealed in air, the donor density is expected to decrease, thus increasing the resistance of the film even further. In this case Mott-Schottky analysis is not possible in a simple way. This is also true for measurements on non-annealed, thicker films. One option would be to use larger contact areas, another option is to exploit the admittance approach, as explained in §1.3.6.
For thin TiO₂ films (less than 100 nm) donor densities are obtained from slopes of the Mott-Schottky plots. The films are deposited at 300°C and are subsequently annealed in air or vacuum at 450°C for 2 hours afterwards. For samples annealed in air, the average donor density is $5 \times 10^{15}$ cm$^{-3}$, while for vacuum annealed TiO₂ the donor density is $4 \times 10^{16}$ cm$^{-3}$. Both numbers are rather low as compared to, for example, donor densities of electron beam evaporated samples (see § 2.3), explaining the high resistance of the films. The flat band potential is around $-1$V, in agreement with literature values$^{20,21}$.

### 2.3 Electron Beam Evaporation

In the preceding section Chemical Vapour Deposition has been described as a technique in which gaseous precursor molecules decompose or react to yield a thin film of a desired product on a substrate. Another class of deposition techniques is Physical Vapour Deposition (PVD), in which also thin films are formed from the gas phase, but here without a chemical transition from precursor to product. This is, therefore, only possible with substances that can be brought into the gas phase without decomposing or reacting. The most common of these PVD techniques is thermal evaporation, in which a material is evaporated from a crucible and deposited onto a substrate. PVD is a so-called line-of-sight technique, i.e., the gaseous stream of material follows a straight line from source to substrate. This leads to shadow effects, which are not strongly present in CVD. The substrate can be at room temperature, or heated/cooled, depending on the requirements. In most set-ups the substrates are placed straight above the source, but other arrangements are also possible. In most cases evaporation takes place under reduced pressure to minimize collisions of gas molecules and to prevent pollution of the deposited films. In Electron Beam (E-beam) Evaporation a focussed beam of electrons heats the selected material. These electrons in turn are thermally generated from a tungsten wire that is resistively heated by a current.

TiO₂ films, deposited with E-beam Evaporation, have superior characteristics over CVD grown films if smoothness, conductivity, presence of contaminations, and crystallinity are concerned, but on the other hand production is slower and more laborious. The use of reduced TiO₂ powder
(heated at 900°C in a hydrogen atmosphere) is necessary to make it conductive enough to focus the electron-beam in the crucible\textsuperscript{2}.

TiO\textsubscript{2} films have been grown on quartz substrates using E-beam evaporation. Prior to deposition a thin, semitransparent film of titanium metal (40-60 nm) is evaporated to serve as electrical contact. The experimental conditions are summarized in Table 2.4. During deposition of TiO\textsubscript{2} additional oxygen is added to achieve stoichiometry of the films. The growth of the film can be monitored with a quartz crystal microbalance.

\begin{table}[h]
\centering
\caption{Parameters for E-beam deposition of TiO\textsubscript{2} films.}
\begin{tabular}{ll}
\hline
Base pressure (Ar) & \(2\times10^{-6}\) mbar \\
Oxygen partial pressure & \(2\times10^{-4}\) mbar \\
Substrate temperature & 200°C \\
Growth rate & 2 nm/min \\
Emission current & 40 mA \\
\hline
\end{tabular}
\end{table}

After deposition an anneal treatment at 450°C in air is routinely performed. In Fig. 2.10 XRD spectra are shown for films annealed at 450°C for two different periods of time. Although the noise-level is quite high, it is possible to observe the anatase peaks in both films, whereas a rutile fraction occurs for the longer annealed sample.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{xrd_spectra.png}
\caption{XRD spectra for TiO\textsubscript{2} films (100 nm) on quartz annealed at 450°C in air for 0.5 h (bottom curve) and 2 h (top curve). The \# denotes the anatase peaks, the * denotes the rutile peaks.}
\end{figure}
From previous work it is known that the donor density in these kinds of films is in the order of $7 \times 10^{16}$ cm$^{-3}$, which is higher than for CVD grown films. This has advantages for use in solar cells, as it leads to a lower resistance of the film. A higher donor density also yields a higher interfacial electrical field, which splits excitons more effectively.

2.4 Spray Pyrolysis

Spray pyrolysis is an aerosol deposition technique for thin films and powders related to CVD. The main differences are:

1. In spray pyrolysis an aerosol (a mist of small droplets) is formed from a precursor solution instead of a vapour in CVD.

2. In spray pyrolysis, the aerosol is directly focused onto the sample in most cases, whereas diffusion is a dominant process in CVD.

3. In spray pyrolysis the heated substrates are at ambient pressure, while in CVD the set-up commonly is under reduced pressure.

There are several small derivatives of this technique, mainly differentiating in the formation-step of the aerosol. The aerosol can be induced using ultrasonic agitation (see Chapter 6), pressured gas (used in this section), or electrostatic forces (ESD, electrostatic spray deposition). The reaction at the substrate can be categorized into gas-to-particle synthesis (the aerosol turns into vapour above the heated substrates, resembling a CVD process) and droplet-to-particle synthesis (the droplets reach the surface before they react). Less used methods include the encapsulation of droplets and the use of "sieves" to filter out larger droplets.

The first patent on this technique was granted in 1956 and describes the synthesis of MgO powder from a heated mist of a magnesium chloride solution. A broad spectrum of names for this class of techniques has evolved since then, including aerosol decomposition, spray pyrolysis, evaporative decomposition, spray roasting, spray calcination, Anan process, aerosol pyrolysis, atomizing burner technique, Ruthner process, decomposition of
misted solutions, thermal spray deposition, and liquid aerosol thermolysis. It has been used for preparation of (mixed) oxide powders/films and uses mostly metal-organic compounds or metal salts as precursors\textsuperscript{53,35,34}. The process is divided into the following steps:

1. solution droplet formation
2. solvent evaporation
3. precipitation
4. decomposition/reaction

The size of the aerosol droplets is governed by parameters like surface tension, density, molecular weight of the precursor, the process parameters of the aerosol generation (for example gas pressure or ultrasonic frequency), and the concentration of the precursor. The size of the particles formed and the morphology of the resulting film are strongly dependent on deposition parameters like substrate temperature, composition and concentration of the precursor, gas flow, and substrate-nozzle distance. Some of these parameters are mutually dependent on each other.

Compared to other thin-film deposition methods, spray pyrolysis of, for example TiO\textsubscript{2}, has the merits of simplicity, low costs, reproducibility, and the possibility of depositing large areas in a short time\textsuperscript{37}, while the films exhibit good electrical and optical properties. Uniformity is in most cases a problem, as well as the roughness of the films. If the right parameters are chosen, also nanostructured films of TiO\textsubscript{2} can be formed using spray pyrolysis, which could be used in nanostructured heterojunction solar cells\textsuperscript{33}.

In this study a simple spray pyrolysis set-up is used to deposit thin films of TiO\textsubscript{2} and ZnO. The system consists of an electrical heater on which the substrates are placed and a flask containing the precursor solution provided with a nozzle. The spraying system is illustrated in Figure 2.11. By leading pressured air or oxygen through the nozzle, a spray of droplets is formed. The spray head is moved manually over the substrates, keeping it at a fixed height. The temperature of the substrate is measured with a thermocouple on
top of the substrate before the start of the deposition. It is anticipated that the real temperature of the heating plate is somewhat higher (a 25°C difference is possible).

Figure 2.11. Spray pyrolysis set-up. The following parts are shown (A): heater (a) with substrates, thermocouple unit (b), compressed air (or pure oxygen) (c), handle bar (d), and the spray head (e). This last part is shown enlarged in panel (B).

The solvent of the aerosol droplets evaporates leaving the precursor to react to form a thin film on the substrates. An advantage of this technique is the ease with which films can be doped. The dopant can be added in the form of a salt to the precursor solution in the desired concentration. To prevent the precursor to react vigorously with air or water, which would lead to low-quality films, the precursor is stabilized.

For titanium dioxide the employed precursor is the same as for the CVD experiments, i.e., titanium tetraisopropoxide (TTIP), of which 2.4 ml is mixed with 3.6 ml of acetyl acetone, leading to the following exothermic reaction\(^n:\)

\[
\text{Ti(O-} \text{C}_3\text{H}_7)_4 + 2\text{C}_5\text{H}_8\text{O}_2 \rightarrow \text{Ti(O-} \text{C}_3\text{H}_7)_2(\text{C}_5\text{H}_7\text{O}_2)_2 + 2\text{C}_3\text{H}_8\text{O} \quad (\text{R. 2.2})
\]
The Ti(acetyl acetate)$_2$(isopropoxide)$_2$ formed is less reactive than TTIP and is diluted with 54 ml of ethanol.

The precursor solution for the ZnO thin films contains 1.1 g zinc acetate dihydrate (Zn(CH$_3$COO)$_2$•2H$_2$O dissolved in a mixture of 20 ml methanol and 30 ml ethanol. A few drops of glacial acetic acid are added to avoid the precipitation of zinc hydroxide. When the aerosol droplets of the precursor solution have almost reached the heated substrate a pyrolytic process occurs and highly adherent ZnO films are produced according to the following steps:

\[
\begin{align*}
(1) \quad & 4\text{Zn(CH}_3\text{COO)}_2\cdot 2\text{H}_2\text{O (s) } \rightarrow 4\text{Zn(CH}_3\text{COO)}_2\text{(g) } + 8\text{H}_2\text{O(g) } \rightarrow \\
& \quad \text{Zn}_4\text{O(CH}_3\text{COO)}_6\text{(s) } + 2\text{CH}_3\text{COOH(g)} \quad \text{(R. 2.3)}
\end{align*}
\]

\[
(2) \quad \text{Zn}_4\text{O(CH}_3\text{COO)}_6\text{(s) } + 3\text{H}_2\text{O(g) } \rightarrow 4\text{ZnO(s) } + 6\text{CH}_3\text{COOH(g)}
\]

In Table 2.5 the experimental conditions for the spray pyrolysis process are summarized. The temperature, deposition times, and spraying gas (air or oxygen) are varied to study the properties of the deposited films. The spray head is moved over the substrate in order to obtain a homogeneous thickness of the samples and every spray pulse starts and stops outside the substrate area. During deposition, the thickness and the uniformity can be roughly estimated by monitoring the appearing of interference colours of the light refracted from the films.

**Table 2.5. Parameters for the spray pyrolysis of TiO$_2$ and ZnO thin films. TCO is used as substrates material.**

<table>
<thead>
<tr>
<th>Substrate temperature</th>
<th>300-500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas pressure</td>
<td>2.5 bar</td>
</tr>
<tr>
<td>Distance nozzle-heater</td>
<td>10 cm</td>
</tr>
<tr>
<td>Pulse length</td>
<td>3 s continuous spray, 10 s interval</td>
</tr>
<tr>
<td>Deposition time</td>
<td>5-30 min</td>
</tr>
<tr>
<td>After deposition treatment</td>
<td>30 min at spraying temperature</td>
</tr>
</tbody>
</table>
If a continuous spray mode is adopted instead of a pulsed spray mode, inhomogeneous films, consisting of particles with sizes of several hundreds of nm are obtained. This is due to fast reaction rates, limiting the time for the droplets to flow out on the substrate. In Fig. 2.12 SEM pictures are presented, showing the typical morphologies that are obtained.

![SEM micrographs of TiO₂ films on TCO deposited with spray pyrolysis in the continuous mode. The left hand panel is a strong magnification, showing the particles that are formed during spraying. The right hand panel shows an overview of the sample surface.](image)

In the pulsed spray mode, TiO₂ and ZnO films deposited with spray pyrolysis are optically transparent, uniform (no signs of cracks), and well adherent to the TCO substrates. The size of the crystalline domains increases slightly with increasing temperature as can be seen in Fig. 2.13. When going from 300°C to 425°C the crystallites in average increase in size from 200 to 300 nm. At prolonged spraying times, larger crystals start to form, giving rise to inhomogeneity (Fig. 2.13 D).

The thickness of the samples is determined with UV-VIS reflection measurements. The average growth rate is about 25 nm/min, but due to the error in the reflection measurements (around 100 nm) an accurate study of the growth kinetics is in this case not possible.
Grazing Incidence X-ray diffraction is used to investigate the crystal structure of TiO₂ thin films deposited at different temperatures. From the XRD spectra shown in Figure 2.14 is found that anatase TiO₂ is obtained between 325°C and (at least) 425°C, if air is used as a carrier gas. At temperatures below 325°C the anatase structure is not obtained.

For ZnO thin films the XRD spectra are shown in Fig. 2.15. All films have a thickness between 400 and 500 nm, but are deposited at different temperatures. The intensity of the TCO peak at 38° 2θ is indexed at the same value for all films. Crystalline ZnO starts to form at 325°C and the crystalline fraction increases at higher temperatures if air is used as a carrier gas. At temperatures above 425°C crystallinity decreases, while no indication of other
phases is present. Hence, 425°C is the optimum temperature for depositing ZnO with this technique. The reason for the decrease of crystallinity at higher temperatures is at this moment not known.

![Graph](image)

**Fig. 2.14.** Grazing Incidence X-ray Diffraction patterns of TiO₂ on TCO sprayed at various substrate temperatures. The incoming X-ray beam makes an angle of 2° with the substrate. The * denotes the anatase peaks. The other peaks originate from the TCO substrates.

![Graph](image)

**Fig. 2.15.** Grazing Incidence X-ray Diffraction patterns for ZnO films deposited with spray pyrolysis at different temperatures. Film thicknesses are between 400 and 500 nm for all films. The ZnO wurtzite peaks are denoted with *, the other peaks originate from the TCO substrates. The incoming X-ray beam makes an angle of 2° with the substrate and the TCO peak at 38° 2θ has the same intensity for all samples.
It is further investigated whether the carrier gas has an influence on the formation of deposited thin films of ZnO. Compressed air is used in the deposition of ZnO thin films at 350°C and the properties are compared to ZnO films deposited with compressed oxygen at the same temperature. In Fig. 2.16 the XRD spectra are shown for three films prepared under the same conditions and with the same thickness. One film is deposited using air as spray gas, (XRD before and after a thermal treatment at 450°C for 4h is shown) and the other film is deposited using oxygen as spray gas. If oxygen is used, larger XRD peaks are present compared to air at the same deposition temperature. It is concluded that the use of oxygen as carrier gas leads to more films with a higher crystallinity.

![Graph showing XRD spectra for different deposition conditions](image)

**Fig. 2.16. Grazing Incidence X-ray Diffraction patterns of ZnO films on TCO deposited with spray pyrolysis at 350°C using air and oxygen as a carrier gas and after annealing. The ZnO wurtzite peaks are denoted with *, the other peaks originate from the TCO substrates. In all cases the film thicknesses is 400 nm and the incoming X-ray beam makes an angle of 2° with the substrate.**

I-V curves of the TiO₂ films show good rectifying behaviour. TCO and mercury are used as electrode materials. To calculate the donor density, Mott-Schottky measurements are carried out. The value of the donor density is in the order of 1×10¹⁶ cm⁻³ for films deposited at 400°C without any
annealing. This value is similar to the donor density found for CVD-deposited TiO₂ films.

2.5 Nanostructured TiO₂

As described in paragraph 1.3.3 bi-layer solar cells exhibit a low efficiency. Dense flat TiO₂ films are, therefore, not suited for high-efficiency hybrid solar cells. Such films are, however, useful as model systems, in which fundamental properties of the solar cells can be studied. Furthermore, thin TiO₂ films can be used as selective contacts in nanostructured heterojunction cells and they are applied as such many times in the investigations described in this Ph.D. thesis.

Porous, nanocrystalline (nc) TiO₂ is needed for dye-sensitized and nanostructured heterojunction solar cells. These nc-TiO₂ films must comply with the following requirements:

1. The TiO₂ film preferably exhibits the anatase crystal structure.
2. Good electrical contact between the individual TiO₂ particles in the film and to the substrate is desired to enable optimal charge transport and collection.
3. Percolation is necessary to provide a pathway for electrons, while percolation of hole transport in the organic phase is a necessity for nanostructured heterojunctions.
4. The thickness of the nc-TiO₂ film should be chosen such that adsorption of dye molecules yields enough light absorption, while the electrical resistance is not too high.
5. The size of the particles governs the porosity of the nc-TiO₂ film and herewith the depth to which organic molecules can penetrate in the film. On the other hand, the distance between the TiO₂ particles should be in the order of the exciton diffusion length to prevent recombination losses. Both the porosity and the thickness of the film define the total interface area between TiO₂ and the dye, provided that an intimate contact between both compounds is achieved.
6. The TiO₂ film should be free of cracks and pinholes, homogeneous, and smooth.
While in nanosized TiO₂ particles no depletion layer is created if a nc-TiO₂ film is brought into contact with a p-type semiconductor, the conductivity and doping level are not important. For dye-sensitized solar cells, the thickness of the nc-TiO₂ film employed is usually between 5 and 10 µm. For nanostructured heterojunctions, this is usually much smaller, in the order of 3 µm or even less.

Most nc-TiO₂ particles that are commercially obtainable are synthesized using sol-gel methods. This involves the controlled hydrolysis of a Ti(IV) precursor (for example, TTIP or TiCl₄) in water. A sol develops and is treated in an autoclave (a high pressure and high temperature vessel) to allow controlled growth of the particles until they reach the desired size. Oswald ripening takes place during this process, leading to a homogeneous particle size distribution. After this ripening process, substances can be added to prevent, for example, cracking and agglomeration or increase the binding and viscosity. The resulting paste can be deposited on a substrate. The solvent is evaporated and the particles are interconnected by a sintering process, normally at temperatures around 450°C in air. At this temperature also organic additives are removed from the film. Slow heating and cooling is important to prevent cracking of the film. In most cases, the resulting film has a porosity of 50%. In Fig. 2.17 a SEM micrograph is shown of a film consisting of 50 nm particles. Thicknesses can be easily determined using a step profiler, as the nc-TiO₂ film is not extremely hard. Nevertheless, it is recommended to make a scratch before the sintering step.

![SEM image](image-url)

**Fig. 2.17.** SEM picture of a doctor-bladed (see text below) film of 50 nm TiO₂ particles, sol-gel synthesized and annealed at 450°C for 2h in air.
Deposition of a TiO₂ paste on flat substrates can be accomplished in various ways. Most often doctor blading is used. In Fig. 2.18 a schematic drawing of the process is shown. Two lines of Scotch tape (3M®) are placed on the substrate and a small amount of TiO₂ paste is put in between, at an edge of the sample. Using a small glass slide under an angle of about 45°, the paste is spread out over the substrate to form a homogeneous layer. After a short drying period, the Scotch tape is removed and the film of TiO₂ is annealed. Due to the loss of solvent and sintering of the particles, the final thickness of the film (8-10 μm) is much smaller than the thickness of the Scotch tape (100 μm)³⁶. By using tapes with different thicknesses the TiO₂ film thickness can be varied. This method is fast and reliable, but yields quite thick films and is not applicable for large areas. An alternative for the anneal step is to press the dried films. This technique, however, is still in the early stage of development and problems like fractioning of the substrate, cracks in the film, and insufficient inter-particle contact need to be solved. No organic substances can be added to the TiO₂ paste in this case, while they will not be removed during the sintering step which is employed in other techniques³⁶.⁴⁰.

Fig. 2.18. Schematic drawing of the doctor blade process.

Another coating technique, often used in industry, is referred to as screen-printing. It allows fast, inexpensive deposition of films over large areas. Patterned films can be deposited easily and the thickness of the film is less restricted than for doctor blading. In Fig. 2.19 a schematic drawing of the screen-printing technique is shown. A screen, which is similar to a metal
mesh, is placed a few millimetres above the substrate surface. The TiO₂ paste is placed on top of this and with a rubber "stick" the screen is rubbed. Where the screen touches the substrate, a thin film of TiO₂ paste is deposited. The thickness of the TiO₂ film is governed by the mesh parameters, the distance between screen and substrate, and the viscosity of the paste.

![Schematic drawing of the screen-printing technique.](image)

*Fig. 2.19. Schematic drawing of the screen-printing technique.*

A simple method to make a thin nanostructured film from a TiO₂ sol is dip coating (Fig. 2.20). A substrate is dipped into a TiO₂ sol and is subsequently dried. This is repeated several times, until the desired thickness is achieved. Afterwards a sintering step is applied. This method is easy and very thin films can be achieved, but the homogeneity of the film is difficult to control and slow heating is necessary to prevent cracking. With this method also dense films of TiO₂ can be deposited, if the dip coat solution contains a TiO₂ precursor, which is heated to form TiO₂ after each dip coating step.

![Schematic drawing of the dip-coat process.](image)

*Fig. 2.20. Schematic drawing of the dip-coat process.*
Another way to obtain thin nc-TiO$_2$ films is to use a spin coat process (Fig. 2.21). A solution or paste of nanocrystalline TiO$_2$ is placed on a substrate, which subsequently is rotated at high speed (normally somewhere between 1000 and 5000 rpm). The solvent evaporates and a homogeneous thin film is left. This method is also used very often for deposition of organic films. The rotation speed, the amount of solution, and the viscosity thereof determine the film thickness. Again, for TiO$_2$ films a sintering step is required afterwards. Spin coating one drop of nc-TiO$_2$ paste usually yields films with thicknesses of several hundred nanometers, while 1-2 μm thick films can be achieved if prior to spin coating a film of TiO$_2$ paste is applied to the substrate (for example with doctor blading). For diluted pastes these values are lower.

![Schematic drawing of the spin coat process.](image)

**Fig. 2.21.** Schematic drawing of the spin coat process.

### 2.6 Conclusions

Titanium dioxide is a suitable n-type semiconductor to use in solar cells. Visible light absorbing materials are necessary for sensitization due to its large bandgap. Thin films are deposited using Chemical Vapour Deposition, E-beam Evaporation, and Spray Pyrolysis Deposition, yielding dense, flat films of TiO$_2$ with good rectifying characteristics, but a high resistivity. The
donor density of the films depends on the deposition technique and the post-deposition treatment. In Table 2.6 the values are summarized.

Table 2.6. Donor densities of TiO₂ thin films, deposited with different techniques as determined by Mott-Schottky analysis.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Annealed in air (2h, 450°C)</th>
<th>Annealed in vacuum (2h, 450°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Vapour Deposition</td>
<td>5×10¹⁵ cm⁻³</td>
<td>4×10¹⁶ cm⁻³</td>
</tr>
<tr>
<td>E-beam Evaporation</td>
<td>7×10¹⁶ cm⁻³</td>
<td></td>
</tr>
<tr>
<td>Spray Pyrolysis Deposition</td>
<td>1×10¹⁶ cm⁻³*</td>
<td></td>
</tr>
</tbody>
</table>

* annealed at 400°C for 30 min.
References


(4) Thompson, R. *Industrial inorganic chemicals; production and uses*; The Royal Society of Chemistry: 1995.


Phthalocyanine

In this chapter phthalocyanines (Pc's) are discussed. This class of molecular p-
type semiconductors is used frequently in hybrid solar cells. They exhibit strong
light absorption in the visible part of the solar spectrum, good hole mobility, and
are chemically very stable. These properties make them suitable for use in solar
cells. In paragraph 3.1 an introduction to the phthalocyanines is given,
concerning their general and specific properties. In §3.2 experiments are
described on thermally evaporated films of ZnPc and solar cells based on
ZnPc/TiO₂ heterojunctions. In paragraph 3.3 sublimated ZnPc films are
investigated and their morphology is described in detail. With these films a
nanostructured ZnPc/TiO₂ network is synthesized and its photovoltaic
characteristics are discussed.
3.1 Introduction

The name phthalocyanine, from the Greek words naphtha (rock oil) and cyanine (blue), was first used by Linstead in 1933 to describe a new class of organic compounds. The compound phthalocyanine (Pc) itself was discovered by accident in 1907, when during a study of the properties of \( \alpha \)-cyanobenzamide a solution in ethanol was heated and Pc precipitated. Only some 20 years later a patent was filed describing an industrial manufacturing process. Structural studies were performed, which led to the elucidation of the crystal structure, which was one of the first for relatively large organic molecules. Since that time a large number of publications has appeared in which the synthesis and properties of many different Pc's is described.

In Fig. 3.1 the general molecular structure of metal phthalocyanines (MPc) is shown. MPc's consist of a symmetrical 18 \( \pi \)-electron aromatic macrocycle, closely related to the naturally occurring porphyrins. Like the porphyrins, over 70 different metal ions (M) can be incorporated into the central cavity.

![Molecular structure of metal phthalocyanine.](image)

MPc's exhibit properties that make them of interest for various applications like dyes (for plastics, inks, fabrics, and paints), photoconducting materials in laser printers, light absorbing species in recordable CDs, photosensitisers
Phthalocyanine

in laser cancer therapy, non-linear optical materials, chemical gas sensors, and industrial catalysts. Some selected properties are:

- MPC's can be prepared in high purity. They are easily crystallized and sublimated, resulting in materials of an exceptional purity in organic chemistry \((10^{-14}-10^{-16}\text{ impurities/cm}^3)\). This is advantageous for use in solar cells. However, most commercially available MPC's have to be purified to reach this high purity level.

- MPC's are highly thermally and chemically stable. In air they show no degradation until 400-500°C and in vacuum they are stable until 900°C. They are resistant against strong acids and bases. Only strong oxidizing compounds can decompose the molecules.

- MPC's have a high extinction coefficient (in the order of \(2\times10^3\) in solution at their maximum absorption wavelength of about 650 nm) due to their extended conjugated \(\pi\)-system. They show intense absorption in the red and their appearance in the solid-state ranges from dark blue to metallic bronze to green, depending on the charge of the central metal, the crystalline form, the doping level, and the microstructure.

- MPC's provide a versatile chemical system. The phthalocyanine ligand forms a complex with nearly all metals and semimetals from the Periodic Table, either monovalent (for example LiPc), divalent (CuPc), trivalent (forming a metal halide or metal hydroxide, like AlCl and AlOHPC), or tetravalent (forming a metal oxide, metal dihalide or metal dihydroxide, like TiOPc, SiClPc and Si(OH)Pc). The central metal ion influences physical and chemical properties, like, for example, the oxidation-reduction potentials of the MPC. The phthalocyanine ligand can also accommodate two hydrogen atoms (HPC) and form a metal free phthalocyanine. Furthermore, side groups can be attached to the phthalocyanine ring that can enhance the solubility, and alter the morphology and photoconductivity. Unsubstituted MPC's are not soluble.

- The MPC molecule is very flat, offering the possibility to form liquid crystals (see the schematic drawing in Fig. 3.2). Also, studies have been published in which crown-ethers were combined with a HPC
or MPc molecule (Fig. 3.3) These molecules form channels or coils, which may be of interest for new types of solar cells. Another way to induce stacking is to polymerize MPc’s like TiOPc and SiOPc. The oxygen atom can form a bridge between the phthalocyanine cores.

![Chemical structure](image1)

**Fig. 3.2.** Liquid crystalline Pc’s can be formed from substituted Pc’s (in A an example is shown), which can stack to form columns (B). The Pc core is shown as a cross here. In this picture free-base phthalocyanine $H_2Pc$ is shown, but liquid crystals can also be formed with metal phthalocyanines. Picture taken from ref. 7.

![Chemical structure](image2)

**Fig. 3.3.** Molecular structure of crown-ether moieties attached to $H_2Pc$. 
Most MPC’s can be synthesized in one step from the reaction of 1,2-cyanobenzene or derivatives thereof with an appropriate metal or metal salt\(^6\). Usually this (exothermic) reaction is carried out at 250-300°C in organic solvents with a high boiling point. Li\(_2\)Pc is sometimes used as an intermediate, because it is easily produced in high yields and is soluble in organic solvents at room temperature. In Fig. 3.4 the main chemical pathways for the synthesis of MPC’s are shown.

![Synthesis routes for metal phthalocyanines](image)

*Fig. 3.4. Synthesis routes for metal phthalocyanines. Taken from ref 6 and 7.*

In their solid state, most MPC’s exist in different polymorphs. The \(\beta\)-form is mostly obtained by crystallisation at higher temperatures (i.e., sublimation) and leads to needle-shaped crystals that have a bcc monoclinic lattice with the molecules orientated in a herringbone configuration. Evaporated thin films (in vacuum on substrates at room temperature) usually exhibit the \(\alpha\)-phase, which is comparable to the \(\beta\)-form, but has larger lattice spacing. The \(\alpha\)-polymorph is obtained by milling of the \(\alpha\)-form. In Fig. 3.5 a
schematic drawing of the three main polymorphs is shown. Variations on these three major types, as well as other polymorphs are possible.\textsuperscript{14}

Fig. 3.5. Polymorphs of MPc with unit cell orientation and lattice spacing.\textsuperscript{13}

MPc's have two intense absorption bands, one in the 300-400 nm region (Soret band) and the other in the 600-700 nm region (Q-band). These bands are in most cases not sensitive to the central metal ion, while additional bands in the UV normally are. From theoretical calculations, it is shown that both the Soret and the Q-band primarily arise from $\pi \rightarrow \pi^*$ transitions of the Pc ring.\textsuperscript{12}

Oxidation of MPc's is possible by removing electrons either from a $\pi$-orbital of the macrocyclic ring or from the central metal ion, depending on the nature of the metal ion. They can also be reduced, accepting up to four electrons. MPc's also are sensitive to doping with oxygen, which diffuses rapidly and oxidizes MPc's easily in the solid state. Oxygen doping of MPc's
is investigated in detail in Chapter 4. This doping process, which can also be induced by other reagents, leads to higher conductivities, both in the dark and under irradiation.

Phthalocyanines are widely studied as p-type semiconductors in hybrid solar cells. Combined with perylene tetracarboxy diimide (PTCDI) being an n-type semiconductor, cells with an energy conversion efficiency a little over 1% have been made\textsuperscript{15-18}. In these cells the PTCDI also absorbs visible light and contributes to the photovoltaic effect. The combination of Pc's and titanium dioxide has not been studied widely\textsuperscript{15-18}, although the energy levels of the two compounds make a solar cell possible in theory. In Fig. 3.6 energies of the band edges of TiO\textsubscript{2} and ZnPc are shown. ZnPc is chosen here, because this material will be used in the present investigations of bi-layer and nanostructured solar cells. It is cheap, readily available and studied in depth.

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{energy_diagram.png}
\caption{Energy diagram for TiO\textsubscript{2} and ZnPc. For clarity also the Fermi-levels for fluor doped SnO\textsubscript{2} (Transparent Conducting Oxide (TCO)), Au and Ca are shown. NHE stands for Normal Hydrogen Electrode with a defined energy of 0 eV.}
\end{figure}
3.2 Evaporation of zinc phthalocyanine

Because ZnPc is not soluble, but stable enough to be evaporated, thermal deposition methods are suitable for thin-film synthesis. In Fig. 3.7 a schematic drawing of the used evaporation set-up is shown. In §2.3 the principals of physical vapour deposition, to which thermal evaporation belongs, have already been discussed. In short the procedure is as follows: inside a glass bell, a tungsten crucible is filled with ZnPc powder. Samples are placed above this crucible at a distance of approximately 10 cm. The system is evacuated to a pressure of $\sim 1 \times 10^{-5}$ mbar. Subsequently, a high current is put through the crucible (usually 20-60 A) resulting in evaporation of the ZnPc powder, which is deposited on the substrates above it. This evaporation is a rather fast process: the average deposition rate is 1 nm/s, depending on the current employed.

![Schematic drawing of thermal evaporation set-up.](image)

*Fig. 3.7. Schematic drawing of thermal evaporation set-up.*

The morphology of the ZnPc films is investigated using Scanning Electron Microscopy (SEM). In Fig. 3.8 results are shown. The ZnPc is present as small crystallites on the surface, with a size of 100-200 nm as confirmed by AFM measurements*. The film adheres not very well to the TCO substrate, as is
seen in the left-hand micrograph, which shows that part of the film has peeled off.

![Fig. 3.8. SEM photographs of thermally evaporated ZnPc on TCO. The right-hand picture is a detail from the left-hand picture (the size of the scale bar is 1 μm).](image)

For some evaporation experiments ZnPc powder is first purified using zone sublimation. More information on the sublimation set-up will be presented in §3.3. In Fig. 3.9 XRD spectra of the powder are shown before and after sublimation. No change in peak positions can be observed, although the relative intensity of some peaks is slightly different after sublimation. All peaks match the reported spectrum of ZnPc and it is, therefore, concluded that no structural changes are induced by sublimation.

![Fig. 3.9. XRD spectra of ZnPc powder before and after sublimation.](image)
Kelvin probe measurements (see §1.3.6) have been performed at the Weizmann Institute, Rehovot, Israel, in the group of Prof. David Cahen. A ZnPc film of 30 nm thickness on TCO was placed in the vicinity of a vibrating gold grid. The whole set-up was placed in a nitrogen filled glove box and was grounded. Using a white light source and neutral density filters, the light intensity on the sample is increased stepwise, while the CPD was measured continuously. In Fig. 3.10 a plot of the contact potential difference (CPD) is shown as a function of time. The light induces a flattening of the bands (Fig. 1.13) and saturation can be observed at higher light intensities. The band bending (BB) is completely removed at full light intensity and its value is the difference between the CPD in dark and in full light. The work function of the gold grid is taken as 5.34 ±0.09 eV\(^7\) and the work function of the ZnPc in dark is, therefore, 4.63 eV and under full illumination 4.79 eV. This leads to a band bending of 0.16 eV. As mentioned before, ZnPc is a p-type semiconductor and the Fermi-level will be close to the valence band edge when the band bending is removed. The measured value matches very well with the position of the valence band shown in Fig. 3.6.

Fig. 3.10. Kelvin probe measurements on ZnPc (30 nm) on TCO in nitrogen. Compensating voltage (i.e., -CPD) as a function of time, under stepwise increase of white light intensity.

ZnPc films (30 nm) are deposited on top of TiO\(_2\) to investigate the solar cell characteristics of the device. TiO\(_2\) films are deposited with CVD (see §2.2) at 300°C and the thickness is varied between 100 and 420 nm. The influence of
the thickness on the solar cell characteristics is studied. Some TiO\textsubscript{2} films are annealed prior to ZnPc deposition, either in air or in vacuum and the effects thereof are investigated. In Fig. 3.11 an I-V plot of a 100 nm thick TiO\textsubscript{2} film with ZnPc is shown, as recorded in dark and under white light illumination (approximately 100 mW/cm\textsuperscript{2}, but not calibrated to the solar spectrum). The open circuit voltage ($V_\infty$) was found to be 0.5 V and the short circuit current is discussed in more detail in the following section.

![I-V plot](image)

**Fig. 3.11.** I-V plot for TCO/TiO\textsubscript{2}(100 nm)/ZnPc (30 nm)/Hg, measured in dark (dotted line) and under white light illumination (solid line).

With increasing TiO\textsubscript{2} film thickness, the photocurrent decreases. This is caused by the increase of resistance of the cell and shows that thin TiO\textsubscript{2} films are preferred in solar cells (used either as n-type semiconductor or as selective contact in nanostructured heterojunction solar cells). Annealing the TiO\textsubscript{2} film prior to ZnPc deposition, has a strong effect, as can be seen in Fig. 3.12A. Annealing in air leads to lower currents, while annealing in vacuum increases the photocurrent with a factor of 4. The detrimental effect of annealing in air can be (partly) cancelled by an additional anneal step in vacuum. The anneal time also plays a role, as can be seen in Fig. 3.12B. For longer anneal times in vacuum, the photocurrent increases and the optimum is more than 2 hours. The effect of annealing seems to be stronger for thinner TiO\textsubscript{2} films To be able to compare the different annealing steps, they need to be performed at the same temperatures.
**Fig. 3.12.** Photocurrents at 0V for TCO/TiO₂/ZnPc (30 nm)/Hg. A: as a function of TiO₂ film thickness for different annealing steps; (□) not annealed, (○) annealed in air (2 hr, 450°C), (■) annealed in vacuum (1x10⁻⁴ mbar, 1hr, 300°C), (●) annealed in air and in vacuum (2h, 450°C and 1 hr, 300°C, respectively). B: as a function of anneal time in vacuum (1x10⁻⁴ mbar, 300°C) for 100 nm (■) and 140 nm (○) of TiO₂.

It is expected that the donor density and, therefore, the conductivity of the TiO₂ will increase by annealing in vacuum and will decrease if annealed in air (see §2.2). In Fig. 3.13 a Mott-Schottky plot for ZnPc on TiO₂ (not annealed) is shown, recorded at 20 kHz in dark and under white light illumination. Like for TiO₂ films, a hysteresis is observed (compare Fig. 2.9). In the inset, the Bode plots of the impedance spectrum at 0V for this system are shown. Straightforward Mott-Schottky analysis is in fact not allowed at a frequency below 100 kHz, hence the data will be used here only for an indication of the trend of the donor density. The slope of the Mott-Schottky curve decreases under illumination, revealing a photo-induced increase of the donor density from 1.3x10⁷ cm⁻³ in the dark to 1.7x10⁸ cm⁻³ under illumination. To obtain more information from Mott-Schottky measurements, advanced techniques, like impedance spectroscopy at low frequencies, are tried, but it appears that the donor density under illumination is not stable in ZnPc. This is described in more detail in Chapter 4.
Fig. 3.13. Mott-Schottky plots for TCO/TiO$_2$(100 nm)/ZnPc (30 nm)/Hg in dark (black line) and under white light illumination (grey line) at 20 kHz. Inset: Bode plots of the impedance of this system at 0 V. A 400 nm high pass filter is used, to prevent light absorption of the TiO$_2$.

The photoaction spectrum of the TiO$_2$/ZnPc cells is compared to the optical absorption spectrum in Fig. 3.14A. Although the shape of the spectra are much alike, the peak positions are not exactly the same. It is not clear what the reason is for this effect. The maximum photocurrent at 680 nm (Q-band absorption) is about 0.5 $\mu$A/cm$^2$. A correction is made for the flux of incident photons ($3.10^6$ photons/cm's at every wavelength) but not for the fraction of absorbed photons. In Fig. 3.14B the effect of different annealing steps on the photoaction spectrum is shown. The same trend as for the I-V curves is observed, i.e., annealing in vacuum leads to an increase of the current, while annealing in air leads to a decrease. The shape of the spectrum is slightly changed upon annealing in air. The peak around 600 nm varies in intensity. This indicates that more effects than the change in donor density of the TiO$_2$ may play a role, but their nature is not known yet.
3.3 Sublimation of zinc phthalocyanine

In the preceding paragraph it has been shown that thermal evaporation of ZnPc powder leads to films that consist of small crystallites (Fig. 3.8). Changing the evaporation velocity and the substrate temperate influences the morphology of the deposited film. Sublimation has been used as a technique to study the influence of these deposition parameters. In Fig. 3.15 a schematic drawing of the set-up is shown. It consists of a gradient furnace in which a crucible with ZnPc powder is placed in the middle and substrates at the ends. The system is evacuated with a rotation and turbopump to $1 \times 10^{-3}$ mbar. The crucible is heated to a temperature of 350°C, while the substrates are kept at a temperature of approximately 150°C. The ZnPc powder evaporates and sublimates at the colder parts of the furnace where the samples are located. Typically, the deposition rate is 0.3 nm/s.

Fig. 3.15. Schematic drawing of the sublimation set-up.
A cold finger can be placed on one end of the furnace, which consists of a water-cooled support for substrates. This cold finger is kept at a temperature of 10°C and the variation in morphology for different substrate temperatures can be studied. The same set-up is used to purify ZnPc powder. No substrates are present during the purification and the furnace is heated for 48 h after which the sublimated crystals are collected.

The morphology of the samples is investigated with Scanning Electron Microscopy (SEM). In Fig. 3.16 some micrographs are shown for ZnPc powder sublimated at 350°C with the substrates at 150°C or at 10°C (cold finger). A very specific structure is observed, which consists of long and thin wires of ZnPc. The aspect ratio of these wires is very high, as the length can reach up to 10 μm and the width is 100 nm or less. The samples are quite vulnerable, as the wires can easily be scraped of the substrate. In several instances the wires exhibit thicker parts (Fig. 3.16C). At 10°C much shorter wires are formed. The wires in all cases form interconnected porous networks.

![SEM photographs of sublimated ZnPc](image)

**Fig. 3.16. SEM photographs of sublimated ZnPc. The ZnPc powder was at 350°C, while the substrates are kept at 150°C (A-C) or at 10°C (D).**
XRD measurements of these samples show no diffraction pattern. Probably the porosity leaves too little intensity to measure, but more research is needed to clarify this. Using TEM measurements, performed at the National Centre for High Resolution Electron Microscopy, Delft University of Technology by dr. Patricia Kooyman, the structure is studied in detail. In Fig. 3.17 photographs are shown for ZnPc wires, which are directly collected on a TEM grid during a sublimation experiment. The wires in the photograph (Fig. 3.17A) are not as long as those in the SEM pictures, which is probably due to the short deposition time required to deposit a limited amount of material on the TEM grid. In the magnification (Fig. 3.17B) it is clearly seen that the wires are crystalline and the d-spacing is estimated to be 1.08 nm. This is different to the lattice spacing of the unit cells of the α- and β form of phthalocyanine, which is 3.78 and 4.85 Å, respectively (§3.1), so it is possible that these ZnPc wires represent a new polymorph.

_Fig. 3.17. TEM photographs of ZnPc sublimed on a TEM grid. The operating voltage was 300 kV._

This porous network of ZnPc is used as the starting point for the formation of a nanostructured network for solar cells. Using CVD at reasonably low temperatures, the formation of a percolating network of TiO₂ and ZnPc is explored. First a network of ZnPc wires is deposited on a TCO substrate using sublimation. Subsequently, the sample is placed in the CVD reactor (§2.2). CVD of TiO₂ is performed at 350°C for 1 h and the samples are characterized with SEM and I-V measurements. In Fig. 3.18 SEM photographs of the resulting composite films are shown. The wires are covered with TiO₂ during the CVD process, but the network of the ZnPc
wires breaks up and the resulting pieces are encapsulated. The fragments are smaller in the middle of the sample compared to the edge of the sample and are also coated with a thicker TiO$_2$ film. This is probably due to a higher deposition rate in the middle of the CVD reactor. As a result the interconnections in the network are lost. In the I-V curve a diodic behavior is observed, but no photocurrent, consistent with the absence of an interconnected network.

![Image A](image1)

![Image B](image2)

Fig. 3.18. TiO$_2$ deposited on top of a sublimated ZnPc network using CVD at 300°C. A: edge of sample, B: middle of sample.

Using spray pyrolysis (see §2.3) another attempt is made to synthesize an interconnecting network of ZnPc and TiO$_2$. After sublimation of ZnPc wires onto TCO, TiO$_2$ is deposited using spray pyrolysis at 300°C. In Fig. 3.19 SEM photographs of the resulting morphology are shown, which closely resemble the graphs of Fig. 3.18.

![Image A](image3)

![Image B](image4)

Fig. 3.19. TiO$_2$ deposited on top of a sublimated ZnPc network using spray pyrolysis at 300°C. The right-hand picture is an enlargement of the left-hand picture.
In Fig. 3.20 the electrical characteristics of these samples are shown. A minor photovoltaic effect is observed under illumination, but a huge photoconductivity appears if a UV-component is present in the illumination, as a result of photoconductivity of the TiO$_2$. In time the photocurrent under a small bias increases substantially when UV light is present, which indicates that the photoconductivity rises with illumination time.

**Fig. 3.20.** Electrical characterization of TiO$_2$ deposited on top of a sublimated ZnPc network using spray pyrolysis at 300°C. A: I-V plots in dark, under illumination with a UV-component, and under illumination without a UV-component. B: Current-time plots at 0.1V forward bias under illumination with (no filter) and without (400 nm filter) a UV-component. For the illumination without filter the light was switched on at 20 s, off at 105 s, again on at 145 s, and again off at 185 s. For the illumination with a 400 nm high pass filter present, the light was switched on at 0 s, off at 65 s, again on at 135 s, and again off at 170 s.

As a final experiment co-deposition of ZnPc and TiO$_2$ is performed inside the CVD reactor. During CVD deposition of TiO$_2$, a crucible with ZnPc powder is placed in the middle of the furnace, which is kept at 350 °C. Although it is not specifically designed to have a temperature gradient, at the edges of the furnace the temperature is lower and the substrates are placed in such a way that sublimation of the ZnPc will take place. In Fig. 3.21 the resulting
morphology is shown. Some wires can be distinguished in the TiO$_2$ matrix, but again no percolation is obtained. It can, therefore, be concluded that it is not straightforward to manufacture a nanostructured network of ZnPc and TiO$_2$, as the wires are isolated during TiO$_2$ deposition. Nevertheless, more advanced techniques, for example using furnaces with a specific temperature gradient, or lower deposition temperatures might lead to a working cell.

![SEM photograph of co-deposited ZnPc and TiO$_2$ inside the CVD reactor at 350°C.](image)

3.4 Conclusions

Phthalocyanines form a class of p-type semiconductors that is suitable for use in solar cells. They have a high light absorption, versatile chemistry, can be prepared with high purity, and are highly stable. Thin films of zinc phthalocyanine can be deposited by thermal evaporation and consist of small crystallites (100-200 nm). The work function and band bending are determined with Kelvin probe measurements to be 4.63 eV in dark (under illumination 4.79 eV) and 0.16 eV respectively, which matches very well with literature values. These ZnPc films are used to form bi-layer solar cells with TiO$_2$. The photovoltaic characteristics depend strongly on the thickness of the TiO$_2$ film and of the thermal treatment of the TiO$_2$ films prior to ZnPc deposition. The photocurrent decreases with increasing TiO$_2$ film thickness as a result of the increase in resistivity. Annealing in air leads to lower
currents, while annealing in vacuum increases the photocurrent with a factor of 4. Longer annealing times and thinner TiO₂ films enlarge the effect. These effects are thought to originate from the change in donor density of the TiO₂ film upon different annealing steps. Sublimation of ZnPc leads to films that consist of long, thin, crystalline wires that form an interconnected porous network. Coating of these wires with TiO₂ using CVD and spray pyrolysis leads to breaking of the network and encapsulation the ZnPc fragments. No photovoltaic effect is observed, although photoconductivity appears. Co-deposition of ZnPc (sublimation) and TiO₂ (CVD) yield a network without percolation of the ZnPc phase. For both techniques attempting to form a nanostructured heterojunction solar cell more research is needed to answer the question whether or not they can lead to efficient solar cells.
References

(22) Takada, J.; Awaji, H.; Koshioka, M.; Nakajima A.; Nevin, W. A. 
13, 219-222.
(26) Kerp, H. R. Exciton and charge carrier dynamics in molecular 
Netherlands.
482.
Photodoping of zinc phthalocyanine: formation, mobility, and influence of oxygen radicals in phthalocyanine-based solar cells

Organic/inorganic hybrid solar cells are constructed from titanium dioxide (TiO$_2$) and zinc phthalocyanine (ZnPc). Only modest photocurrents are observed originating from excitation of the ZnPc. The photocurrent is not stable, but is found to decrease when measured in ambient atmosphere. The combined presence of oxygen, light, and an electric field is the cause of the photocurrent decay, which is found to be fully reversible. Under illumination, oxygen radical anions are formed, which subsequently drift towards the interface with the titanium dioxide when an interfacial electric field is present. These radicals quench the singlet excitons that are generated in the phthalocyanine film. A decay of the photocurrent is the result. Upon irradiation, the oxygen anion concentration increases up to $6 \times 10^8$ cm$^{-3}$, which is two orders of magnitude higher than the reported O$_2^-$ concentration in the dark. This photodoping effect, combined with the observed mobility of the dopant, is disadvantageous for the working of this kind of solar cells.
4.1 Introduction

In the past decade the performance of organic and dye-sensitized solar cells has been improved strongly. In dye-sensitized solar cells organic molecules are optically excited which leads to a charge-separated state; electrons are injected from the LUMO of the dye molecule into the conduction band of a wide-bandgap semiconductor\textsuperscript{13}. These cells show an energy conversion efficiency of about 10% and offer a promising alternative for the present generation of silicon solar cells. The development of reasonably efficient, cheap solar cells, produced on plastic substrates, is well on its way, although still several problems have to be solved.

Phthalocyanines (Pc’s) are organic p-type semiconductors and are among the most intensively studied dyes in this field. Their strong absorption in the visible part of the solar spectrum, excellent chemical stability, high LUMO energy level, and relative high hole mobility make them suitable to be applied in opto-electronic devices such as photocopiers, and hybrid solar cells. Up to now the best results are obtained when Pc’s are combined with n-type perylene tetracarboxy diimide (PTCDI)\textsuperscript{17}. Efficiencies a little over 1% have been reported. In these cells PTCDI also absorbs in the visible part of the solar spectrum and contributes to the photovoltaic effect. The combination of Pc’s and titanium dioxide has not been studied much\textsuperscript{5,6,8-11}. TiO\textsubscript{2}, however, is a promising material for solar cell application, because of its low price, high stability, and availability of various fabrication techniques. The possibility to make smooth, thin films of TiO\textsubscript{2} with various gas-phase techniques opens routes towards easy and large-scale production of solar cells in which dyes are combined with TiO\textsubscript{2}. These kinds of cells need therefore to be examined in detail.

Pc’s are known to have a pronounced interaction with ambient oxygen, which acts as an electron acceptor\textsuperscript{11}. Oxygen leads to a modification of the opto-electronic properties. Phthalocyanine films, prepared under ultra-high vacuum, have a low hole conductivity and show no rectifying behaviour. Only after contact with oxygen p-type character is observed. It is known that a fraction of the molecular oxygen, which can diffuse easily into and out of
the films, is transformed into radical anions\textsuperscript{12-15}. This reaction creates additional holes, rendering Pc a p-type semiconductor. The exact mechanism of this transformation is still not fully understood, but it is believed to involve complex of a Pc molecule and axially bound oxygen. An electron from the extended π-system, or from a d-orbital of the metal centre (depending on the metal type), is transferred to the oxygen molecule. The radicals formed in this way are able to quench the singlet excitons that are formed in the Pc under irradiation. Since oxygen is difficult to exclude completely in practical devices it is worthwhile to study its influence in detail. In this paper we report on the photovoltaic properties of the combination of ZnPc and anatase TiO\textsubscript{2}. In particular, the formation and migration of oxygen radicals in Pc due to the presence of light and an electric field are investigated in depth. It is found that ionized oxygen can accumulate at the TiO\textsubscript{2}/ZnPc interface and quench the singlet excited state. Photocurrents are inhibited by this effect, which poses a serious bottleneck in the development of this type of solar cell.

4.2 Experimental aspects

4.2.1 Sample preparation

Thin films of anatase titanium dioxide are deposited on SnO\textsubscript{2}:F coated glass (TCO: transparent conducting oxide; 20 Ω cm\textsuperscript{-1}, Libbey Owens Ford) with metal-organic chemical vapour deposition at 300°C. Titanium isopropoxide (TTIP, Aldrich, 98\%) is used as precursor and nitrogen as carrier gas (flow 60 sccm). Saturated TTIP vapour at 50°C is carried into a hot-wall CVD reactor. Before deposition of the TiO\textsubscript{2} and ZnPc films, the substrates are thoroughly cleaned in an ultrasonic bath with ethanol and acetone and are dried with dry nitrogen. The TiO\textsubscript{2} films made with CVD are annealed for 2 hours at 450°C under ambient conditions and ZnPc evaporation takes place directly afterwards. Zinc phthalocyanine (Aldrich 98\%) is purified by vacuum sublimation in a gradient oven (temperature middle: 350°C, substrate temperature: approximately 250°C). The collected crystals are thermally evaporated (vacuum 1×10\textsuperscript{-3} mbar) onto the TiO\textsubscript{2} film in six minutes with a deposition rate of 10 nm/min, yielding a film thickness of about 60 nm.
thick. Mercury drops with a diameter of 2 mm are applied to the phthalocyanine film as a back contact. The construction of the cell is schematically presented in Fig. 4.1. Other Pc’s (MnPc, CuPc, H$_2$Pc) are also investigated. All are obtained from Aldrich and are used without further preparation. Films of these Pc’s are deposited onto TiO$_2$ in the same way as the ZnPc film.

Fig. 4.1. Sample configuration seen in cross-section. For clarity, only two mercury drops are shown, normally each sample contains 6 to 8 mercury contact spots.

4.2.2 Measurements
The opto-electronic properties of the cells are examined in air, argon, or in vacuum ($\leq 1 \times 10^{-3}$ mbar). Grazing incidence X-ray diffraction measurements are performed with a Bruker D8 Advance X-Ray Diffractometer. A Jeol JSM-5800 LV Scanning Electron Microscope is used to study the surface morphology of the films. Optical absorbance spectra are recorded with an intergrating sphere detector. Current-voltage characteristics and photocurrent (pulse) experiments are performed using an EG&G 283 potentiostat and a Keithley 2001 digital multimeter. A 5-mW 670-nm laser (Coherent) is used as irradiation source. Photocurrent action spectra are recorded using a 250W tungsten-halogen lamp in combination with a monochromator (Acton SpectraPro-275) and appropriate high-pass filters. Irradiation always takes place through the transparent TCO electrode.
4.3 Results

4.3.1 Sample characterization
Chemical vapour deposition of thin titanium dioxide films is described in detail elsewhere\textsuperscript{16-18}. Grazing incidence X-ray diffraction measurements show that at 300°C the anatase phase is formed. ZnPc films obtained by thermal evaporation are bright blue. Electron microscope analysis shows that the film consists of microcrystals with a size of approximately 100-200 nm. Since the film thickness is approximately 60 nm, the ZnPc film essentially consists of a single layer of crystals.

4.3.2 Electrical properties
For the TCO/TiO\textsubscript{2}/ZnPc/Hg heterojunctions a clear rectifying behaviour is observed in the dark. When illuminated with 670-nm light a photovoltaic effect occurs, as can be seen in Fig. 4.2. The photocurrent direction is such that electrons flow from ZnPc into TiO\textsubscript{2}. The photocurrent is not stable but decreases in time as can be seen by comparing the I-V curves recorded directly after the onset of irradiation and after a delay of five minutes. In the next section this phenomenon will be described in more detail.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig4_2.png}
\caption{I-V curves in dark (\[\square\]) and under 670-nm 5-mW irradiation: immediately after switching on the irradiation (\[\circ\]) and after 5 min of irradiation (---). In forward direction (positive voltage) the mercury electrode is positive. The right-hand panel is an enlargement of the left-hand panel.}
\end{figure}
The spectral photocurrent response at 0 V external bias is shown in Fig. 4.3A, along with the absorption spectrum of ZnPc on anatase TiO₂. The photoaction spectrum is converted into internal and external (IPCE) quantum efficiencies (Fig. 4.3B/C) after correction for the lamp output and absorption of the ZnPc film.

![Graphs showing absorption and photocurrent spectra](image)

**Fig. 4.3.** Absorption and photocurrent action spectra (A) external (IPCE) and internal quantum efficiencies (B) and magnification of B (C).

### 4.3.3 Bias effect

As mentioned before, a remarkable decrease of the photocurrent is observed if current-voltage scans are recorded under illumination. To study this phenomenon in detail, the photocurrent at 5-mW 670-nm irradiation is followed, while the cell is kept at 800 mV (TCO is the positive electrode). As can be seen in Fig. 4.4A the photocurrent decays rapidly. In contrast, at 0 V
only little decay is observed (Fig. 4.4B). All tested Pc's (MnPc, CuPc, H₂Pc) exhibit a similar decay (not shown).

**Fig. 4.4. Current decay curve as a function of time with an external bias voltage of 0.8 V (A). Photocurrent as a function of time at 0 V external bias, only a minor decrease in photocurrent is observed (B).**

It is important to note that the decay is fully reversible (Fig. 4.5). When irradiation is switched off for a while, the photocurrent starts off at a higher level upon resumption of the irradiation. If this dark period is long enough (typically overnight), the photocurrent recovers completely and starts at the original level. The decay and recovery can be repeated more than 20 times at least, after which we stopped checking the reversibility.

**Fig. 4.5. Reversibility of the photocurrent decay. The second decay curve, starting at 170 s, does not start at the level of the initial decay at 30 s. The dark period of approximately 70 s is too small to restore the system in its original state. A decay curve identical to the first decay curve isn't observed until the dark period exceeds 1 h.**
In Fig. 4.5 another remarkable detail is noticed; the dark currents increase stepwise after each irradiation period. This can also be seen in Fig. 4.6 in which dark I-V curves are presented before and after a period of irradiation. Both at the forward (negative) and the reverse side (positive) of the curve, the dark current is higher after irradiation than before. We conclude that the dark conductivity of the phthalocyanine increases after a period of irradiation.

![Graph showing I-V curves before and after irradiation.](image)

**Fig. 4.6. Increase in dark conductivity after irradiation. Dark I-V curve taken before (■)and after (○) 1000 s of irradiation with 5-mW, 670-nm light.**

To examine whether oxygen from the ambient is involved, TiO₂/ZnPc cells are also studied under argon. Upon introduction of argon in the measurement chamber, the decay becomes less pronounced (Fig. 4.7). After prolonged flushing with argon, the photocurrent has become nearly stable. The same is true when cells are studied in vacuum; no decay of the photocurrent is visible (Fig 4.8). When air is re-admitted the decay immediately occurs again.
Fig. 4.7. Decrease in photocurrent when a TCO/TiO/ZnPc/Hg sample is placed in a box that is flushed with argon. The initial decay is recorded in air, after which flushing with argon started. After prolonged flushing, the decay of the photocurrent has disappeared for the largest part. If air is re-admitted, the decay curve is almost identical to the curve before the start of the argon flushing.

Fig. 4.8. Current at 0.8 V under illumination of 5-mW, 670-nm light in vacuum (1×10⁻⁷ mbar). No decay of the photocurrent is observed in time. Illumination is switched on at 55 s and switched off at 250 s.
In summary, we observe that the photocurrent decays in the combined presence of oxygen, light, and an electric field. In order to understand the underlying mechanism, a set of puls experiments is performed (Fig. 4.9). These experiments enable us to study the effect of the irradiation and the influence of the electric field separately. A cell in air is continuously illuminated with 5-mW 670-nm light at 0 V and for a short period of time (25 s) the bias voltage is set to 1 V. During these 25 s the initial decay is recorded. Now a delay of 400 seconds is applied in which the bias voltage is set to 0 V while the irradiation continues. After this period, the voltage is stepped to 1 V again to record the decay characteristics. If the decay is caused by the irradiation alone and not by the electric field, we expect that during the period of 400 seconds, in which light is present but the electric field is not, the decay continues. This would lead to a much lower photocurrent onset immediately after the second potential step. This is not observed. Both responses are identical which indicates that in the absence of an electric field there is no decay irrespective of the presence of light. It can thus be concluded that the presence of an electric field is a prerequisite for the occurrence of photocurrent decay.

Subsequently, decay curves have been recorded while varying the light intensity and the applied bias voltage. Two examples of these decay curves are shown in Fig. 4.10, where the applied bias voltage is 0.8 V for both, while the light intensity is different. These decay curves can be fitted with a second order exponential of the form

$$I(t) = I_\infty + Ae^{-t/\tau_1} + Be^{-t/\tau_2}$$  \hspace{1cm} (Eq. 4.1)

in which $I_\infty$ is the value of the photocurrent after stabilization at prolonged times, $\tau_1$ and $\tau_2$ are the characteristic decay times for the first and second part of the decay, respectively, and $A$ and $B$ are constants. In Fig. 4.10, fits to the above mentioned example decay curves are shown. It is clear that a fast process is present in the first part of the spectrum, characterized by $\tau_1$, followed by a much slower process, characterized by $\tau_2$. The characteristic time $\tau_2$ is almost independent of the light intensity and of the bias voltage with an average of $17 \pm 7$ s.
Fig. 4.9. Puls experiment as described in the text. At 25 s a photocurrent decay curve is recorded. In the following 400 s no bias potential is applied, while the irradiation continues. At $t = 425$ s, a bias potential of 1 V is again applied and the resulting current decay is recorded. The dotted curve is drawn to simulate the photocurrent behaviour when the decay would continue in the 400 s where no bias potential is present.

Fig. 4.10. Decay curves, measured at an applied bias voltage of 0.8 V and a light intensity of 5 mW and 0.11 mW respectively (\(\rightarrow\)) and second order exponential fits (\(\rightarrow\)) to these curves. From the fit of each curve the characteristic times $\tau_1$ and $\tau_2$ are estimated.
In Fig. 4.11, the characteristic time, \( \tau \), and the ratio between the stabilized current and the initial current at the end of the decay \( (I/I_0) \) are plotted as a function of light intensity (Fig. 4.11a), and bias voltage (Fig. 4.11b). It can be observed that \( \tau \) is not influenced by the light intensity is varied, but is strongly dependent on the bias voltage. On the other hand, \( I_0/I \), shows an opposite trend: it is independent of the bias voltage and strongly dependent on the light intensity.

![Graphs showing characteristic time and current ratio as functions of light intensity and bias voltage.](image)

**Fig. 4.11.** Characteristic time, \( \tau \), of the current decay and the ratio between initial and final values of the current, \( I_0/I \), as a function of light intensity (A), and applied bias (B). When the light intensity is changed, the applied bias is kept constant at 0.8 V and when the bias voltage is changed the light intensity is kept constant at 5 mW. The lines are drawn as a guide to the eye.

In the last experiment (Fig. 4.12), a current transient is measured. A cell is illuminated continuously with 5-mW, 670-nm light with a reverse bias of 0.8 V for a long period of time (> 1000 s). After this period, both light and electric field are switched off simultaneously and the current is monitored. A negative current characteristic is seen which rises to zero in about 200 s. From this curve the concentration of oxygen radical anions will be calculated in the discussion section of this paper.
**Fig. 4.12.** Current response of a TCO/TiO$_2$/ZnPc/Hg solar cell in air after a period (> 1000 s) of irradiation with 5-mW, 670-nm light and 0.8 V of bias potential.

### 4.4 Discussion

#### 4.4.1 Electrical properties

From the current-voltage and spectral response curves (Fig. 4.2 and 4.3A) it is clear that the combination TiO$_2$/ZnPc exhibits a photovoltaic effect. Photoexcited ZnPc injects electrons into the conduction band of the TiO$_2$ and the holes are transported to the mercury electrode. In the dark a clear rectifying behaviour is present; while under irradiation photoconductivity is observed. The photocurrent follows the absorption spectrum of the ZnPc, indicating that the photovoltaic effect originates from photo-excited phthalocyanine molecules injecting electrons into TiO$_2$. As can be seen in Fig. 4.3b, the quantum efficiency of the cells is rather moderate. At 670 nm the external quantum efficiency is maximal and is 0.25%, which is around 1.5% when corrected for absorption of the film (internal quantum efficiency). Compared to perylene diimide/ZnPc cells$^{44}$, which have an incident power to current efficiency of about 15%, these cells have an efficiency performance, which is roughly a factor of 10 lower. Because TiO$_2$ only absorbs in the ultraviolet part of the spectrum, the contribution of the absorption of the n-type semiconductor is missing here.
4.4.2 Bias effect

The decay of the current observed in the TCO/TiO₂/ZnPc/Hg samples when a reverse bias is applied is caused by the simultaneous presence of oxygen, light, and an electric field. Superoxide $O_2^-$ species are present in phthalocyanine films as a result of doping with oxygen. The conductivity of Pc films deposited in vacuum increases several orders of magnitude if they are placed in ambient atmosphere. However, we observe also an increase of conductivity when the Pc films are illuminated in air, indicating that more $O_2^-$ species are formed under influence of light (photodoping). It is thus of interest to know how many of these radical anions $O_2^-$ are formed and whether they are mobile or not. The experiments show that if an external bias voltage is applied the photocurrent decays and, in addition, the dark conductivity increases. The following two-step mechanism is proposed in order to explain these observations:

**STEP I:** Oxygen radicals are formed under influence of light.

\[ \text{hv} \]

\[ \text{ZnPc} + O_2 \rightleftharpoons (\text{ZnPc}^*O_2^-)^* \rightleftharpoons \text{ZnPc}^+ + O_2^- \quad (R. 4.1) \]

The nature of the intermediate charge transfer complex $(\text{ZnPc}^*O_2^-)^*$ is not fully known, but is tentatively ascribed to a complex in which an oxygen molecule has an axial coordinated bond to the central Zn²⁺ ion. This photodoping effect leads to the observed increase in dark conductivity. The donation of an electron from the ZnPc to the $O_2^-$ occurs from the $\pi^*$-excited state of the ZnPc. A small amount of $O_2^-$ species may already have been formed in the dark as a result of thermal activation. However, light boosts the formation rate to a much higher level. If illumination is switched off, most superoxide radicals slowly transform back to oxygen, which consumes holes and lowers the conductivity.

**STEP II:** The superoxide species drift to the interface between TiO₂ and ZnPc under the influence of the electric field. This accumulation leads to a charge build-up, which quenches the created singlet excitons before they are separated at the TiO₂/ZnPc interface. As a result the photocurrent decreases significantly.
According to this two-step model, the electric field and not the light intensity determines the decay rate. This is indeed observed in Fig. 4.11B. In contrast, the ratio between initial and final values of the photocurrent is determined by the concentration of oxygen radicals created by irradiation. Therefore, it is independent of the applied bias voltage, but increases at lower light intensity.

A reasonable estimate of the diffusion coefficient of these oxygen radical ions in this system can be obtained using a simple model. Combining the following equations leads to an expression for the mobility of the ions:

\[
\begin{align*}
V &= E L \\
\nu &= \mu E \\
L &= \nu \tau_{\text{ion}} \\
\mu &= \frac{L^2}{\tau_{\text{ion}} V}
\end{align*}
\]  
(Eq. 4.2)

In which \(V\) is the potential drop over the ZnPc film, \(E\) is the electric field, \(\mu\) is the mobility of the oxygen anions, \(\nu\) is the velocity with which the created oxygen radicals move towards the TiO\(_2\)/ZnPc interface, \(\tau\) is the time-of-flight (i.e. the time oxygen radicals need to travel through the ZnPc film), and \(L\) is the thickness of the film. The Einstein relation expresses the ionic mobility in terms of the diffusion coefficient:

\[
\mu = \frac{ZD_{\text{ion}} e}{kT}
\]  
(Eq. 4.3)

In which \(k\) is the Boltzmann constant, \(T\) is the temperature, \(Z\) is the charge of the ion, \(D_{\text{ion}}\) is the diffusion coefficient (for ionic species) and \(e\) the elemental charge. Combining this with equation 4.2 yields an expression for the diffusion coefficient of the ZnPc radicals:

\[
D_{\text{ion}} = \frac{kT}{Ze} \times \frac{L^2}{\tau_{\text{ion}} V}
\]  
(Eq. 4.4)

Using average values for the TiO\(_2\)/ZnPc system (\(L = 60\) nm, \(\tau = \tau_{\text{ion}} = 1000\) s at \(V = 0.2\) V) we find that the mobility of the oxygen radicals is in the order of \(2\times10^{-3}\) cm\(\text{V}^{-1}\text{s}^{-1}\) and the diffusion constant, \(D_{\text{ion}}\), is in the order of \(5\times10^{-5}\) cm\(^2\)s\(^{-1}\), which is not unrealistic.
The fast process, characterized with $\tau_i$, does not depend on bias voltage nor on light intensity and is therefore associated with diffusion of an uncharged species. The diffusion coefficient for this case is given by:

$$D_{\text{neutral}} = \frac{L^2}{2\tau_{\text{neutral}}} \quad \text{(Eq. 4.5)}$$

and equals $1 \times 10^{-8}$ cm's$^{-1}$ for a value of 17 s for $\tau_i = \tau_{\text{neutral}}$. At present the nature of this diffusing species is unknown, but it seems unlikely that it concerns molecular oxygen, as this has a reported$^{35}$ diffusion coefficient of around $3 \times 10^{-8}$ cm's$^{-1}$. Assuming this value to be correct, molecular oxygen diffuses across the film in less than a millisecond.

Accumulating charges at the interface between ZnPc and TiO$_2$ create an ionic space-charge region. Turning off the electric field stops the build-up of O$_2^-$ species at the interface, resulting in diffusion of the oxygen radicals from the interface throughout the film. In Fig. 4.12 the current associated with this charge redistribution is presented. The integral of the curve corresponds to the released amount of charge. In this case $3.8 \times 10^n$ cm$^{-2}$ elementary charge units are released. If these charges are equally distributed through the entire ZnPc film the concentration of oxygen radicals is $6 \times 10^8$ cm$^{-3}$. This, of course, is a minimum concentration, because oxygen radicals slowly reduce back to oxygen molecules during the time the curve is taken. According to Kerp et al.$^{35}$ an amount of $1 \times 10^{20}$ cm$^{-2}$ oxygen molecules is incorporated in a ZnPc film in ambient atmosphere. We find that roughly one out of every 16 oxygen molecules is ionized, which is more than 100 times the value for ZnPc films in dark.

The migration of oxygen radical anions through the ZnPc film towards the interface with the TiO$_2$ can be considered as ionic charges moving through a solid electrolyte. Ions will gather at the interface between the electrode and the electrolyte to counterbalance the charge on the electrode. This leads to the formation of a diffusion layer, also called a double layer, the theory of which is described by Helmholtz. Following the the Gouy-Chapman-Stern model$^9$, it is possible to calculate the distribution of the potential in the ZnPc
layer and the concentration profile of the oxygen radical anions close to the interface with the TiO$_2$. The accumulated charge can be calculated as:

$$\sigma = (8kT\varepsilon_{ZnPc} \varepsilon_0 N)^{1/2} \sinh\left(\frac{Ze\Phi_z}{2kT}\right), \quad \text{(Eq. 4.6)}$$

in which the potential as a function of distance $x$ from the surface is:

$$\Phi = \frac{4kT}{Ze} \arctanh\left[\tanh\left(\frac{Ze\Phi_z}{4kT}\right)\exp[-\kappa(x - \lambda)]\right] \quad \text{(Eq. 4.7)}$$

with:

$$\kappa = \left(\frac{2NZ^2e^2}{\varepsilon_{ZnPc} \varepsilon_0 kT}\right)^{1/2} \quad \text{(Eq. 4.8)}$$

$\Phi_z$ is the potential of the inner Helmholtz plane, i.e. at a distance $\lambda$ from the electrode, $\varepsilon_{ZnPc}$ is the dielectric constant for zinc phthalocyanine and $\varepsilon_0$ is the permittivity of vacuum. $N$ is the concentration of oxygen radical anions, which have a charge $Z = 1$. $k$ is the Bolzmann constant, $e$ the elemental charge, and $T$ the temperature. Using this model, the potential as a function of distance is plotted in Fig. 4.13, for two different voltages. The voltage is the total potential difference between TiO$_2$ and ZnPc, i.e. the sum of the built-in voltage and the applied bias voltage. Approximated numbers are used: $N = 6.10^{24}$ m$^{-3}$ oxygen radicals, $\varepsilon_{ZnPc} = 3$ and $\lambda = 1$. It is clear that the accumulation of charges at the interface changes when a larger bias voltage is used, the sheet of charge becoming smaller and the concentration near the interface increasing substantially. The transfer of excitons through this highly doped region will be inhibited, which leads to a reduction of the photocurrent.

As can be seen in Fig. 4.3 there is a substantial increase in photocurrent and efficiency of the cell below ca. 400 nm. This is due to direct hole transfer from photo-excited TiO$_2$ to the ZnPc. TiO$_2$ contributes to the photovoltaic effect when illuminated with sub bandgap wavelengths. During this UV illumination also the conductivity of the TiO$_2$ increases but this is thought to be of little influence on the overall performance of the cell.
Fig. 4.13. Plot of the concentration of oxygen radical anions as a function of the distance from the TiO₂ interface. The Gouy-Chapman-Stern model is used with the following parameters: \( \varepsilon_{\text{ZnPC}} = 3.0 \), \( N_{\infty} = 6 \times 10^{11} \text{ m}^2/\text{mol} \), \( \phi \), \( \lambda = 1 \text{ nm} \), potential in outer Helmholtz layer 0.1 V (A) and 1.0 V (B).

Recombination losses are to our opinion the biggest bottleneck for the photovoltaic process and these are almost exclusively occurring in the ZnPC film. Furthermore, there is a possibility that excited holes in the valence band of TiO₂ oxidize oxygen radical anions, present at the interface between the TiO₂ and ZnPC film. At 0 V only few radical anions are present at this interface, which means that under normal operating conditions this possible photoelectrochemical process is of minor importance. Yet it is interesting to investigate whether the oxidation of oxygen radical anions by photoexcited TiO₂ is possible, but this topic falls outside the scope of this paper.

4.5 Conclusions

In TiO₂/ZnPC heterojunctions a photocurrent can be generated by excitation of the ZnPC molecules. When an electric field is present, samples in air show a strong decrease of the photocurrent, while samples kept under argon or in vacuum do not show this effect. The decay curves can be fitted using a second order exponential function. The ‘fast’ process is independent of bias voltage and light intensity and has a characteristic time of 17 ± 7s. The ‘slower’ process is dependent on bias voltage, but not on light intensity. The
magnitude of photocurrent loss is governed by the irradiation intensity. The characteristic decay time is governed by the electric field at the junction. When light and air are both present, O$_2^-$ species are generated that are mobile and drift towards the TiO$_2$/ZnPc interface due to an external electric field. These O$_2^-$ species accumulate at the TiO$_2$/ZnPc interface and quench the $\pi\pi^*$ singlet excitons, decreasing the photocurrent significantly. From the release of charge after prolonged irradiation at 0.8 V bias a minimum concentration of $6\times10^9$ cm$^{-3}$ radical anions in the ZnPc film is calculated. This is more than two orders of magnitude higher than the O$_2^-$ concentration in the dark. The Gouy-Chapman-Stern model is used to quantify the accumulation of charges at the interface.
References

(1) Green, M. A. Solar cells; operating principles, technology and system applications, University of New South Wales: Kensington, 1992.


Sexithiophene and poly(3-octylthiophene): bi-layer and nanostructured heterojunctions with TiO$_2$

In this chapter the class of thiophenes is discussed. These organic semiconductors can be synthesized both in oligomeric and in polymeric form, with as well as without side groups attached to the backbone. In the first section a general introduction will be given to these compounds with emphasis on their properties. In §5.2 sexithiophene (the hexamer of thiophene) is used in combination with TiO$_2$ to investigate the solar cell characteristics of this bi-layer system. In §5.3 nanostructured heterojunction solar cells are discussed that are prepared from TiO$_2$ and poly(3-octylthiophene), a soluble polymer of thiophene.
5.1 Introduction

Polymers consist of repeating units of one or more small monomers. They are used extensively in industry in the form of plastics, fibers, and additives. Conjugated polymers have special properties as a result of alternating double and single bonds. The delocalisation of the π orbitals over the backbone leads to characteristics like: non-linear optical properties, semiconductivity, flexibility, and chemical resistance. If aromatic or heteroaromatic rings are incorporated even more possibilities emerge. Although some of the basic compounds were known for a long time, research on conjugated polymers only started blooming in the late 1960’s. In Fig. 5.1 a selection of the most studied compounds is shown. If the repeating number of units is small (mostly between 1 and 10), the compound is called an oligomer. These oligomers can be very interesting compounds for study purposes, as they often already exhibit most properties of the polymer, while they are easier to handle, can be synthesized much more monodisperse, and show a higher degree of ordering as compared to their matching polymers. Some oligomers have already found application in organic transistors and Light Emitting Diodes (LED’s).

\[
\begin{align*}
\text{polyacetylene} & \quad \text{poylaniline} & \quad \text{polypyrrole} & \quad \text{polythiophene}
\end{align*}
\]

*Fig. 5.1. Chemical structure of some conjugated polymers. n is the number of repeating units.*

Polyacetylenes represent the first group of polymers that revealed high electrical conductivity upon doping. In the mid 1970’s MacDiarmid, Shirakawa, and Heeger discovered that the conductivity of polyacetylene increases with a factor of 10⁶ upon exposure to iodine vapour\(^{14}\). Their research was awarded the Nobel Prize for Chemistry in 2000. These polyacetylene results were the first indication that electrical conductivities
comparable to those of inorganic compounds could be reached with organic compounds, which was believed to be impossible until then. Since that time, the number of papers on semiconducting polymers has increased enormously and numerous groups in the world have undertaken research in this field, either with a fundamental (i.e., computations), a chemical (i.e., synthesis of new compounds), a physical-chemical (i.e., properties), or an application-oriented point of view. The major results can be summarized as a better control of properties and ordering (for example using oligomers instead of polymers) and higher conductivities.

The monomer of thiophene was discovered in 1882 by the German organic chemist Viktor Meyer, who extracted it from benzene. The ion is the Greek word for sulfur and the name thiophene is referring to the similarity with benzene. Thiophene is a colourless, volatile liquid, which amongst others occurs in coal-tar and is extracted by shaking with concentrated sulphuric acid. Thiophene is a parent substance for a number of derivatives, differing in side-groups and polymerisation degree. In nature it is also present, for example, a tetrahydrothiophene unit is contained in Biotin (vitamine H) and occurs in yeast and eggs. A simple pyrolysis of butane with sulfur is employed to date to produce thiophene in industry.

The inverse of resistivity is called conductivity. It is measured in Sm$^{-1}$ ($S=\Omega^{-1}$) and is a material property. The conductivity depends on the number of charge carriers ($n$) and the mobility of these charge carriers ($\mu$, also a material property) according to:

$$\sigma = n|zq|\mu$$

(Eq 5.1)

The unit of mobility is cm$^2$V$^{-1}$s$^{-1}$, $q$ is the electron charge, and $z$ is the valence state of the charge carrier. In Fig. 5.2 a scheme is shown in which materials are classified according to their electrical conductivity. Of course, the borders between the different categories are not strict. Doped polyacetylene, as researched by MacDiarmid, Shirakawa, and Heeger, exhibits a conductivity of $10^{-1}-10^7$ Sm$^{-1}$, depending on the cis/trans ratio of the double bonds and the dopant. Polyacetylene is sensitive to water and oxygen and is, therefore, not suited for commercial application. Polthiophene and polypyrrole are much more stable in ambient conditions and can be synthesized in the doped form.
in one step with a conductivity around $10^4$ Sm$^{-1}$ at present, which still is sufficient for practical applications.

Fig. 5.2. Electrical conductivities of different materials. Figure taken from ref. 3

To date, many conductive polymers are commercially used. For example:

- Polypyrrole is tested as radar-invisible coating and as active material for sensors
- Polyethylene dioxythiophene (PEDOT) doped with polystyrene sulfonic acid is used as an anti-static coating in photography and as electrode material in LED's. It was recently used as an infra-red detector.
- Doped polyaniline is used as a corrosion inhibitor as well as for electromagnetic shielding of electronic circuits.
- Polyphenylene vinylene (PPV) and polydialkyfluorene derivatives are tested as light-emitting materials for displays.
- Polythiophene derivatives are promising candidates for field-effect transistors.

Other applications of these materials are emerging as research continues. In order to obtain processable polymers (i.e. from melt or solution), side-groups have to be attached to the backbone. For polythiophenes it is found that poly(3-alkythiophenes) (PATs) with alkyl groups longer than butyl are
easily soluble (for example in chloroform) and can be deposited as thin films, which subsequently can be oxidized to yield conductivities of 100-500 Sm⁻¹. Regioregular polymers (i.e., all monomers are coupled head-to-tail) have a higher conductivity than regiorandom / irregular polymers in which also head-to-head and tail-to-tail coupling is occurring. Because of the steric hindrance caused by the substituents a twist of the thiophene rings occurs, which leads to a decrease of conjugation and, therefore, of conductivity. This difference can easily be a factor of 10-50. As the demands on the polymers grow, the synthesis methods also become more elaborate. The organic chemistry involved falls outside the scope of this thesis, but can be found in textbooks and mostly involves an oxidative coupling of thiophene monomers. Side groups are in most cases already present in the starting materials. Electrochemical polymerisation is also widely applied, but usually yields lower molecular weight polymers.

There is a strong correlation between structure and absorption spectra in thiophenes. First of all, the band gap has an influence on the peak position. In Chapter 7 this is illustrated for oligothiophenes. Another major contribution is ordering, which causes an increase in overlap of the backbones. In the solid state, this leads to a red shift compared to the absorption of the solution, which is clearly visible with the naked eye. Side-chains in most cases hinder stacking and the absorption is blue-shifted, but some end-capping groups may lead to increased ordering and subsequently to red-shifted absorption spectra. Regioregularity, temperature, solvent molecules, molecular weight, and doping can also influence the absorption spectrum, so care should be taken in comparing literature data.

Neutral polythiophene derivatives have a low conductivity (10⁻⁴-10⁻⁵ Sm⁻¹) and have to be oxidized (p-type doped) or reduced (n-type doped) to increase their conductivity to values, high enough for practical applications. Oxidative doping by FeCl₃ (also used often in the polymerisation reaction) or iodine is most effective, although the latter evaporates in time from the material. While the conductivity is highly anisotropic, being largest along the polymer backbone, an increase of the polymerisation degree can lead to higher conductivities. Stretching of thin films can increase the conductivity in one
direction even further. Cross-linking on the other hand decreases the anisotropy and most of the time also the conductivity. Furthermore, it diminishes the processability, yielding mostly powders. In principle, longer alkyl sidegroups lead to lower conductivities, because of larger interchain distances, but often these long alkyl chains are advantageous for regioregular polymerisation and ordering, which results in higher conductivities. In general, it is very difficult to predict the conductivity on the basis of a chemical structure. Synthesis details, molecular weight, and structural ordering are very important factors and the conductivity can vary with manufacturer or even synthesis batch.

Photoconductivity in these compounds is generally described in terms of bound electron-hole pairs (excitons) rather than as photogeneration of free electrons and free holes. These excitons dissociate usually at an interface (for example the pn-junction) or at a trap. Oxygen, like in phthalocyanines (see Chapter 4), is considered to serve as a deep trap for electrons and can dope thiophene materials.

Thin films can be deposited from soluble polythiophenes using spin coating or tape casting. For oligothiophenes thermal evaporation/sublimation is the most common technique, as they are usually not soluble. For insoluble polythiophenes this is not an option, as their backbone will break down at elevated temperatures. The morphology and structure of oligothiophene crystals and thin films are described in various articles, showing the importance of orientation, side groups, and preparation method. Detailed information on this structural characteristics is beyond the scope of this thesis, but can be found in various reviews\textsuperscript{56}. In general, oligothiophenes adopt a herringbone-like structure in the solid state and in thin films the oligothiophenes molecules prefer to stand upright on the substrate surface. This orientation can be influenced by choice of substrate (for example, metal vs. insulator) or by "rubbing" and shows to have a pronounced influence on the solar cell characteristics\textsuperscript{78}. Polymorphism occurs for some oligothiophenes (for unsubstituted oligothiophenes in the case of quaterthiophene (α-4T) and sexithiophene (α-6T)), depending on the deposition characteristics. For instance, the high-temperature (HT)
polymorph of $\alpha$-6T is formed if crystals are grown from the melt, while the low-temperature (LT) form is obtained if crystals are grown from the vapour phase. Polythiophenes inherently exhibit low crystallinity, but calculations show that two stable conformations can exist: one with a linear and nearly planar all-trans structure (i.e., rod formation) and one with a helical all-cis structure (i.e., coil formation). Experiments on powders and thin films seem to support these calculations.

Oligothiophenes, in general, show a lower conductivity than polythiophenes with the conductivity increasing with increasing chain length. This is caused by the lower conjugation length. Empirically it is found that the conductivity decreases logarithmically with the inverse chain-length. But again, the structural order and doping level influence the conductivity a great deal, so care has to be taken in comparing data from different articles. The conductivity for undoped oligothiophenes is two to three orders of magnitude lower in dark than under illumination and if oxygen and illumination both are present the conductivity can be another order of magnitude higher. The conductivity is roughly linear with the square root of the light intensity. The band gap decreases with increasing oligomer length going from 3.53 eV (2T), 2.74 eV (4T), 2.25 (6T) to 1.9-2.1 eV for polythiophene as can be determined from UV-VIS absorption measurements. The oxidation potential is linearly dependent on the inverse of the conjugation length and the energy of the HOMO level is believed to follow the same trend. Both can be determined from cyclic voltammetry (CV) plots. The LUMO level can then be calculated from the HOMO level and the band gap. In Fig. 5.3 a schematic energy diagram is shown for poly(3-alkythiophene) in combination with TiO$_2$. Fermi levels can be determined using Kelvin-probe measurements and are normally found to be close to the valence band, showing the p-type character of polythiophene. For clarity also the Fermi-levels of gold and ITO (high workfunction) and of Ca (low workfunction) are shown. From theory it is predicted that polythiophene should form an ohmic contact with high work function electrodes, while it should form a Schottky barrier with low work function metals. Care should be taken with energy values in literature, while they can be scaled vs. vacuum, normal hydrogen electrode (NHE, 4.5 eV below vacuum), saturated
silver electrode (Ag/AgCl, 0.20 V above NHE) or saturated calomel electrode (SCE, 0.24 V above NHE)\(^5\). As mentioned earlier (§1.3.3), the bands of the polythiophene can be regarded both as HOMO/LUMO levels or as valence/conduction bands.

![Schematic energy diagram for poly(3-alkylthiophene) in combination with TiO\(_2\). For clarity also the Fermi-levels for fluor doped SnO\(_2\) (Transparent Conducting Oxide (TCO)), Au and Ca are shown. NHE stands for Normal Hydrogen Electrode with a defined energy of 0 eV.](image)

Solar cells are synthesized using both oligothiophenes and polythiophenes. If a similar arrangement as the Tang cell (perylene/phthalocyanine) is employed using a combination of sublimed \(\alpha\)-octithiophene and perylene, an efficiency of 0.6% is achieved which is in the same order of magnitude as
for the original Tang cell\textsuperscript{4-5}. Small oligomers (less than 6 units) in general do not absorb enough visible light to lead to high efficiencies and it is shown that orientation plays a role\textsuperscript{7}. Polythiophene is more often applied in solar cells, but again bi-layer devices show a limited efficiency\textsuperscript{7}. In nanostructured heterojunctions they are promising as is shown for the C60/PT cells\textsuperscript{16-20}. Using TiO\textsubscript{2}, some results have been obtained for bi-layer devices as well as for nanostructured heterojunctions\textsuperscript{21-23}. Recently, Huyn, Dittmer, and Alivisatos reported on the combination of polythiophene and nanorods of CdSe, which exhibits an overall efficiency of 1.7\%\textsuperscript{24}.

5.2 Bi-layer devices with sexithiophene and TiO\textsubscript{2}

Bi-layer devices of TiO\textsubscript{2}, deposited with e-beam evaporation (§ 2.3), and sexithiophene (α-6T), deposited on top using thermal evaporation are prepared. As substrate material quartz is used, on which a thin film of titanium metal (40 nm) is deposited by e-beam evaporation prior to deposition of the TiO\textsubscript{2} film (80 nm). The quartz/Ti/TiO\textsubscript{2} sample is annealed at 450°C for 2h in air before sexithiophene is evaporated. Thermal evaporation of α-6T is performed at the Nano Physics group, Nanoscience Department, Faculty of Applied Physics, Delft University of Technology. The set-up is similar to the thermal evaporation set-up described in § 3.2 to deposit ZnPc films. The base-pressure of the set-up is around 10\textsuperscript{-7} mbar and a quartz crystal microbalance is installed to measure the film thickness during growth. Sexithiophene powder is obtained from Syncom (Groningen, the Netherlands) and is purified by zone-sublimation (courtesy of D. Fichou, Laboratoire des Matériaux Moléculaires, C.N.R.S. (CEA Saclay), Thiais, France. In Fig. 5.4 an optical microscopy image is shown of evaporated α-6T. A uniform film of crystallites of 1-2 μm in size is formed. From literature it is known that the growth rate and the substrate temperature strongly affect the crystal size. The pressure in the evaporation set-up, the purity of the material, the film thickness, and the substrate material are also of influence. Different articles have appeared that present investigations on the relation between crystal size and substrate temperature\textsuperscript{25-26}. Fast deposition rates (a few nm per minute) combined with a substrate at room temperature usually leads to
non-oriented films with small crystallites (below 100 nm). Slow evaporation (a few Å per minute) and a heated substrate produce orientated films with larger grains (several μm). Although the applied deposition rate of 0.4 nm/min is quite high, large uniform crystallites are observed, possibly due to the pure starting material. It is also important to mention that directly after deposition the sample is cooled to room temperature at a high rate using a water-cooled substrate holder. This prevents evaporation of the deposited sexithiophene film. Various film thicknesses of α-6T have been deposited.

![Image](image_url)

**Fig. 5.4.** Optical (fluorescence) microscopy photograph of sexithiophene crystals, thermally deposited on TiO₂. The substrate temperature during evaporation is 180°C and the sexithiophene powder is evaporated at 300°C. Growth rate: 0.4 nm/s, film thickness: 500 nm.

The photovoltaic effect of the TiO₂/α-6T is measured in vacuum (1×10⁻³ mbar) using mercury as a back contact. In Fig. 5.5 the device geometry is shown.

In Fig. 5.6 the I-V curve in dark and under illumination with a 5-mW 435.5-nm laser is shown. Although the fill factor is rather low, the open circuit voltage (0.62V) and the short circuit current (9 μA/cm²) are good.
Fig. 5.5. Device geometry for electrical measurements on quartz/Ti (40 nm)/TiO$_2$ (80 nm)/α-6T (80 nm)/Hg. Mercury is applied in holes (diameter 2 mm) cut from a piece of foam tape. On top of the mercury droplets another piece of foam tape is placed, to prevent leakage. The sample is attached with the quartz side on a glass support. Platinum wires are connected to the mercury droplet and are attached to the support by silver paint (conducting silver glue). The Ti film is also connected with silver paint. The left hand picture is a top view, the right hand picture is a side view.

Fig. 5.6. I-V curve of quartz/Ti (40 nm)/TiO$_2$ (80 nm)/α-6T (80 nm)/Hg, measured in vacuum in dark (grey line) and under 5-mW 435.5-nm laser illumination (black line).

Photoaction spectra with different applied bias voltages are measured to study the influence of the electrical field. In Fig. 5.7A photoaction spectra are
shown, measured in vacuum at different voltages. In Fig. 5.7B the same spectra are shown, now corrected for the change in current caused by the voltage change (base line correction). It is expected that a change in shape of the spectra as a result of the bias voltage can be related to the active interface region of the α-6T film near the TiO₂. Especially the tails of the photoaction peaks are expected to be sensitive to a change in active interface region, as the penetration depth of wavelengths that are absorbed in small yield is higher than the penetration depth of wavelength that are absorbed at maximum. No major changes in shape are observed, in particular not at the tail of the absorption peak (around 550 nm). It is, therefore, concluded that the electrical field does not induce a change in the active interface region.

![Graph A](image1.png)

**Fig. 5.7.** Photoaction spectra of quartz/Ti (40 nm)/TiO₂ (80 nm)/α-6T (80 nm)/Hg, measured in vacuum and at different bias voltages. A: as-measured, B: after baseline correction.

To determine the acceptor density in the sexithiophene film, Mott-Schottky analysis is performed. In Fig. 5.8 a Mott-Schottky plot is shown, measured with a frequency of 10 kHz in the dark and under illumination (white light). As can be seen from the Bode plot of the impedance (inset of Fig. 5.8) straightforward Mott-Schottky analysis as discussed in §1.236 is in fact only allowed beyond 100 kHz, but we can use the slope of this Mott-Schottky plot as an indication of the acceptor density. In the dark a value around 2.4×10⁹ cm⁻³ is found, while under illumination this increases to 7.7×10⁹ cm⁻³, which agrees with literature values⁴.
A hysteresis is observed when scanning to and from -1V in the dark, but not under illumination. This effect is possibly related to storing of charges in the first half of the potential scan that are released at a slow rate in the second half. In Chapter 3 (Fig. 3.13) this effect is also observed for TiO₂/ZnPc devices. Under illumination the electrical conductivity of the 6T is increased, which increases the charging/discharging speed and prevents the occurrence of a hysteresis. The hysteresis leads to a deviation in the value of the flat-band potential for the second half of the scan in the dark.

To investigate the influence of oxygen on these samples, the current as a function of time is measured in the dark and under illumination both in reverse and in forward bias in ambient atmosphere. In Fig. 5.9 these time-dependent current plots are shown. In forward bias the dark current increases in time. This is attributed to a reduction of α-6T, caused by the injection of electrons. In reverse bias the current is stable in the dark and under illumination with monochromatic light that is only absorbed by the α-6T and not by the TiO₂ (i.e., 450 nm light). If illumination is applied that can
be absorbed by the TiO$_2$ (i.e., 360 nm light) a steady increase of the current is seen. This is attributed to an oxidation of the α-6T, caused by the injection of holes from the TiO$_2$ into the sexithiophene. Electron-hole pairs are formed under UV-illumination and holes are injected into the α-6T at the junction. It can thus be concluded that sexithiophene is subject to oxidation and reduction reactions in air.

**Fig. 5.9.** Current-time plots for quartz/Ti (40 nm)/TiO$_2$ (80 nm)/α-6T (80 nm)/Hg in air. A: in forward bias (-0.5 V, Hg is positive) in dark, B: in reverse bias (1 V, Ti is positive) under illumination with 450 nm or 360 nm light.

5.3 **Nanostructured blends of poly(3-octylthiophene) and TiO$_2$**

To explore the possibility to design a nanostructured heterojunction solar cell using thiophenes and TiO$_2$, several methods are investigated. The restrictions on the employed techniques are mainly related to solubility and temperature stability of the polymer. Oligothiophenes that are suited for solar cells are in most cases not soluble, excluding methods in which infiltration in a nanoporous TiO$_2$ film takes place from solution. Gas-phase synthesis methods like CVD and ALD could possibly be employed, but this is outside the scope of this thesis. In Chapter 7 an alternative method is described, in which small, soluble, oligothiophenes are infiltrated into nanoporous TiO$_2$ and are polymerized using UV-illumination. Formation of a nanoporous oligothiophene film may be possible by controlled evaporation processes, much like the phthalocyanine sublimation described in §3.3, but the subsequent filling of the pores with TiO$_2$ will cause stability problems, as
the temperature to obtain crystalline TiO₂ (either by gas-phase synthesis or post-deposition treatment) is such that the oligothiophene fraction will evaporate or degrade. For polythiophenes the same problems apply, even more so because evaporation is in most cases not possible. Applying side-groups, like in the poly(3-alkylthiophenes) lifts the solubility problem, but infiltration into nanoporous TiO₂ is difficult as a result of the size of the polymer. In Chapter 6 this is discussed in more detail. Premixing the polymer (or precursor thereof) with TiO₂ nanoparticles (or precursor thereof) is a possibility, but again, a high temperature step is necessary to obtain crystalline TiO₂, which may lead to degradation of the polymer.

While it is clear from Thermo Gravimetric Analysis (TGA) (Fig. 5.10) that poly(3-octylthiophene) (P₃OT) is stable up to temperatures well above 300°C, codeposition of TiO₂ and P₃OT using spray pyrolysis deposition (SPD) is studied. Devices, stepwise built-up from TCO, a thin (ca. 100 nm) film of sprayed TiO₂, a sprayed mix of TiO₂ and P₃OT, and a thin spincoated film of PEDOT are fabricated and their electrical characteristics are studied. The substrate temperature for spraying is 300°C and the solvent is either ethanol or chloroform. The spraying time is either 15 or 30 minutes and the mass fraction of P₃OT in TiO₂ is varied between 5% and 10%. The cells are slightly coloured; in the case of ethanol as solvent they are purple and in the case of chloroform as solvent they are orange. The purple cells do not look completely homogeneous, as they seem to contain some grains. For polythiophene-based devices, it is known that interaction between the polymer chains (for example by stacking) leads to a purple colour, while separated polymer chains lead to an orange colour. The purple colour of the cells with ethanol and especially the grains that are visible lead us to believe that P₃OTT is agglomerated, which is due to the fact that P₃OT is not very soluble in ethanol. In chloroform this problem is circumvented and the cells appear homogeneous and have an orange colour. In Fig. 5.11 current-voltage plots are shown for four different cells. All cells exhibit diode behaviour in the dark. The dark currents in forward direction (negative potential) are relatively small, indicating that the film has a high resistance. Under
illumination all cells show clear photoconducting behaviour, but a very limited photovoltaic effect.

![Diagram](image)

Fig. 5.10. TGA measurement of poly(3-octylthiophene) powder heated from 25 to 630°C at 10.0°C/min under argon. The weight of the sample is monitored with a quartz crystal microbalance.

![Graphs](image)

Figure 5.11. Current-voltage plots for TCO/TiO$_2$/TiO$_2$ + P3OT/PEDOT/Hg cells in dark (black) and under illumination (grey, white light approx. 15 mW/cm$^2$, UV excluded). (A):5% P3OT, ethanol used as solvent, spray time 15 min. (B): 10%, ethanol, 15 min. (C): 10%, ethanol, 30 min. (D): 10%, chloroform, 15 min.
From XRD measurements it is concluded that anatase TiO$_2$ is formed (Fig. 5.12), but no peaks from the P$_3$OT are observed. A cross-section of a film deposited in 15 min is measured with scanning electron microscopy and shows that the film is about 1 μm thick. This might well be too thick and explains the high resistance.

![XRD spectrum](image)

*Figure 5.12. XRD spectrum of a co-sprayed TiO$_2$/P$_3$OT cell with 10% PT, ethanol as solvent, spraying time 15 min, substrate temperature 300°C. The asterisks denote the anatase peaks; the other peaks originate from the TCO substrate.*

Because the cells with chloroform in the precursor solution exhibit the highest photocurrent, a photoaction spectrum is recorded at 0V (Fig. 5.13). The spectrum follows the absorption curve of P$_3$OT, indicating that P$_3$OT is indeed the photo-excited species that creates an hybrid solar cell with TiO$_2$, but the maximum is clearly blue-shifted, which means that the π-overlap is less than for a dense film of P$_3$OT. Although the results of this type of cells are not good enough yet, it is concluded that spray pyrolysis co-deposition can yield cells that exhibit a photovoltaic effect. This is very promising and calls for further research.
Figure 5.13. Photoaction spectrum of a co-sprayed TiO$_2$/P$_3$OT cell with 10%PT and chloroform as solvent (squares). The spraying time was 15 min and the substrate temperature 300°C, a 360 nm high pass filter was used. Absorption curve (optical density) of a bi-film of TiO$_2$ (100 nm, deposited with spray pyrolysis) and P$_3$OT (60 nm) (solid line).

Another approach to pre-mixing of this kind of solar cell components is to make a film of nanoparticles TiO$_2$ without a heat treatment. This can be done by pressing a TiO$_2$ paste on a substrate. The heat treatment and the pressing both are able to connect the individual TiO$_2$ particles together, so they form a connecting network. A soluble polythiophene can be added to the paste and by controlling the percentage of both components percolation can be reached. Some studies have appeared on this subject recently$^{27,28}$. It is important to note that organic additives cannot be added to the paste, as they cannot be removed from the TiO$_2$ film. Commercial TiO$_2$ nanoparticles (P25, Degussa, average particle size 20 nm) are ultrasonically deagglomerated in ethanol and P$_3$OT is added. A film of this paste is doctor bladed on a TCO/TiO$_2$ (100 nm deposited with spray pyrolysis) substrate. Subsequently, a pressure of 1000 kg/cm$^2$ is applied on the sample and afterwards a PEDOT
film is spincoated on top. Surprisingly, in most cases the samples did not break under this high pressure.

In Fig. 5.14 a SEM photograph of a cross-section of a pressed film of P3OT and nanocrystalline TiO₂ is shown. As can be seen, the film thickness is 3.5 μm and the film is not everywhere dense.

![SEM of P3OT film](image)

**Fig. 5.14. SEM recording of a TCO/TiO/nc-TiO₂ + P3OT film, pressed at 1000 kg/cm².**

In Fig. 5.15 the I-V curve and photoaction spectrum of this cell are shown. A short-circuit current of 5 μA/cm² and an open circuit voltage of 0.5V is obtained. Although the photovoltaic effect is rather limited, it would be interesting to investigate this system in more detail. It is, for example, possible that percolation of the P3OT is not yet reached. If this system could yield good quality solar cells, it would be a large step forward, as no high-temperature step is needed, which opens up a way to construct effective nanostructured heterojunction solar cells.
**Fig. 5.15.** Electrical characterization of TCO/TiO/nc-TiO$_2$ + P3OT/PEDOT/Hg, uniaxially pressed at 1000 kg/cm$^2$. A: I-V curve in the dark (squares) and under white light illumination (solid line). B: photoaction (360 nm high pass filter) and absorption spectrum.

### 5.4 Conclusions

Oligomers and polymers of thiophene are a promising class of compounds for use in solar cells. Their high hole conductivity, chemical versatility, and easy deposition makes them suitable for nanostructured heterojunctions. However, a lot of challenges have yet to be met in order to come to commercial applications. Bi-layer devices of sexithiophene and TiO$_2$ have been prepared, which show a pronounced photovoltaic effect, but no effect of applied bias voltage on the active interface region. The acceptor density inside the sexithiophene film is found to be $2.4 \times 10^{15}$ cm$^{-3}$ in the dark, which under illumination (white light) increases to $7.7 \times 10^{14}$ cm$^{-3}$. Sexithiophene is subject to reduction under forward bias in the dark and to oxidation under reverse bias and UV-illumination. Nanostructured blends of poly(3-octylthiophene) and TiO$_2$ are synthesized with codeposition using spray pyrolysis. Under illumination a clear photoconducting behaviour is found, but a limited photovoltaic effect. Premixing of poly(3-octylthiophene) and TiO$_2$ nanoparticles, followed by uniaxial pressing leads to cells with a small photovoltaic effect. For both systems more research is needed to assess whether efficient solar cells can be obtained.
References


(3) see http://www.nobel.se/chemistry/laureates/2000/chemadv.pdf


Aerosol synthesis of anatase titanium dioxide nanoparticles for hybrid solar cells

Using an aerosol technique, in which ultrasonically formed droplets of titanium isopropoxide are pyrolyzed, thin films of nanosized anatase titanium dioxide (TiO₂) particles are deposited. The size of the particles and the morphology of the films depend on the deposition parameters, i.e., reaction temperature, concentration of the precursor, and gas flow. Under optimal conditions, films can be deposited that consist of stoichiometric anatase TiO₂ particles with diameters of 50-300 nanometer. With these films, solar cells are constructed by spin casting poly(3-octylthiophene) (P3OT) on top. Devices with a 1 μm film of porous TiO₂ and P3OT inside the pores have a short circuit current (Iₚₜ) of 0.25 mA/cm², an open circuit voltage (Vₚₜ) of 0.72 V, a fill factor (FF) of 0.35 and an efficiency (η) of 0.06% under white light illumination (1000 W/m²). The efficiency is a factor of 20 higher compared to cells with a flat film of anatase TiO₂, while the O.D. for both systems is comparable (flat film equivalent of 60-nm P3OT). The Incident Photon to Current Efficiency (IPCE) for the nanostructured solar cell is 2.5% at 488 nm. Devices, prepared by adding P3OT during the deposition of the porous TiO₂ show the same performance as the cells where P3OT is applied after porous TiO₂ deposition. This shows that penetration of the polymer is quite effective in this system. It is found that P3OT can penetrate these porous TiO₂ films as deep as 1 μm.
6.1 Introduction

Titanium dioxide is a key chemical and attracts a lot of interest for optical and optoelectronic applications. TiO$_2$ is a wide-bandgap semiconductor, easy to synthesize in either the anatase or the rutile crystal structure, with a high dielectric constant, and high temperature stability. It is also chemically stable, highly scattering and an excellent UV absorber, explaining its use in bulk products like paint, toothpaste, sun cream, and cosmetics. TiO$_2$ also exhibits photocatalytic properties, which can be employed for waste water purification, organic synthesis, and production of hydrogen from water. For specialized applications TiO$_2$ can, for example, be used in anti-reflection coatings, photonic crystals, and solar cells. In the last decade especially nanostructured anatase TiO$_2$ is studied for interfacial area enlargement in combination with visible light-absorbing sensitizers. In 1991 O'Regan and Grätzel showed that a solar cell comprising a porous film of anatase TiO$_2$ particles of 15 nm in combination with a sensitizing ruthenium complex and a liquid electrolyte exhibits an energy conversion efficiency of 8%$. At present, these cells have an efficiency of around 10%$. However, the presence of a liquid electrolyte in the system is a major bottleneck for further development, as time- and money-consuming sealing has to be applied to prevent leakage.

Several attempts have been undertaken to design dye-sensitized solar cells excluding the liquid electrolyte. It can be replaced by an ion-conducting polymer$^{**}$ or hole-conducting material$^9$. Another possibility is to use organic or inorganic compounds that do not only absorb visible light and inject electrons into TiO$_2$, but also transport the holes to the back contact. In this concept the pores in nanostructured TiO$_2$ are filled with a visible light-absorbing and hole-conducting material$^{**}$. A problem in constructing these cells is the necessity of a high-temperature sintering step to obtain good-quality nanostructured anatase titania films. Most organic dyes are not stable at these temperatures and can only be applied afterward. This is a problem when bulky molecules have to penetrate into the nanosized pores. Synthesizing a network of TiO$_2$ and organic dye at the same time would be an
elegant solution to this dilemma, leading to a high interfacial area and intimate contact between the components". It is important to achieve this without any high-temperature steps. Most synthesis methods for nanocrystalline anatase TiO₂ particles are wet-chemical, posing an additional constraint on fabrication of interpenetrating networks in one-step. Uniaxial pressing of nc-TiO₂ films could open up a way to avoid the sintering step, making it possible to blend the organic phase with the TiO₂ particles beforehand⁹⁻¹⁰. Nanostructured heterojunctions of PPV/C60 (poly phenylene vinylene/ buckminsterfullerene) are well-known and have an efficiency as high as 2.5% under simulated solar light irradiation⁹⁻¹⁰. At present, morphology studies are conducted to investigate in detail the characteristics of the blend⁹. Recently, a bulk heterojunction of CdSe nanorods and poly-(3-hexylthiophene) was reported to have an efficiency of 1.7% under AM 1.5 conditions⁹. For an overview of recent progress in hybrid solar cells we refer to ref. 22.

In this chapter we report on a route to synthesize nanostructured anatase TiO₂ films, in which a sintering step after deposition is not necessary. Using ultrasonically generated aerosols of a precursor, films of nanoparticles TiO₂ can be formed in a controlled way in ambient atmosphere. It is shown that these films can be used in solar cells. After spin coating poly(3-octylthiophene) on top of these porous TiO₂ films, solar cells are obtained. It is clearly shown that the interfacial area enlargement improves the conversion efficiency. It is also possible to add polymer to the film during deposition, yielding TiO₂/P₃OT interpenetrating networks in one step.

The employed aerosol synthesis technique for nanosized TiO₂ particles is known in literature under a variety of names including aerosol decomposition, spray roasting, and spray pyrolysis⁹⁻¹⁲. The average size of the produced droplets (dₐ) depends on the density of the precursor solution (ρₚ), the surface tension of the precursor solution (γ), and the ultrasonic frequency (f) as follows:
\[ d_a = \left( \frac{\gamma \pi}{4 \rho_p f^2} \right)^{1/3} \]  

(Eq. 6.1)

The size of the formed oxide particles \(d_p\) depends on the droplet size \(d_a\), the molecular weight of the oxide \(M_o\), the molecular weight of the precursor \(M_i\), the concentration of the precursor \(c\), and the density of the oxide \(\rho_o\) in the following way:

\[ d_p = d_a \left( \frac{M_a c}{M_i \rho_o} \right)^{1/3} \]  

(Eq. 6.2)

According to these equations, we expect an average droplet size of 930 nm and an average TiO_2 particle size of 146 nm for a concentration of 5% titanium isopropoxide (TTIP) in ethanol and an ultrasonic frequency of 1.63 MHz.

Semiconducting polymers have attracted a lot of attention over the past years. They are easy to process and especially their hole-conducting properties have greatly improved since their first appearance in literature. Hence, they are promising candidates to serve as light-absorbing and hole-conducting material in combination with an n-type semiconductor. The class of polythiophenes is investigated by numerous groups, owing to their relative stability in ambient atmosphere and under illumination in comparison to, for example, poly vinylene phenylenes (PPV's). The backbones of the conjugated units of the polymer are able to stack, leading to higher hole mobilities and increased exciton diffusion lengths compared to isolated polymer chains\(^a\). Nevertheless, for successful application in solar cells, the distance that both excitons and holes have to travel must be kept as small as possible. There have been a number of reports on heterojunctions of TiO_2 and oligo- or polythiophenes\(^{9,21,39-40}\).

### 6.2 Experimental aspects

Fig. 6.1 shows the set-up for aerosol synthesis of nanocrystalline TiO_2 particles. It comprises a commercial ultrasonic nebulizer (oscillating frequency 1.63 MHz) in which a diluted precursor solution is agitated to form small droplets. As precursor titanium isopropoxide (TTIP, Aldrich
98%+) diluted with absolute ethanol is used, kept at a constant temperature of 40°C. Part of the aerosol is transported along with an argon carrier flow through a quartz tube, which passes a furnace at the end. The temperature inside the furnace is measured with an internal thermocouple. A flow of oxygen is added just before the furnace. When the droplets of the titanium precursor solution travel through the furnace, they are pyrolyzed to form TiO₂ particles, which are subsequently deposited on a horizontal substrate placed at the exhaust of the tube. The substrate is attached to a spincoater, which is rotating at 3000 rpm. At the tube exhaust droplets of a P3OT solution in chloroform can be added from a syringe. As substrate material fluor-doped SnO₂ is used (Transparent Conducting Oxide, Libbey Owens Ford, 20 Ω/cm). Substrates are thoroughly cleaned in an ultrasonic bath with ethanol and acetone successively and are dried in a dry nitrogen stream. Most substrates are covered with a thin dense film of anatase TiO₂ (70 nm, deposited by spray pyrolysis) prior to deposition of the nanocrystalline TiO₂ particles⁴. This film serves as a selective contact to prevent short-circuiting.

**Fig. 6.1. Setup for synthesis of TiO₂ particles using an ultrasonically generated aerosol.**
The crystal structure of the films is studied with grazing incidence X-ray diffraction by using a Bruker D8 Advance X-ray Diffractometer. Raman spectra are recorded on a home-built set-up, using a SpectraPhysics Millenia Nd:YVO₄ laser with a wavelength of 532 nm. Raman scattering is recorded in the backscattering mode, using a set of notch filters to remove Raleigh scattering, a liquid nitrogen cooled CCD camera (Princeton Instruments LN/CCD-1100PB), and a Spex 340E monochromator equipped with a 1800 grooves/mm grating. The morphology and film thickness are studied with (high-resolution) scanning electron microscopy using a JEOL JSM-5800 LV Scanning Electron Microscope (SEM) and a JEOL JSM 6500 F Field Emission SEM (High Resolution SEM).

On top of the TiO₂ films, a solution of poly(3-octylthiophene) (Aldrich, regioregular) is spincoated. The polymer is used without additional purification. A solution of 5 to 20 mg/ml in chloroform is freshly prepared and ca. 5 drops are applied to the substrate until the whole surface is covered with a solution layer. Subsequently, the substrate is spinned at 1500 rpm for 20 s, leading to a polymer film with the same optical density (O.D.) as an equivalent film of 30 to 115 nm (depending on the concentration) deposited on a flat substrate. After spin coating of P3OT, the samples are annealed for 30 min at 100°C to remove remaining chloroform. For the samples that are prepared in one step, the P₃OT solution is added dropwise from a syringe during the aerosol deposition of nc-TiO₂. The number of drops that are added, the concentration of the solution, and the interval are varied.

Current-voltage characteristics and wavelength-dependent photocurrent spectra are recorded using a Keithley 2400 digital source meter. A 250 W tungsten-halogen lamp in combination with an Acton Spectra-Pro-275 monochromator is used to illuminate the samples through the TCO substrate with an intensity of 100 mW/cm², in the case of white light, and with ca. 2 mW/cm² in the case of monochromatic light. A 360 nm high-pass filter is used for the wavelength-dependent photocurrent spectra and a 400-nm high pass filter is used to remove UV-light during the measurements.
under white light illumination. Gold contacts with a diameter of 2 mm and a thickness of 50 nm are evaporated on top. Contact to these gold contacts is made with a gold-coated tip, attached to a spring with a spring constant of \(7 \times 10^3 \text{ Nm}^{-1}\) (Ingun Prüfmittelbau GmbH). Some measurements are carried out using a mercury back contact, yielding the same results as for gold. Measurements are performed in ambient atmosphere and at room temperature. Care is taken to measure samples directly after the polythiophene film is spincoated and to avoid exposure to light, as this is known to cause degradation of semiconducting polymers\(^{38,42}\).

Solar cell characteristics are measured for cells, which consist of a TCO substrate, a dense film of TiO\(_2\) (70 nm), an aerosol-deposited film of nanoparticles TiO\(_2\) (various thicknesses), and a spincoated film of P3OT (either applied during or after deposition) subsequently.

To examine the penetration depth of P3OT inside the porous TiO\(_2\) network in detail, mixtures of nc-TiO\(_2\) and P3OT are sandwiched between two electrodes. In this case no selective TiO\(_2\) contact is present and the thickness of the nc-TiO\(_2\) film is varied between 200 and 2200 nm. For comparison, some devices are made with the nc-TiO\(_2\) film formed from commercially available TiO\(_2\) powder. Films are made consisting of either Solaronix HT paste (average particle size: 9 nm, thickness of the film 300 nm and 3 \(\mu\)m) or a 50-nm particle size paste, prepared by a sol-gel method (thickness of the film 50 nm and 2 \(\mu\)m). On top of all these nc-TiO\(_2\) films, P3OT is spincoated from a 10 mg/ml solution in chloroform, leading to an amount of polymer in the pores with the same O.D. as an equivalent flat film of 60 nm.

6.3 Results and discussion

6.3.1 Preparation of nanoporous TiO\(_2\)
To study the influence on the structure and the morphology of the TiO\(_2\) particles, the following process parameters are systematically varied: the concentration of TTIP in the precursor solution, the distance between tube
exhaust and substrate, the temperature of the furnace, the flow of argon, and the flow of oxygen.

In Fig. 6.2 grazing incidence X-ray diffraction patterns are shown of TiO₂ films produced at different furnace temperatures. Below 550°C, only peaks originating from the tin dioxide substrate are present; the TiO₂ film is amorphous. At temperatures above 550°C, additional peaks appear, which can be assigned to the anatase phase of titanium dioxide. The temperature at which anatase is formed in these experiments is much higher than, for example, in Chemical Vapour Deposition of TiO₂, where anatase already forms at 300°C.[4–6] This apparent increase in anatase formation temperature is caused by the short residence time of the precursor droplets in the furnace (typically less than a second). In this short period, they are not fully heated to the temperature of the furnace and only when the furnace temperature is sufficiently high, complete thermolysis of TTIP to anatase TiO₂ takes place. To check for the presence of possible minor fractions of other phases, which cannot be detected by XRD, Raman measurements are performed. In Fig. 6.3 Raman spectra are shown for TiO₂ deposited at different furnace temperatures. Again, it is clear that at temperatures lower than 550°C the TiO₂ formed is amorphous, while above 550°C the particles exhibit the anatase structure.[6] No other phases are detected, but it is possible that a small amorphous fraction is present in the films, because this is not visible in either Raman or XRD.

![Fig. 6.2. Grazing incidence X-ray diffraction patterns of nanocrystalline TiO₂ for different deposition temperatures. The crosses denote the tin dioxide peaks; the asterisks denote the anatase peaks. The spectra are offset for clarity.](image)
Using (HR)SEM the morphology of the TiO₂ films is studied. Fig. 6.4A shows a SEM micrograph of anatase particles, deposited at a furnace temperature of 550°C, 100% TTIP as precursor, a distance between tube exhaust and sample of 2 cm, an oxygen flow of 13 l/h, and an argon flow of 20 l/h. The particles are spherical and the size distribution ranges from 50 nm to 1 µm. Fig. 4B shows a detailed HRSEM recording of a TiO₂ film, deposited at a furnace temperature of 640°C, 5% TTIP in ethanol as precursor, a distance between tube exhaust and sample of 0.5 cm, an oxygen flow of 53 l/h, and an argon flow of 1.1 l/h. The particle size distribution is now much smaller, ranging from 50 to 300 nm.

![Graph showing Raman spectra for different temperatures. Peaks are marked with asterisks.](image)

Fig. 6.3. Raman spectra of nanocrystalline TiO₂ for different deposition temperatures. The asterisks denote the anatase peaks. The spectra are offset for clarity.

It is found that at higher precursor dilution and with a smaller argon flow, the size dispersion decreases. This can be explained by the fact that the smallest particles are formed from one single droplet of precursor solution. Part of the precursor droplets fuse before pyrolysis takes place, leading to larger particles. Lower carrier gas flows and a more diluted solution yield a smaller concentration of droplets and, therefore, a more homogeneous particle size distribution with a higher fraction of the smallest particles. The particle size is smaller than calculated. This is probably due to deviations of the values for surface tension and porosity of the oxide from the assumed values used in the calculations.
Fig. 6.4. (A): SEM micrograph of TiO₂ particles deposited with a furnace temperature of 550°C, 100% TTIP as precursor, a distance from tube to sample of 2 cm, an oxygen flow of 13 l/h, and an argon flow of 20 l/h. The length of the scale-bar is 5 μm. (B): HRSEM recording of TiO₂ particles, deposited on SnO₂:F with a furnace temperature of 640°C, 5% TTIP in ethanol as precursor, a distance from tube to sample of 0.5 cm, an oxygen flow of 10 l/h, and an argon flow of 1.1 l/h.

In Fig. 6.5 SEM micrographs are shown for samples obtained with different process parameters. If the distance between tube exhaust and substrate is small (0.5 cm), sintering between the TiO₂ particles occurs as a result of the hot gas-flow. Exactly beneath the tube exhaust, where the temperature is highest, an almost smooth layer develops in which the individual particles are hardly visible anymore (Fig. 6.5A). More to the edges of the sample, the particles are still present, but form large agglomerates, with cracks between them (Fig. 6.5B). These cracks are probably stress-induced and are caused by the fast cooling rate after deposition. At the edge of the sample, the temperature is low enough to prevent sintering (Fig. 6.5C). If the distance between the tube exhaust and the substrate is increased, no sintering is observed (see Fig. 6.4A for a distance of 2 cm). Although the temperature of the substrate is not monitored, an estimated temperature of about 100°C can be reached if the distance between tube exhaust and substrate is 0.5 cm, while the temperature stays below 50°C if the distance is increased to 2 cm. Locally
much higher temperatures can be reached, which explains the observed sintering of the particles. The TiO$_2$ particles are very hot when they come from the tube exhaust and they only partly cool down before they reach the substrate. There, they cool down rapidly, as their mass is very small and the sample is spinning at high speed. Although extensive sintering is detrimental for the morphology of the TiO$_2$ film, we have reason to believe that a certain increase of substrate temperature is beneficial for the creation of a well-conducting TiO$_2$ network, while it allows the formation of necks between the individual particles. In commercial nc-TiO$_2$ films these interconnections are formed during an annealing step at around 450$^\circ$C. To prevent degradation of the polymer in the experiments where devices are prepared by adding P3OT during TiO$_2$ deposition, a “cool-down” time of 30 s is introduced before the P3OT solution is added. Still, hot TiO$_2$ particles come into contact with the polymer when deposition is resumed, but only a limited contact area between P3OT and new TiO$_2$ exists, as the P3OT penetrates the underlying porous film. No colour change is observed for the samples that are prepared during TiO$_2$ deposition as compared to the samples that are prepared by postdeposition addition of P3OT, indicating that no major degradation is occurring.

At prolonged deposition times a thick, porous network is formed (Fig. 6.5D-F). Substrates become opaque and the film can be removed rather easy by brushing gently with a tissue.
Fig. 6.5. Scanning electron micrographs of TiO₂ particles, deposited on SnO₂:F with different process parameters. Middle of the sample (A), halfway between centre and edge (B), at the edge (C). TiO₂ networks are formed for thicker samples (D,E). Cross-section of a thick film (F).

If TiO₂ particles are deposited without additional oxygen the films become grey. This is caused by the presence of oxygen vacancies compensated by conduction-band electrons and the product is best described as TiO₂-x. Supplying a flow of oxygen to the tube leads to the formation of stoichiometric TiO₂ films. Thick films (more than 2 μm) appear opaque, but thinner films are transparent. The effect of additional oxygen on the solar cell characteristics will be discussed in more detail later.

By measuring the thickness using cross-sections of TiO₂ films deposited with different argon flow rates, it is possible to determine the growth-rate as a
function of argon flow. A graph of this relationship is shown in Fig. 6.6. The growth-rate is roughly linearly dependent on the flow rate. The growth rate increases when the distance between tube exhaust and substrate is decreased. With a typical argon flow of 1 l/h and a distance of 2 cm, films are deposited at about 200 nm/min. As is visible in Fig. 6.6, the linear fit does not pass the origin. At zero argon flow, still a small growth-rate is visible. This is caused by the evolving aerosol in the nebulizing chamber. Even without argon, part of the generated droplets are diffusing through the quartz tube towards the sample.

![Graph](image)

**Fig. 6.6.** Growth rate of nc-TiO$_2$ films as a function of argon carrier gas flow. The distance between tube exhaust and substrate is kept constant at 2 cm. The oxygen flow is 10 l/h. The concentration TTIP in the precursor solution is 5%, kept at a constant temperature of 40°C. The temperature of the furnace is kept constant at 630°C. The solid line is a linear fit to the data points.

In Table 6.1 the optimal process parameters for the deposition of stoichiometric anatase TiO$_2$ particles with a homogeneous particle size distribution are summarized. In short, we find that the distance between tube exhaust and sample must be large enough to prevent extensive sintering but small enough to form interconnected TiO$_2$ particles. The supply of additional oxygen is necessary to prevent the formation of oxygen vacancies. The temperature of the furnace should be higher than 550°C to obtain anatase
TiO₂. For most samples a higher temperature is used, to ensure a high percentage of crystalline TiO₂. The argon carrier flow rate determines the growth-rate and the size distribution, whereas the concentration of the precursor also influences the latter. The values given in Table 6.1 are used to deposit films for the devices with poly(3-octylthiophene).

<table>
<thead>
<tr>
<th>Table 6.1. Optimal process parameters for thin films of nc-TiO₂.</th>
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<td>Furnace temperature</td>
</tr>
<tr>
<td>TTIP concentration</td>
</tr>
<tr>
<td>Distance tube exhaust-substrate</td>
</tr>
<tr>
<td>Oxygen flow</td>
</tr>
<tr>
<td>Argon flow</td>
</tr>
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6.3.2 Devices with poly(3-octylthiophene)

Electrical and photovoltaic properties are investigated of devices of TiO₂ and polymer. These cells are prepared by spincoating a P3OT solution either during or after deposition.

In literature, dye-sensitized solar cells contain TiO₂ particles with a size around 15 nm⁹. But to allow polythiophene to penetrate into a TiO₂ film, the pore diameters should not be too small. Furthermore, a maximum penetration depth of spincoated polymer is expected, leading to an optimal thickness for the TiO₂ film. In the remainder of this paper, we will investigate the relation between pore size, penetration depth and photovoltaic properties in more detail. The size of the particles shown in Fig. 6.5 is about 50 nm, although agglomerated particles are also present. The pores are of similar size. These are the minimum sizes we could obtain using the aerosol technique.

First, cells are investigated, that consist of nc-TiO₂ on top of which P3OT is spincoated after deposition. The thickness of the nc-TiO₂ film is varied and current-voltage characteristics are recorded in the dark and under
illumination. In Fig. 6.7A, the photocurrent at 0 V (I_p) short circuit current) is plotted as a function of deposition time for two different distances between tube exhaust and substrate. When converted into film thicknesses (using the calculated growth rate), it is clear that the maximum of the photocurrent is reached at a TiO_2 film thickness of approximately 1 μm for both distances (Fig. 6.7B). Furthermore, it is observed that the maximum is higher at a smaller tube exhaust to substrate distance. This is probably caused by an increase of the substrate temperature for smaller tube exhaust to substrate distances leading to an improved contact between the TiO_2 particles. At very small distances, the particles sinter completely and no nanostructured film is no longer formed (vide infra).

![Graph A](image1)

**Fig. 6.7.** Short circuit current of TCO/TiO_2 (dense, <100 nm)/nc-TiO/P3OT as a function of the thickness of the nc-TiO_2 film. See Table 1 for deposition parameters. Illumination with white light (100 mW/cm², not AM 1.5, 400 nm high pass filter to remove UV-light) takes place through the SnO₂ electrode. A: I_p plotted vs. deposition time. The distance from tube exhaust to substrate is 1 cm (■) or 2 cm (○). B: I_p plotted after conversion to thickness of the TiO_2 film, using the growth rate for the two distances. The lines are drawn as guide for the eye.

To find the optimum flow of oxygen in the deposition process, devices are prepared under the same conditions while the oxygen flow rate is varied. In Fig. 6.8 the short circuit current of the TCO/TiO/nc-TiO/P3OT/Au cells is plotted as a function of the oxygen flow. For low oxygen flows the
photocurrent increases linearly with the amount of oxygen, whereas it levels of at flows rates around 50 l/h. Therefore, this oxygen flow rate is chosen for all TiO$_2$ film depositions (see Table 6.1).

![Graph](image)

*Fig. 6.8. Short circuit current, $I_s$, of TCO/TiO$_2$ (dense, <100 nm)/nc-TiO$_2$/P$_3$OT devices as a function of oxygen flow. Illumination with white light (100 mW/cm$^2$ and a 400 nm high pass filter to remove UV-light) takes place through the tin dioxide electrode.*

Other devices are prepared by adding P$_3$OT during the deposition of the porous TiO$_2$ while systematically varying the process parameters. In table 6.2 photovoltaic characteristics are summarized for a number of devices. As can be seen, these cells yield at maximum about the same photovoltaic characteristics as postdeposition spincoating of P$_3$OT. This indicates that the penetration of P$_3$OT occurs quite effectively in this porous system.

To investigate the penetration of poly(3-octylthiophene) into a nanoporous network of TiO$_2$ in more detail, experiments without selective contacts are carried out. When an interpenetrating film of TiO$_2$/P$_3$OT (spincoated after nc-TiO$_2$ deposition) mixture is sandwiched between TCO and Au two situations can be distinguished. In the first case, the nc-TiO$_2$ film is thin enough for the P$_3$OT to penetrate completely from top to bottom. P$_3$OT makes an ohmic contact to both TCO and gold contacts, and a linear I-V graph, with the reciprocal of the resistance of the P$_3$OT film as slope, is
observed when the voltage is scanned. In the second case, the nc-TiO$_2$ film is too thick for the P$_3$OT to reach the bottom. Hence, a clear interface between

<table>
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<th>P$_3$OT concentration (mg/ml)</th>
<th>Number of drops</th>
<th>Interval between drops (s)</th>
<th>Film thickness (µm)</th>
<th>$I_n$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
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</table>

TiO$_2$ and P$_3$OT will be present at some location in the film and a diode-type I-V characteristic is observed. For different thicknesses of the nanoporous TiO$_2$ film I-V curves are recorded of TCO/nc-TiO$_2$/P$_3$OT/Au devices with a spincoated P$_3$OT film (10 mg/ml, leading to a flat film equivalence of about 60 nm) on top of the nc-TiO$_2$. In figure 6.9 I-V curves are shown for TiO$_2$ films with a thickness of 340 (A) and 1780 nm (B), respectively. It can be seen that in the dark the 340-nm film shows a symmetrical curve (I), although not completely linear. The 1780-nm film shows diode-type behaviour (V). If illuminated, both samples show an increase in slope at 0V (II and VI), which is equivalent to a decrease in resistance. This is caused by the light-induced formation of electrons and holes in the P$_3$OT (photoconductivity). The UV light is filtered out to prevent TiO$_2$ from being optically excited. Upon
heating the samples kept in air and in darkness even steeper curves are measured (III, IV and VII), indicating that the resistance of the heated films decreases. This is ascribed to the temperature dependence of the specific resistance of poly(3-octylthiophene). From the I-V curves measured in the dark it can be concluded that for the 340 nm thick film the P3OT penetrates all the way to the bottom and touches the TCO electrode. For the 1780 nm thick film this is not possible and at some location in the film interpenetration ends, which excludes contact between the TCO electrode and P3OT. Note that we cannot distinguish between complete and incomplete pore filling, as only information on how deep the P3OT penetrates the nanoporous TiO₂ is obtained. The change of the slope, if the samples are illuminated or heated, reveals that the resistance clearly originates from the P3OT film inside the TiO₂ pores and excludes pinholes or short-circuiting being the reason for the symmetrical or linear I-V curves. For the 340 nm thick TiO₂ film the resistance of the P3OT is around 2700 Ω in the dark, 2130 Ω if illuminated, and decreasing to 1630 Ω and even further to 450 Ω, if heated to about 40°C and 60°C, respectively. For the 1780 nm thick TiO₂ film the resistance in the dark is a combination of TiO₂ and P3OT. If illuminated and heated, the resistances show remarkable resemblances with the resistances for the 340-nm thick film (2520 Ω as compared to 2130 Ω for the illuminated sample and 1370 Ω compared to 1630 Ω for the sample heated to 40°C). This indicates that in the dark the resistance of the TiO₂ is higher than the P3OT resistance, but upon illumination or heating the resistance of TiO₂ drops under that of P3OT and only the resistance of the P3OT is observed. Apparently, a substantial decrease of TiO₂ resistance is accomplished easily by injection of electrons.

The current-voltage measurements without selective TiO₂ contacts are repeated for different film thicknesses of the nc-TiO₂ film and the resistance is calculated from the slope of the I-V curves at zero volts. All curves are recorded in the dark. For nc-TiO₂ films of 200 nm to around 1 μm the I-V curves show a straight or symmetrical line with a resistance of 500-1400 Ω (not shown). This variation in resistances can be explained by assuming that
the pore sizes of the TiO$_2$ film and the pore filling of the P3OT are not completely homogeneous over the sample. If the film thickness increases beyond approximately 1 μm, the shape of the I-V curves changes from linear/symmetrical to a more diode-like type of curve. The resistances increase to values of 4-10 kΩ. From this we conclude that the maximum penetration depth of P3OT in this system is approximately 1 μm. This matches very well with the maximum of the short-circuit current, which occurs also for 1 μm thick films as shown in Fig. 6.7B. In general, it is expected that the maximum penetration depth depends on of the concentration of the spincoated P3OT solution, the amount of spin-coated material, and the spin-coat method (for example, whether multiple coatings are applied), and the pore size of the TiO$_2$ films.

![Graph](image_url)

**Fig. 6.9. I-V curves for TCO/nc-TiO$_2$/P3OT/Au.** The concentration of spincoated P3OT is 10 mg/ml in chloroform. A: Film thickness of nc-TiO$_2$ is 340 nm. I: measured in dark, $R = 2750\Omega$. II: measured under illumination (white light, 100 mW/cm$^2$, 400 nm high pass filter to remove UV-light), $R = 2130\Omega$. III: measured in dark, heated with hot air to about 40°C, $R = 163 \, \Omega$. IV: measured in dark, heated to about 60°C, $R = 450\Omega$. B: Film thickness of nc-TiO$_2$ is 1870 nm. V: measured in dark, $R = 8350\Omega$. VI: measured under white light illumination, $R = 2520\Omega$. VII: measured in dark, heated to about 40°C, $R = 1370\Omega$.

The influence of the latter parameter is studied by performing the same experiment with titanium dioxide powder of different particle sizes. In the
case of 50 nm particles (prepared using a sol-gel method) the pore size is larger than that for the aerosol-synthesized TiO₂ as confirmed by SEM (not shown). For both the 50-nm and the 2-μm thick samples the I-V curve shows ohmic behaviour, indicating that the P₃OT reaches all the way to the TCO electrode. The maximum penetration depth for this system is, therefore, substantially larger than for the aerosol synthesized TiO₂. For commercial 9 nm particles (Solaronix HT) the pore size is around 10 nm. For both 300-nm and 1-μm thick samples the I-V curve shows diode-type behaviour, indicating that the P₃OT does not penetrate all the way to the TCO contact. The maximum penetration depth for this system is, therefore, substantially less than that for the aerosol synthesized TiO₂.

These experiments also address the question as to whether small TiO₂ particles are always the best for making solar cells based on interpenetrating networks. In the case of polymers, it might well be that a small pore size is inhibiting the formation of a good TiO₂/polymer blend. On the other hand, if the pore-size is larger than the exciton diffusion length inside the polymer, excitons will recombine, which has a negative effect on the solar cell characteristics. Recently, it has been shown that the exciton diffusion length in regioregular P₃OT is only 3-5 nm⁴⁸-⁵⁰. Designing solar cells based on interpenetrating polymers and TiO₂ will, therefore, be a trade-off between pore-filling capability and recombination losses.

Figure 6.10 shows the current-voltage response for a 1 μm thick film of aerosol-synthesized anatase TiO₂ with interpenetrating P₃OT (10 mg/ml). Also a current-voltage curve is shown for a solar cell comprising a flat dense TiO₂ film (70 nm) with an equal amount of P₃OT spincoated on top (dotted curve). Although the light source is not AM1.5 calibrated, the efficiency can be determined to provide an indication of the cell performance. The values for the nanostructured cell are: \( I_\infty = 0.25 \) mA/cm², \( V_\infty = 0.72 V \), FF = 0.35, and \( \eta = 0.06\% \), and for the flat cell: \( I_\infty = 37 \) μA/cm², \( V_\infty = 0.66 V \), FF = 0.25, and \( \eta = 0.003\% \). The nanostructured cell has a 20 times higher efficiency than the flat cell. The photocurrent is linearly dependent on the irradiation intensity
between 0.1 and 200 mW/cm². If the cells are kept in the dark at room temperature or at elevated temperatures (100°C), the photovoltaic characteristics are stable for several weeks. If illuminated continuously, the photocurrent decreases slightly at a time scale of a few hours indicating that photodegradation is occurring. This process is irreversible.

![Graph](image.png)

**Fig. 6.10. I-V curve for TCO/TiO₂ (70 nm)/nc-TiO₂/P3OT/Au.** The nanocrystalline TiO₂ film is 1 μm thick and consists of 50-nm particles. The dotted curve is a current-voltage graph of TCO/TiO₂ (70 nm)/P3OT/Au. Illumination with white light (100 mW/cm², not AM 1.5) takes place through the tin dioxide electrode and a 400 nm high pass filter is used to prevent excitation of the TiO₂.

In Fig. 6.11 the wavelength-dependent photocurrent spectra for these same cells are shown, converted to the Incident Photon to Current Efficiency, together with the absorption spectra. The IPCE curve matches the shape of the absorption spectrum. The O.D.'s of the nanostructured and flat cell are comparable, showing that indeed an amount of polymer similar to a flat film of 60 nm is penetrated inside the nc-TiO₂. When we estimate the nc-TiO₂ film to be around 50% porous (as for the TiO₂ in dye-sensitized cells'), a pore filling of slightly more than 10% is estimated. This is quite low and could possibly be increased by spincoating of multiple layers of P₃OT, higher concentrations, or soaking of the nc-TiO₂ in a polymer solution. A better pore-filling could lead to higher efficiencies. Another interesting option is to use polymers that can form a chemical bond with the TiO₂ surface. Acid side-
groups will form such a covalent bond, which likely leads to an increase of the amount of absorbed polymer in the pores and possibly also to fast injection of electrons.

![IPCE curve for TCO/TiO₂ (70 nm)/nc-TiO₂/P₃OT/Au (solid line). The nanocrystalline TiO₂ film is 1 μm thick and consists of 50-nm particles. The dotted curve is an IPCE plot of TCO/TiO₂ (70 nm)/P₃OT/Au. The dashed curve is the absorption spectrum for the nanostructured cell and the dashed-dotted curve is the absorption curve for the flat cell. Illumination with monochromatic light (around 1 mW/cm²) takes place through the tin dioxide electrode and a 360 nm high pass filter is used.](image)

Gebeyehu et al.\textsuperscript{14,39} have reported on similar cells, using poly(3-octylthiophene) spincoated on top of 2-μm thick films consisting of 13-nm particles of anatase TiO₂. These cells have an efficiency of 0.08% under solar simulated white light of 80 mW/cm². When Ru 535-dye (cis-[L₂Ru(SCN)₃] in which L is 2,2’-dipyridine-4,4’-dicarboxylic acid) is applied between TiO₂ and polymer, like in dye-sensitized solar cells, the efficiency becomes twice as high. The Ru-dye absorbs visible light and injects electrons very efficiently into the TiO₂ network. The P₃OT has a double function: light-absorption/carrier injection and hole conduction. Still, these efficiencies are small compared to cells functioning with a liquid electrolyte. The authors remark that the limiting step for these devices is probably the hole transfer from the Ru-dye to the polymer, because injection of electrons from the Ru-dye to TiO₂ is expected to be very fast and there is sufficient hole transport in
the polymer. In the present study the transport of excitons to the TiO₂ particle surface is probably also a bottleneck of the device. Nevertheless, the area enlargement is effective, as nanostructured cells exhibit a remarkable efficiency enhancement of a factor of 20 compared to that of bi-layer devices.

6.4 Conclusions

Using an aerosol synthesis route, thin films of nanocrystalline, stoichiometric anatase titanium dioxide are deposited. The minimum size of the particles is 50 nm; at higher concentrations and carrier gas flows agglomeration occurs. The growth rate is linearly dependent on the flow rate of the carrier gas. Spincoating poly(3-octylthiophene) on top of these TiO₂ films leads to solar cells, which show efficiencies 20 times higher than that of cells with "flat" TiO₂. Maximum photocurrents are obtained for cells with 1 μm thick TiO₂ films, consisting of 50 nm particles. These cells exhibit a short circuit current of 0.25 mA/cm², an open circuit voltage of 0.72 V, a fill factor of 0.35 and an overall efficiency of 0.06%. The IPCE is 2.5% at 488 nm. Devices for which the P3OT is spincoated during TiO₂ deposition show similar efficiencies, indicating that the penetration of the P3OT in the porous TiO₂ network is quite effective. By analysis of current-voltage characteristics of intermixing layers of aerosol-synthesized TiO₂ and P3OT (10 mg/ml in chloroform), sandwiched between two electrodes, we have found that the maximum penetration depth of P3OT inside the nano porous TiO₂ is around 1 μm. Larger pore sizes facilitate penetration of P3OT, but due to the small exciton diffusion length more recombination occurs. Interpenetrating solar cells with polymers and TiO₂ will be a trade-off between pore-filling ability and recombination losses. An increase of the amount of P3OT in the pores will probably increase the efficiency. We have shown that it is possible to make interpenetrating networks of TiO₂ and P3OT both in one and in two steps, but an increase in efficiency is demanded before practical application of these kinds of cells comes into view.
References


UV-polymerization of oligothiophenes and their application in nanostructured heterojunction solar cells

Thin films of 2,2'-bithiophene (2T) and 2,2'-5',2''-terthiophene (3T) are polymerized by UV irradiation. The polymerization process can be observed by UV-VIS and photoluminescence spectroscopy. If 2T is used as starting material, predominantly 4T (quarterthiophene) is formed, while 6T (sexithiophene) is formed if 3T is used as starting material. If polymerisation is carried out at or below room temperature, a non-ordered structure is formed. The same polymerization reaction can take place in solutions of 2T or 3T in chloroform or toluene, or in a film of nanocrystalline titanium dioxide (nc-TiO₂), soaked with a 2T or 3T solution. In the latter case the pores are (partly) filled with 4T or 6T, which acts as hole conductor. A photovoltaic response is observed when nc-TiO₂/4T or nc-TiO₂/6T interpenetrating structures are irradiated with visible light. The increase of oligomer length from 2T to 3T and the corresponding decrease in orientational freedom of the molecules strongly affects the ease of polymerisation and the structural order of the compounds formed. Illumination of a 2T thin film on quartz leads to the formation of a non-ordered 4T film. The same transformation occurs inside nc-TiO₂, but in this case a more ordered structure is formed. If these samples are heated to 200°C even more ordering is observed. For 3T non-ordered structures are formed, both for thin films on quartz as well as inside nc-TiO₂, while no evidence is found for the occurrence of ordering at higher temperatures.
7.1 Introduction

Conjugated oligomers and polymers of thiophenes have found application in various optical and electrical devices, like electrochromic windows and organic thin-film transistors. Unsubstituted, unbranched oligothiophenes are abbreviated by $\alpha$-$n$T, in which $n$ stands for the number of repeating units. $\alpha$ indicates the position of the thiophene ring where monomers are linked together (see Fig. 7.1).

![Oligothiophene nT](image)

*Fig. 7.1. Structure of $\alpha$-$n$T.*

Because of $\pi$-stacking in the solid state, hole mobilities for the higher oligomers and polymers can reach a few $10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$. The electronic structure of oligothiophenes largely depends on the number of repeating units. As the HOMO-LUMO gap decreases for increasing $n$, the absorption and luminescence peaks shift to the red. Also the oxidation potential and the energy of the excited states are influenced. The fluorescence quantum yield of $\alpha$-4T is around $2 \times 10^{-3}$, but for $\alpha$-5T to $\alpha$-8T this yield is much lower ($\leq 10^{-5}$), while it decreases further for more ordered films. In Table 7.1 literature values for absorption and luminescence maxima of oligothiophenes are presented.

Hybrid solar cells (also referred to as organic solar cells) have been developed in the past decade as an alternative for silicon-based solar cells. A wide bandgap metal oxide, like TiO$_2$, is sensitized by a visible light-absorbing species that can be inorganic or organic in nature. Other combinations of
materials are also possible. A bi-layer device structure has shown to yield cells with limited efficiency (<1%) due to the limited interfacial area, which leads to extensive recombination, as the exciton diffusion length in most

Table 7.1. Absorption and fluorescence peaks for solutions and thin films of oligothiophenes (α-nT). All values are taken from ref. 1, but similar values have been found in other articles.

<table>
<thead>
<tr>
<th></th>
<th>Absorption</th>
<th>Fluorescence</th>
</tr>
</thead>
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<tr>
<td></td>
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<td>film (nm)</td>
</tr>
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<td>α-2T</td>
<td>302</td>
<td>362</td>
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<td>513</td>
</tr>
<tr>
<td>polythiophene</td>
<td>-</td>
<td>486</td>
</tr>
</tbody>
</table>

* Measured in chloroform. In other reports EPA, dichloromethane, and dioxane/acetonitrile are used as solvent, showing no apparent differences for the peak positions.

organic semiconductors is only a few nanometers. Enlargement of the interfacial area is accomplished in dye-sensitized solar cells, in which a highly porous film of titanium dioxide nanoparticles is covered with a monolayer of a metal-organic sensitizer that absorbs visible light. Although to date the energy conversion efficiency exceeds 10%\(^{16,17}\), the necessity of a liquid electrolyte to accomplish regeneration of the oxidized dye calls for elaborate sealing techniques, which has hindered commercialization thus far. One especially interesting approach to eliminate the need for a liquid electrolyte inside the device is the use of solid organic or inorganic hole conductors. These compounds can function as light-absorbing species and inject electrons into the conduction band of the n-type semiconductor, while, at the same time, they conduct the holes to the back contact. For inorganic compounds this concept has been successfully proven in the extremely thin
absorber (ETA) TiO$_2$/CuInS$_2$ solar cell\textsuperscript{a,22}. For organic systems, blends of PPV and C60 derivatives are intensively studied and show an efficiency of 2.5\% under simulated solar light\textsuperscript{23,24}. Oligo- and polythiophenes have been studied for incorporation into hybrid solar cells, where they act as visible light absorbers and electron donors in combination with, for example, metal oxide or fullerene electron acceptors. Recently, a bulk heterojunction of CdSe nanorods and poly-(3-hexylthiophene) has been developed with an efficiency of 1.7\% under AM 1.5 conditions\textsuperscript{25}. In solar cells a large overlap between the absorption spectrum of the active material and the solar spectrum is desired. Hence, the higher oligomers are more suited for this purpose. Sexithiophene is regarded to exhibit already most of the properties of polythiophene, because shifts in absorption and hole mobility as a function of $n$ are levelling off for higher oligomers. Adding alkyl chains to the thiophene backbone induces peak shifts, in most cases to the red, as a result of less $\pi$-overlap between adjacent chains\textsuperscript{1}. End substitution or addition of long alkyl chains (more than six carbon atoms) to the backbone, on the other hand, leads to better orientation\textsuperscript{1,26} and to higher hole mobilities.

To synthesize a similar system based on nc-TiO$_2$ several challenges are encountered. First of all, the pores of the system should be rather small in order to prevent extensive bulk recombination inside the organic phase. However, for smaller pore sizes it becomes increasingly more difficult to fill them with bulky dyes. Recently, we have investigated the penetration depth of poly(3-octylthiophene) (P3OT) inside nanoporous TiO$_2$ and observed this depth to be limited to about 1 $\mu$m for an average particle size of 50 nm. For TiO$_2$ particles of about 9 nm the maximum penetration depth of P3OT is less than 300 nm\textsuperscript{37}. Because a high-temperature step is necessary to obtain good-quality anatase TiO$_2$ and most organic materials are not stable at these high temperatures, pre-mixing with TiO$_2$ particles is not possible. Recently, a nanostructured heterojunction of MDMO-PPV and TiO$_2$ was investigated, in which amorphous TiO$_2$ was formed from a precursor in the presence of the polymer\textsuperscript{38}. Another approach is to infiltrate the TiO$_2$ pores with small organic molecules from solution, which will have a larger penetration depth,
compared to large oligomers or polymers. For oligothiophenes, however, only the smallest oligomers are soluble, which merely absorb in the ultraviolet part of the solar spectrum. From literature, it is known that oligothiophenes can be polymerized wet-chemically (using, for example, FeCl₃)³⁹-⁴⁰ as well as electrochemically⁴¹,⁴². Both methods are not suitable for in-situ polymerisation in a nanoporous system, because of size constraints. There are indications that polymerisation of thiophene and bithiophene films can be induced by electron beam or X-ray irradiation⁴³,⁴⁴. Photochemical polymerisation of oligothiophenes has not been reported in great detail, but some studies indicate that small oligomers are formed⁴⁵,⁴⁶.

This paper presents an investigation of the photochemical polymerisation of 2,2'-bithiophene (α-2T) and 2,2'-5',2''-terthiophene (α-3T) thin films using UV irradiation. The polymerisation reaction is monitored by UV-VIS absorption and fluorescence spectroscopy. Evidence is shown for the occurrence of a dimerisation reaction that transforms 2T into 4T and 3T into 6T. This transformation can be established in thin films, solutions and inside nanoporous TiO₂. The peak positions in the absorption and photoluminescence (PL) spectra indicate that a non-ordered structure is formed for the thin films, which can be crystallized at higher temperatures for 2T → 4T films. In nc-TiO₂ the absorption and PL peaks of 2T before and after irradiation are at higher wavelengths, indicating that a more ordered structure is formed. The orientational freedom for 2T molecules is larger than for 3T molecules, leading to more facile polymerisation and the formation of more ordered structures. We will also describe that filling of a nanoporous TiO₂ film with 2T or 3T solutions yields, after UV-irradiation, cells that clearly show a photovoltaic effect.

7.2 Experimental aspects

2,2'-bithiophene (97%) and 2,2'-5',2''-terthiophene (99%) are obtained from Aldrich and are used without further purification. Solutions of either 1 mg/ml or 40 mg/ml are prepared in chloroform (Aldrich, anhydrous 99+%). Thin films are prepared by spin coating; first 5 drops of a 40 mg/ml solution of 2T or 3T are applied on a substrate, which is subsequently rotated
at 1500 rpm for 20 s. The films are immediately used for experiments to prevent evaporation of the volatile 2T and 3T. The film thickness of the 2T/3T films is estimated to be around 300 nm.

For the optical measurements quartz substrates (1×1 inch, ESCO) are used. Quartz does not show any absorption for wavelengths above 250 nm. As substrate material for the photovoltaic measurements fluor-doped SnO₂ is used (Transparent Conducting Oxide, Libbey Owens Ford, 20 Ωcm⁻¹). Substrates are thoroughly cleaned in an ultrasonic bath with ethanol and acetone successively and then dried in a dry nitrogen stream. The TCO is covered with a thin dense film of anatase TiO₂ (70 nm), deposited by spray pyrolysis⁸ and subsequently a nanoporous TiO₂ film is deposited on top by doctor blading of a paste of 15 nm TiO₂ particles (Solaronix T, BN 91/21051T). The nc-TiO₂ film is annealed at 450°C for 2 h, yielding an electron-conducting network. For several experiments the nc-TiO₂ particles are covered with a monolayer of ruthenium dye (Ru535, cis-[L₂Ru(SCN)₂] in which L stands for 2,2’-dipyridine-4,4’-dicarboxylic acid, Solaronix BN 119,0898, 0.3mM in ethanol).

For comparison with the polymerized 3T, a fluorescence spectrum is recorded for a 120 nm thin film of 6T, deposited using a thermal evaporation set-up with a rate of 2 nm/s. The 6T is purchased from Syncom (Groningen, The Netherlands) and is purified by zone-sublimation.

UV-VIS absorption spectra are recorded on a Varian Cary 1 UV-Visible spectrophotometer. Thin films of 2T and 3T on quartz as well as inside nanoporous TiO₂ are measured before and after different times of UV irradiation. A similar experiment is performed with quartz cuvets containing solutions of 2T and 3T in chloroform. The reflection of the samples is neglected.

For UV-irradiation of the samples a 150 W water-cooled Xenon lamp is used, which emits light in the region between 250 and 1100 nm. Because the heat
dissipated by the lamp evaporates the oligothiophene films from the quartz substrates, the samples are cooled by placing them on a “cold finger”, cooled with liquid nitrogen. The distance from lamp to sample is kept constant at 15 cm.

Photoluminescence spectra are recorded with a home-built set-up, using the third harmonic of a pulsed Nd:YAG laser (355 nm, 10 Hz) as excitation source. An intensity of 0.25 mW per pulse and a pulse length of a few ns are used. Fluorescence is recorded in a 90° geometry for quartz substrates and cuvets, using two high pass filters of 380 nm to remove the laser light. Spectra are recorded using a liquid nitrogen cooled CCD camera (Princeton Instruments LN/CCD-1100PB) and a Spex 340E monochromator equipped with a 100 grooves/mm grating, blazed at 500 nm. For low-temperature measurements a closed-cycle helium cryostat is used. In-situ measurements are performed on the polymerization of pristine 2T or 3T thin films on quartz or inside nc-TiO₂ and in 2T/3T solutions in quartz cuvets by the UV light of the pulsed laser, while changes in the PL-spectra are recorded simultaneously. No corrections for the filters and the sensitivity of the CCD camera and the monochromator are applied.

Current-voltage characteristics and wavelength-dependent photocurrent spectra are recorded using a Keithley 2400 source meter. A 250 W tungsten-halogen lamp in combination with an Acton Spectra-Pro-275 monochromator is used to illuminate the samples through the TCO substrate with an intensity of 100 mW/cm² in the case of white light and with ca. 2 mW/cm² in the case of monochromatic light. The light source is not AM1.5 calibrated. A 360 nm high-pass filter is used while measuring wavelength-dependent photocurrent spectra. Evaporated gold contacts with a diameter of 2 mm and a thickness of 50 nm are used as back contacts. Contact to the gold is made with a gold-coated tip, attached to a spring with a spring constant of 7×10⁻⁶ Nm⁻¹. (Ingun Prüfmittelbau GmbH). Some measurements are carried out using mercury contacts, yielding the same results as for gold contacts. Measurements are performed at ambient conditions. To lower the resistance of the cells, a film of PEDOT:PSS
(poly(3,4-ethylenedioxythiophene) : poly(styrene sulfonate) (Bayer AG, Baytron P) is spincoated on top of the TiO₂/oligothiophenes blend. PEDOT-PSS is a highly doped p-type material, selectively conducting holes⁴. First the sample is moistened with a few drops of acetonitril (Aldrich, p.a.) to increase the wetability of the surface. A solution of PEDOT:PSS in water, containing about 5 vol% of acetonitril is spincoated on the sample, yielding a thin film of about 50 nm.

7.3 Results and discussion

7.3.1 UV-irradiation of 2T and 3T thin films: Absorption spectra
2,2'-bithiophene and 2,2'-5',2''-terthiophene are transparent crystals and light yellow powders, respectively. They dissolve easily in polar solvents like chloroform, toluene, water, and acetone. During UV-irradiation, thin films or solutions of 2T and 3T turn orange/brown. For solutions it is observed that in time precipitation occurs.

In Fig. 7.2 the absorption spectra of thin films of 2T and 3T on quartz before and after 10 minutes of UV-irradiation are shown. In the spectra of the irradiated 2T/3T samples a new peak, about 80 nm shifted to the red, is clearly visible. For clarity, the spectrum of the sample before irradiation is subtracted, as starting material is still present. As mentioned above, the absorption peak of α-νT shifts to the red with increasing oligomer length. As a result of the UV-irradiation the 2T and 3T are (partly) transformed into higher oligomers. To which extent the oligomers are polymerized will be discussed in the next section.
Fig. 7.2. Absorption of thin films of 2T and 3T on quartz before and after 10 minutes of UV-irradiation. The illuminated spectra are corrected for the presence of starting material and the spectra are normalized.

7.3.2 UV-irradiation of 2T and 3T solutions: Absorption spectra

Fig. 7.3 shows absorption spectra for 2T in chloroform (1 mg/ml) before and after different UV-irradiation times. Also the difference spectra before and after irradiation are shown. It is clearly visible that a new peak appears, shifted about 60 nm to the red as a result of the irradiation. An isobestic point is observed, indicating a complete transformation from one starting material to one product.

Fig. 7.3. (A) Absorption of 2T in chloroform before and after 10, 30, 60, 100, and 130 minutes of UV-irradiation. (B) difference spectra between irradiated and pristine (non-irradiated) solution. The concentration of the illuminated solution is 1 mg/ml, which is diluted to 0.01 mg/ml for the measurements.
In Fig. 7.4 the same experiment is shown for 3T in chloroform. Again a new peak appears, shifted approximately 80 nm to higher wavelengths. Also here, an isobestic point is observed.

**Fig. 7.4.** (A) Absorption of 3T in chloroform (1 mg/ml) before and after 10, 50, 135, 225, and 330 minutes of UV-irradiation. (B) Difference spectra between irradiated and pristine solution. The concentration of the illuminated solution is 1 mg/ml, which is diluted to 0.01 mg/ml for the measurements.

Comparing the peak data with the literature values in Table 7.1, it is clear that 2T is transformed into 4T and 3T into 6T. A polymerization reaction is taking place, induced by the UV-irradiation. For thin films on quartz, the absorption peak values are similar to those of solutions. This indicates that a non-ordered structure is formed, since normally films have an absorption that is more red-shifted (see Table 7.1).

### 7.7.3 UV-irradiation of 2T and 3T thin films: Luminescence spectra
To investigate the polymerization reaction in detail, photoluminescence (PL) experiments are performed. In Fig. 7.5 the PL spectra are shown for thin films of commercially obtained 2T, 3T, and 6T. Although, literature data for 3T films are not available, the peak positions of 2T and 6T are in agreement with the literature (see Table 7.1).
Fig. 7.5. PL spectra of 2T, 3T and 6T thin films on quartz, measured at ambient pressure and temperature. Laser excitation is performed at 355 nm, with a pulse length of a few ns and an intensity of 0.25 mW per pulse.

Fig. 7.6 shows an in-situ experiment, in which a freshly deposited film of 2T on quartz is continuously irradiated with 355 nm laser pulses, while the PL spectrum is measured every 2 seconds. Clearly a transformation in the spectra is observed as a result of the irradiation and the peak positions shift about 80 nm to the red. An isobestic point is observed, indicating that the transformation is complete and one reaction product is formed. After about 250 s, the intensity of the spectra decreases over the whole wavelength range and no intersection with the isobestic point is present anymore. It can be concluded, that a decomposition or evaporation process occurs, leaving less luminescent material on the substrate.

Fig. 7.6. In-situ polymerisation of a 2T thin film on quartz at ambient pressure and temperature. (A) PL-spectra are taken at 2, 4, 6, 8, 10, 14, 24, 34, 44, 54, 64, 74, 84, 104, 154, 254, 354, 554, 754, and 1015 s after the start of the irradiation. (B): PL-spectra at t=2 s and at t=354 s.
In Fig. 7.7 the same experiment is shown for 2T inside a porous nc-TiO$_2$ film. Again a clear transformation is observed, exhibiting an isobestic point. The peak positions are at higher wavelengths than for a thin 2T film on quartz, indicating a higher ordering inside nc-TiO$_2$.

![PL-spectra of a thin film of 2T inside nc-TiO$_2$ at ambient pressure and temperature. Laser excitation is performed at 355 nm, with a pulse length of a few ns, and an intensity of 0.25 mW per pulse. PL-spectra are taken at 90, 150, 210, 270, 360, and 900 s after the start of the irradiation.](image)

The same experiment is repeated with thin films of 3T on quartz, but no change in spectra is observed, except for a continuous decay in time over the full wavelength range. Afterwards, no film is present on the substrate, indicating that evaporation occurs during irradiation. Lowering the intensity of the pulsed laser prevents evaporation, but the PL spectra remain unchanged in time, indicating that no polymerization reaction is induced at lower energies. In Fig. 7.8, the time evolution of PL spectra is shown for a thin film of 3T on quartz, cooled down to 6 K under vacuum, irradiated at 355 nm. The peaks are more resolved than at room temperature (compare Fig. 7.5), but similar to the experiment performed at room temperature merely a decrease in intensity is seen. Again, afterwards, the film turned out to have evaporated during the experiment.
Fig. 7.8. PL-spectra of 3T on quartz in vacuum at 6 K. PL-spectra are taken at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, 25, 75, and 175 s after the start of the irradiation.

7.3.4 UV-irradiation of 2T and 3T inside nc-TiO₂: Absorption spectra
The experiment is repeated at room temperature with a nanoporous film of TiO₂ soaked with 3T. In this case a change in spectra is observed during laser irradiation (Fig. 7.9), but no isobestic point is present. This indicates that some evaporation still takes place during irradiation. After the experiment, an orange-brown spot is observed on the sample. In Fig. 7.10A the absorption spectra of the coloured region, the substrate (TCO/TiO₂/nc-TiO₂) as well as the difference between the two are plotted. A peak appears, which is at the same position as the peak of irradiated 3T on quartz in the absorption spectra shown in Fig. 7.2. Hence, it is concluded that indeed the same reaction has occurred in the laser experiment as during UV-irradiation using the Xenon lamp. In Fig. 7.10B the same absorption spectra for 2T/nc-TiO₂ after the in-situ PL experiment are shown.

7.3.5 UV-irradiation of 2T and 3T solutions: Luminescence spectra
In-situ PL experiments are also performed on solutions of 2T and 3T. Because chloroform is a strong luminescent solvent, toluene is chosen instead. In Fig. 7.11 PL spectra are shown for a 1 mg/ml solution of 2T in toluene, measured as a function of irradiation time. As can be seen from the difference spectrum before and after irradiation a new peak appears, shifted 90 nm to the red. For the same experiment with 3T in toluene (Fig. 7.12) no new peaks occur during irradiation, but only a decrease in intensity is
observed over the full wavelength range. After the experiment, the 3T/toluene solution was coloured orange/brown. Tentatively, the absence of a clear transformation in the PL-spectra is ascribed to the formation of a compound, which shows only limited or even no luminescence. From literature it is known that the fluorescence quantum yield of 6T is lower than

**Fig. 7.9.** PL-spectra of a thin film of 3T inside nc-TiO₂ at ambient pressure and temperature. (A): PL-spectra are taken at 33, 36, 39, 51, 60, 90, 120, 180, 240, 300, 450, 510, 570, 600, 615, 645, 675, 765, and 843 s after the start of the irradiation. (B): PL-spectra at t=3 s and at t=843 s.

**Fig. 7.10.** Absorption spectra of 2T (A) and 3T (B) inside nanoporous TiO₂, after 10 minutes of irradiation at ambient pressure and temperature at 355 nm, with a pulse length of a few ns, and an intensity of 0.25 mW per pulse. Spectra of the substrate: TCO/TiO₂/nc-TiO₂, the substrate with 2T (A) or 3T (B) after irradiation, and the difference spectrum of sample and substrate are shown.
of 4T (see introduction), so it may very well be also lower than of 3T. This could lead to a situation where the formation of 6T is not seen in the PL spectrum.

**Fig. 7.11.** PL-spectra of 1 mg/ml 2T in toluene at ambient pressure and temperature. (A): PL-spectra are taken at 12, 20, 160, 200, 300, 400, 500, and 600 s after the start of the irradiation. The asterisk denotes the excitation wavelength (355 nm). (B): PL spectrum at t=12 s, normalized by taking the intensity at 355 nm as 100, normalized PL spectrum at t=600 s, and difference spectrum of normalized spectra at t=600s and t=12 s.

**Fig. 7.12.** PL-spectra of 1 mg/ml 3T in toluene at ambient pressure and temperature. (A): PL-spectra taken at 2, 20, 200, 400, and 490s after the start of the irradiation. The asterisk denotes the excitation wavelength (355 nm).
7.3.6 Heat treatment of polymerized 2T and 3T thin films: Absorption spectra
In Fig. 7.13A absorption spectra of 2T on quartz are shown, before and after 45 minutes of UV-irradiation and after subsequent annealing at 100-300°C. From the difference spectra (Fig. 7.13B) it can be seen that at a temperature of 200°C the absorption peak shifts about 45 nm to the red. Higher temperatures do not induce a further change and at 300°C a decrease of the absorption over the full wavelength range is observed, indicating that a decomposition or evaporation reaction is taking place. For 3T, either on quartz or inside nc-TiO₂, no peak shift in the absorption spectrum is observed if a comparable annealing experiment is performed.

7.3.7 Absorption and luminescence peak positions
In Table 7.2 the measured peak values for all absorption and PL-spectra are summarized. A comparison of these values with those from literature (Table 7.1), reveals differences. While the experimentally obtained peak positions for the solutions are comparable to the literature data, the experimentally obtained peak positions for the thin films are close to the solution values. Furthermore, for the reaction of 2T to 4T inside nc-TiO₂, the experimentally obtained peak positions are in between the literature data for solutions and films, while for the reaction of 3T to 6T inside nc-TiO₂ the experimentally obtained peak positions are comparable to the literature solution values.

Fig. 7.13. Absorption spectra of an irradiated 2T film on quartz during annealing. (A): before and after 45 minutes of UV-irradiation, and after subsequent heating at 100°C for 2h, at 200°C for 2h, at 250°C for 2h, and at 300°C for 2h. (B): difference spectra between the absorption spectra after the heating steps and before UV-irradiation and annealing.
Table 7.2. Experimentally obtained values for absorption and fluorescence maxima for oligothiophenes (nT) in solution, thin films, and inside nc-TiO₂. 2T and 3T are starting materials, 4T and 6T are formed by UV induced polymerization.

<table>
<thead>
<tr>
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<th>Absorption</th>
<th>Fluorescence</th>
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<tr>
<td></td>
<td>solution (nm)</td>
<td>film (nm)</td>
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<tr>
<td>2T</td>
<td>328</td>
<td>310</td>
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<tr>
<td>3T</td>
<td>343</td>
<td>364</td>
</tr>
<tr>
<td>4T</td>
<td>352</td>
<td>392</td>
</tr>
<tr>
<td>6T</td>
<td>416</td>
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From literature it is known that the α-position of the thiophene ring is most reactive. Polymerization takes place through the formation of radicals. In this system two oligothiophene units are coupling, indicating that two radicals react with each other. This explains that polymerization is only observed if a high light intensity is applied, as a high concentration of radicals is necessary for this coupling to occur. In the photoluminescence experiments, it is observed that a light intensity beyond a certain threshold is required in order to start the polymerization reaction. Longer oligomers have less orientational freedom, explaining the inhibited transformation of 3T to 6T as compared to 2T to 4T. In nc-TiO₂ more oligomer molecules are present, which also have a higher orientational freedom. This could explain that 3T inside nc-TiO₂ is more easily polymerized. The experimentally obtained peak positions for the reaction of 2T to 4T inside nc-TiO₂ are in between the literature data for solutions and films, while for the reaction of 3T to 6T inside nc-TiO₂ the experimentally obtained peak positions are comparable to the solution values. This indicates that a more ordered structure is formed inside nc-TiO₂ for 2T as compared to 3T. This effect may also be related to the size and corresponding freedom of the oligomers during the polymerisation reaction. After the light-induced polymerisation of 2T the peak position is shifted to the literature values for thin films, if a temperature of 200°C is applied (see Fig. 7.13). The structural order is increased, while for 3T at elevated
temperatures such an increase is not observed, showing once more that structural changes involving molecular reorientations are inhibited for longer oligomers.

7.3.8 UV-irradiation of 2T and 3T inside nc-TiO₂: Solar cells

Nanoporous TiO₂ films are soaked with 2T or 3T solutions (40 mg/ml in chloroform) and are subsequently irradiated with a Xenon lamp. I-V curves and wavelength dependent photocurrent spectra are recorded afterwards. Film thicknesses, particle sizes, and irradiation times are varied to investigate the photovoltaic characteristics of the cells. Cells that consist of TCO/TiO₂/nc-TiO₂/(2T or 3T)/Au exhibit a high resistance and low currents both in the dark and under irradiation. Applying a thin film of PEDOT:PSS improves the hole transport and yields a good diodic behaviour in the dark and a photovoltaic effect under irradiation. In Fig. 7.14A I-V curves are shown for a system with irradiated 3T inside the TiO₂ pores and for a system in which the nc-TiO₂ is first sensitized using a ruthenium dye, after which the sample is soaked in a 3T solution and irradiated. If the ruthenium dye is present, the short-circuit current is increased by a factor of 5 and the open-circuit voltage is also slightly higher.

In Fig. 7.14B wavelength-dependent photocurrent spectra are presented for these cells, corrected for the lamp spectrum. If ruthenium dye is added, the photocurrent increases substantially. Therefore, light absorption, exciton transport towards the TiO₂, or electron injection of the oligothiophene are possible bottlenecks for the cells without Ru-dye. The overall PV-effect, if the ruthenium dye is present, could be limited by various reasons, including incomplete filling of the pores of the nc-TiO₂ and low electronic conductivity inside the oligothiophenes (and hence, ohmic losses). More research is needed to clarify these issues.

7.4 Conclusions

High-intensity UV-irradiation is capable of polymerizing bi- (2T) and terthiophene (3T). Radicals of these oligothiophenes, formed as a result of the irradiation, merge, forming an oligomer twice as long as the starting compound. This polymerization reaction can be observed using UV-VIS
absorption and fluorescence spectroscopy. The systems investigated include solutions, thin films on quartz, and oligothiophenes inside nanoporous TiO₂.

It is concluded that the increase of oligomer length from 2T to 3T and the corresponding decrease in orientational freedom of the molecules has a negative effect on the ease of polymerisation and the structural order of the product. For 2T a thin film on quartz is transformed into an amorphous 4T film, while the same reaction occurring inside nc-TiO₂ yields a more ordered structure. Elevated temperatures lead to crystalline films. For 3T non-ordered structures are formed both for thin films on quartz and inside nc-TiO₂, while no evidence is found for ordering at higher temperatures. Furthermore, the fluorescence intensity during the reaction of 3T to 6T is decreasing (for nc-TiO₂) or disappearing (for toluene solutions) in time, while for the reaction of 2T to 4T a clear isobestic point is observed, indicating that the former reaction is indeed inhibited compared to the latter. For polymerized 2T and 3T inside nc-TiO₂ a photovoltaic effect is observed. The reason for the limited photocurrent in this system requires more research. However, it is shown that an interpenetrating network of nc-TiO₂ and oligothiophenes can indeed be formed using in-situ UV polymerisation.
References


UV-polymerization of Oligothiophenes


The application of inverse titania opals in nanostructured solar cells

In this chapter, we report on the synthesis and characterization of nanostructured heterojunction solar cells based on inverse opal titanium dioxide (TiO₂) films. Photonic films with thicknesses of 0.9 and 3.7 µm are deposited using self-organisation of latex spheres with diameters of 100 nm and 400 nm. The voids between the spheres are filled with a TiO₂ precursor and a subsequent heat treatment yields a highly organized porous structure. Sensitization with Ru 535-dye (cis-[L,Ru(SCN)₂] in which L is 2,2'-dipyridine-4,4'-dicarboxylic acid), yields solar cells with a power conversion efficiency of 0.6% under simulated solar light. At present, the small area of the ordered structure is limiting the performance of the cells. These cells may be promising for future applications, if improved fabrication techniques will enable an enlargement of the ordered area.
8.1 Introduction

To date, ordered mesoporous materials are attracting widespread attention. Periodicity on an optical length scale can lead to materials that exhibit a full photonic bandgap, i.e., a wavelength band in which photon propagation is forbidden. These photonic materials can be used in novel applications, in which the flow of light is manipulated. In most cases the building blocks for photonic crystals (opals) are monodispersed colloids. Next to periodicity with a well-chosen lattice spacing, also a high porosity and a high refractive index are prerequisites to obtain a photonic bandgap. This can be achieved by inversion of the opals using infiltration, followed by removal of the template (calcination). Synthetic opals can be formed by self-organisation using, for example, centrifugation, (controlled) drying, or confinement of a suspension of monodispersed colloidal spheres. Silica or polymer spheres are available in a wide range of sizes and can be obtained in a narrow size distribution. Once the opal is formed, it can be infiltrated with nanosized crystallites or a precursor of an insulator, semiconductor, or metal. The template opal can be removed selectively thermally (in the case of latex spheres) or chemically (in the case of silica spheres). Inverted opals of various inorganic and organic compounds have been synthesized in this way. TiO$_2$-inverted opals can be made from infiltration of metal-organic alkoxide precursors or nanosized crystallites.

At present, the main challenges in the synthesis of inverted opals are to enhance the speed of formation, to obtain high-quality opals over a large area, to infiltrate the pores completely with the desired compound, and to prevent shrinkage-induced cracking. New approaches, like the use of uniform oil droplets or molds as templates can be a step forward in this regard. Advanced techniques, like gas-phase deposition and electrodeposition, are employed to improve the pore filling quality. Reports have also been published on the synthesis of a synthetic opal while infiltrating the voids with a semiconductor in one step.

For solar cells, porous materials are also of interest. Heterojunction solar cells consist of a combination of a p- and an n-type semiconductor, both
either organic or inorganic, in which visible light excites electrons that can be injected in the n-type material. The increase in interfacial area, if nanosized composites are employed, has been shown to increase the efficiency of these types of solar cells to much higher values compared to bi-layer devices\textsuperscript{36-41}. This is due to a decrease in resistance and an increase of active interface area between the p- and the n-type semiconductor. However, if organic dyes are incorporated, recombination is a major bottleneck, as the exciton diffusion length is in most cases limited to 2-60 nm. If an exciton is formed at a distance from the active interface larger than the exciton diffusion length it will be lost and does not contribute to the photocurrent. Therefore, highly ordered structures on a nanometer length scale can lead to higher efficiencies\textsuperscript{41}. The use of inverse TiO\textsubscript{2} opals for solar cells has not yet been investigated, although in a recent study an ordered TiO\textsubscript{2} matrix, synthesized using block copolymers, has been infiltrated with regioregular poly(3-hexylthiophene)\textsuperscript{41}. The photoluminescence of the polymer is partially quenched, indicating that indeed photoinduced charge transfer is taking place from the polymer into the TiO\textsubscript{2}. It has also been shown that inverted TiO\textsubscript{2} opals can be used as a separate layer in dye-sensitized solar cells to improve the absorbance in the red\textsuperscript{46}. To successfully design a photonic solar cell the employed colloids should be small enough to ensure that the voids of the inverted TiO\textsubscript{2} opals are in the order of the exciton diffusion length. The use of small colloids (typically with a diameter smaller than 150 nm) also causes the photonic bandgap to be in the ultraviolet part of the spectrum and hence, does not inhibit visible light to penetrate the crystal. An additional constraint is to fabricate these photonic crystals in the form of a thin film with controllable thickness. In this study, the confinement method, as described by Xia et al., has been selected, using latex colloids to build up a synthetic opal\textsuperscript{47}. This is a simple and relatively fast method that has been used successfully to synthesize large area opals. An additional advantage of this method is the possibility to fabricate complete devices, including front- and back contacts. Inverse TiO\textsubscript{2} opal films are fabricated from these latex templates and are used as an n-type semiconductor in nanostructured solar cells. Using Ru-535 dye and/or poly(3-octylthiophene), solar cells are constructed, which are investigated with opto-electronic techniques.
8.2 Experimental aspects

Fluoride-doped SnO₂ (TCO, Libbey Owens Ford, 20 Ω/cm) is used as substrate material. Substrates are thoroughly cleaned in an ultrasonic bath with ethanol and acetone successively and are dried in a dry nitrogen stream. Some TCO substrates are covered with a thin dense film (70 nm) of anatase TiO₂, deposited by spray pyrolysis⁶.

The confinement method to make synthetic opals from polystyrene latex or silica spheres is described in detail elsewhere⁵⁻⁹,⁴¹⁻⁴⁹. In short the procedure is as follows: a TCO substrate is covered with a rectangular mask, cut out of Mylar foil (polyethylene terephthalate, obtained from Goodfellow with a thickness of 0.9 or 3.7 μm). By soft rubbing in one direction small channels are scratched in the foil. A second TCO substrate, which contains a hole to which a glass tube is connected, is placed on this mask. Using binding clips the cell is assembled, in which the mylar mask is now sandwiched between two substrates. A dilute solution of polystyrene spheres is injected into the glass tube and an air-filled balloon provides a small pressure. Monodisperse polystyrene beads are obtained from Bangslab (10 wt%, 400 nm mean diameter) and from Duke Scientific (1 wt%, 100 nm mean diameter). The colloidal solutions are diluted to 0.5 wt% using ultra-pure water. The complete cell is placed inside an ultrasonic cleaner (Ultrawave Limited), which operates at half-hour-on, half-hour-off intervals. The synthetic opals are allowed to grow for 7 to 30 days before excess solution is removed and the samples are dried under ambient conditions. A few droplets of a mixture of titanium tetra-isopropoxide (TTIP, Aldrich 98% +) and ethanol (1:1) are added via the glass tube and the cell is subsequently heated to 80°C for 30 minutes in air followed by cooling to room temperature (rate: 3°C/min). This filling process is repeated five times, to ensure complete filling of the voids. Finally, the cell is heated at 450°C for 4 h in air and is slowly cooled down to room temperature (heating and cooling rate: 3°C/min). In this calcination step anatase TiO₂ is formed, while at the same time the latex template is removed. Only now, the cell is dismantled. It is also possible to
leave the complete cell intact and to use the top substrate as second contact. This will also prevent the occurrence of defects when dismantling the cell.

The inverted titanium dioxide opals are placed in a Ru 535-dye solution (cis- [RuL₂(SCN)₂] in which L is 2,2'-dipyridine-4,4'-dicarboxylic acid) obtained from Solaronix, 0.03 mM in ethanol) for several hours to allow the dye to adsorb to the TiO₂ surface. Electrical measurements are performed on cells that contain an iodine-based electrolyte solution, as well as on solid state cells that contain poly(3-octylthiophene) (P₃OT, Aldrich, regioregular). P₃OT is infiltrated in the pores by spin casting of a P₃OT solution (10 mg/ml in chloroform) or by melting. In this case, a few droplets are placed on the sample, which is subsequently heated at 200°C in air and darkness. This has recently been reported to be a promising method to achieve pore filling of polymers in nanoporous compounds⁴.

The morphology and film thickness of the opals and inverted opals are studied with scanning electron microscopy (SEM) using a Jeol JSM-5800 LV Scanning Electron Microscope. No conducting film is deposited on top of the samples, as this tends to block the pores. Transmission electron microscopy (TEM) measurements are performed using a Philips CM30T electron microscope, equipped with a LaB₆ filament, which is operated at 300 kV. Samples are prepared by removal of a part of the photonic film from the substrate. A few droplets of this material, suspended in ethanol are placed on a TEM grid, followed by drying at ambient conditions.

Current-voltage characteristics are recorded under a solar simulator (SolarConstant 1200 from Steuernagel Lichttechnik GmbH, 1000 W/m², AM 1.5 calibrated). For wavelength-dependent photocurrent spectra, a 250 W tungsten-halogen lamp in combination with an Acton Spectra-Pro-275 monochromator is used and the samples are monochromatically illuminated through the transparent tin dioxide film with an intensity of ca. 2 mW/cm². A 360 nm high-pass filter is used to remove UV-light. Current-voltage and wavelength-dependent photocurrent spectra are recorded using a Keithley
2400 digital source meter. The electrolyte contains a 0.3 mM I/I solution in propylene carbonate and platinum-covered TCO is used as a back contact. For the solid state cells, evaporated gold contacts with a diameter of 2 mm and a thickness of 50 nm are used as back contacts. Some measurements are carried out using a mercury back contact, yielding the same results as for gold. Measurements are performed in ambient atmosphere and at room temperature. Care is taken to measure samples directly after the polythiophene film is spincoated and to avoid exposure to light, as this is known to cause degradation of semiconducting polymers. Contact to the gold is made with a gold-coated tip, attached to a spring with a spring constant of $7 \times 10^{-3}$ Nm$^{-1}$ (Ingun Prüfmittelbau GmbH).

8.3 Results and discussion

In Fig. 8.1A a Scanning Electron Micrograph is shown for a synthetic opal formed from 400 nm latex spheres using 3.7 μm thick Mylar foil. Ordered crystals of close-packed spheres are formed at the edges of the rectangular mask. The total area of ordered material is a few mm$^2$ and the size of the crystals is on average 400×600 μm. Cracks between the crystals result most likely from drying; the defects at the top are caused by removal of the top substrate. At a higher magnification (Fig. 8.1B) the hexagonal ordering and the presence of defects is visible. The inverse opals of TiO$_2$, after infiltration and calcination, are shown in Fig. 8.1C and D. The opal template is well copied, resulting in a highly ordered porous structure. Some shrinking is observed, consistent with observations in the literature. For opals and inverse opals formed from 100 nm latex spheres, the resolution of the SEM is insufficient and TEM micrographs are recorded (Fig. 8.2). Because the TiO$_2$ inverted opal is studied after partial removal of the film from the substrate and while only very thin parts can be visualized, no ordered portions can be observed. Spherical pores are visible, though, and it is clear that the TiO$_2$ phase consists of particles with an average size of 10 nm. From the diffraction pattern it is confirmed that the particles are crystalline. As the calcination temperature is 450°C, it is expected that the TiO$_2$ is in the anatase crystal structure.
**Fig. 8.1.** A, B: Scanning Electron Micrographs of opals formed from 400 nm latex beads. The thickness of the sample is 3.7 μm and the substrate material is TCO. C, D: SEM graphs of inverted opals after infiltration with titanium tetraisopropoxide and subsequent calcination.

The photovoltaic characteristics of inverted TiO₂ opals are investigated by sensitization with ruthenium dye and/or poly(3-octylthiophene). In Fig. 8.3 current-voltage plots are shown for cells that contain ruthenium dye (measured with electrolyte solution, solid curve) or P3OT (measured with a gold electrode, dashed curve), respectively. Solar cells can be characterized by the open-circuit voltage (Vₐ) and the short-circuit current (Iₚ), which are taken from the intercepts with the V- and the I-axis, respectively. The fill factor (FF), and the conversion efficiency (η) are calculated using the maximum power point according to:
\[ FF = \frac{V_{mp} \cdot I_{mp}}{V_{oc} \cdot I_{sc}} \quad \text{(Eq. 8.1)} \]

\[ \eta = \frac{V_{mp} \cdot I_{mp} \cdot FF}{P_{in}} = \frac{V_{oc} \cdot I_{sc} \cdot FF}{P_{in}} \quad \text{(Eq. 8.2)} \]

\( P_{in} \) is the power of the incoming light, which is 0.1 W/cm\(^2\) in this case. The maximum power point can be found by finding the intercept of the largest possible rectangle that can be fitted inside the curve. The parameters for the cell with Ru-dye are \( V_{oc}=0.56 \text{ V}, I_{sc}=1.8 \text{ mA/cm}^2, FF=0.6 \), and \( \eta=0.6\% \). For the cell that contains P3OT these parameters are \( V_{oc}=0.58 \text{ V}, I_{sc}=0.2 \text{ mA/cm}^2, FF=0.25 \), and \( \eta=0.03\% \).

Fig. 8.2. Transmission Electron Micrograph of an inverted TiO\(_x\) opal templated against a 0.9 \( \mu \text{m} \) thick crystal of ordered 100 nm latex spheres. Part of the inverted opal film is scraped off the substrate and placed on a TEM grid.

Fig. 8.4 shows wavelength-dependent photocurrent spectra and Incident Photon to Current conversion Efficiency (IPCE) curves for these two cells.
The IPCE is defined as the ratio between the number of collected electrons and the number of incident photons per geometrical area per second. An IPCE value of 7.5% is reached at 515 nm for the cell containing ruthenium dye (solid curve).

Fig. 8.3. Current-voltage plot of TCO/inverse opal TiO₂/Ru-dye/I₂I electrolyte/Pt coated TCO (solid line) and TCO/inverse opal TiO₂/P₃OT/Au (dashed line). Illumination takes place through the TCO substrate and the measurement is performed under a solar simulator (AM 1.5 calibrated).

Fig. 8.4. Wavelength-dependent photocurrent spectra and Incident Photon to Current conversion Efficiency (IPCE) curves for TCO/inverse opal TiO₂/Ru-dye/I₂I electrolyte/Pt coated TCO (solid line) and TCO/inverse opal TiO₂/P₃OT/Au (dashed line). Illumination takes place through the TCO substrate with an intensity of ca. 2 mW/cm².
Cell characteristics of inverse TiO₂ opal crystals with different thicknesses (0.9 and 3.7 μm), different pore sizes (template spheres 100 and 400 nm), and different substrates (TCO and TiO₂-covered TCO) are measured. In general the short circuit current of cells on TCO is a factor of 2 to 3 better compared to cells on TiO₂-covered TCO. This is probably caused by the additional resistance of the TiO₂ film. The 0.9 μm thick cells have a short circuit current a factor of 2 lower than the 3.7 μm thick cells. This is due to less light absorption. The open circuit voltage is comparable for both types of cells. No apparent difference between 100 and 400 nm template spheres is observed. The use of P₃OT instead of Ru-dye as sensitizer deteriorates the photovoltaic properties of the cells drastically. First of all, P₃OT has a small exciton diffusion length, which is even smaller if it is not highly ordered. Therefore, other dyes, with better charge-transfer characteristics, may give a better result. Secondly, the P₃OT has to conduct holes to the back contact, whereas this process is performed by the liquid electrolyte in the case of Ru-dye. This poses constraints on the filling of the pores (i.e., percolation) of the TiO₂, which is already hard for these bulky polymer molecules.

It is clear that the efficiency of the investigated system should be increased substantially before a successful solar cell can be obtained. The efficiency of the cells containing Ru-dye is much lower than for similar cells, consisting of nanosized TiO₂ particles. These dye-sensitized solar cells, however, are much thicker (10 μm or more) than the cells investigated here (0.9 or 3.7 μm). Light absorption in these thin films is limited, which lowers the overall efficiency. However, the major bottleneck is most probably the limited area of the ordered TiO₂. Therefore, a large portion of the illumination reaches non-ordered portions of the substrate, which will lower the overall efficiency for the illuminated area substantially. Using a 543.5-nm HeNe-laser with a spot diameter of 1 mm yields a photocurrent 10 times larger at an ordered part of the sample compared to a non-ordered part. If the fabrication process can be improved to grow larger inverted TiO₂ opals, significantly higher efficiencies can be achieved.
8.4 Conclusions

Thin films of highly ordered latex spheres are formed using a confinement method. By infiltration of a precursor solution and subsequent calcination, inverse opals of TiO$_2$ are formed. These can be employed in a novel type of heterojunction solar cells. Sensitizing the porous TiO$_2$ with a Ru-535 dye leads to cells with an overall efficiency of 0.6%. The efficiency is primarily limited by the small area of the opals. If the TiO$_2$ photonic crystalline area is enlarged, higher efficiencies will result, as we have observed that by ordering the TiO$_2$ nanoporous network, the photovoltaic response improves significantly.
References


Summary


In view of the environmental problems (i.e., global warming as a result of CO₂ emission) caused by the use of fossil fuels, the demand for sustainable energy is increasing. New, cleaner technologies to generate electricity are needed. The Netherlands wants to increase the percentage of energy generated by sustainable sources from 1% at present to about 12% in 2010, as a result of the Kyoto agreement. Wind, water, geothermal, biomass, and solar energy have to be developed to a large extent to achieve this goal. Furthermore, technologies for storage of energy will have to be developed, for example, in the form of rechargeable batteries and hydrogen.

Solar energy is abundant, clean, inexhaustible, applicable at many places in many ways, and at many scales. In this thesis we will concentrate on the photovoltaic application of solar energy; to convert sunlight directly into electricity. There are many types of solar cells; some of them already commercially established, some of them only in the research phase. Commercially available solar cells for urban application are mostly based on silicon. Single-crystalline and poly-crystalline silicon cells exhibit quite a high efficiency (12-16% for panels), but their high prize is a serious drawback. A lot of developments (for example, multi-junction cells, improved production) will hopefully increase the efficiency and/or lower the production costs of these inorganic solar cells. In contrast to these “first generation solar cells”, semiconductors are investigated that are cheap, abundant, and less demanding concerning purity. Titanium dioxide is a promising candidate, while it is produced in bulk quantities for use as white pigment in paints, plastics and paper, and in cosmetics. Its properties are suitable for use in solar cells, but as it absorbs only in the UV part of the solar spectrum, a sensitizer that absorbs visible light is necessary to form a hybrid solar cell. Background information on semiconductors and the working mechanism of solar cells can be found in paragraph 1.3.
The properties of titanium dioxide and research on thin and nanostructured films are described in Chapter 2. Titanium dioxide is easy to deposit in the form of thin films using gas-phase synthesis techniques like Chemical Vapour Deposition (CVD), Electron Beam Evaporation, and Spray Pyrolysis Deposition (SPD). The ease, quality of the films and concentration of oxygen vacancies of these three techniques are investigated and compared.

In Chapter 3 phthalocyanines (Pc’s) are discussed. This class of molecular p-type semiconductors is used frequently as sensitizers in hybrid solar cells. Their properties are discussed in §3.1. Thin films of zinc phthalocyanine can be deposited by thermal evaporation and consist of small crystallites (100-200 nm). The work function and band bending are determined with Kelvin probe measurements and match very well with literature values. These ZnPc films are used to form bi-layer solar cells with CVD-deposited TiO₂ films. The photovoltaic characteristics depend strongly on the thickness of the TiO₂ films and of the thermal treatment on the TiO₂ films prior to ZnPc deposition. The photocurrent decreases with increasing TiO₂ film thickness as a result of the increase in resistivity. Annealing in air leads to lower currents, while annealing in vacuum increases the photocurrent with a factor of 4. A longer annealing time enlarges the effect. Also, this annealing effect is stronger for thinner TiO₂ films. These effects are thought to originate from the change in donor density of the TiO₂ film as a result of different annealing steps. Sublimation of ZnPc leads to films that consist of long, thin, crystalline wires that form an interconnected porous network. It is possible that these wires represent a new polymorph of ZnPc. Attempts to fill this network with TiO₂ using CVD or SPD unfortunately did not lead to working solar cells. The wires are encapsulated during TiO₂ deposition and are no longer interconnected. No photovoltaic effect is observed, although photoconductivity is observed. Co-deposition of ZnPc (sublimation) and TiO₂ (CVD) yields a network without percolation of the ZnPc phase. For both techniques more research is needed to answer the question as to whether they can lead to efficient nanostructured heterojunction solar cells.
During the research of bi-layer devices of TiO$_2$ (CVD) and ZnPc (thermal evaporation) it is observed that the photocurrent is not stable, but is found to decrease if measured in ambient atmosphere. This photocurrent decay is investigated in depth in Chapter 4. It is caused by the combined presence of oxygen, light, and an electric field and is found to be fully reversible. If light and air are both present, oxygen radical anion (O$_3^-$) species are generated, which are mobile and drift towards the TiO$_2$/ZnPc interface due to an external electric field. These O$_3^-$ species accumulate at the interface and quench the singlet excitons that are generated in the phthalocyanine film, decreasing the photocurrent significantly. The decay curves can be fitted using a second order exponential function. The 'fast' process is independent of bias voltage and light intensity. The 'slower' process is dependent on bias voltage, but not on light intensity. The magnitude of photocurrent loss is governed by the irradiation intensity. The characteristic decay time is governed by the electric field at the junction. Upon irradiation, the oxygen anion concentration increases up to $6 \times 10^{18}$ cm$^{-3}$, which is two orders of magnitude higher than the reported O$_3^-$ concentration in the dark. The The Gouy-Chapman-Stern model is used to quantify the accumulation of charges at the interface.

Thiophenes are the subject of Chapter 5. The properties of these organic semiconductors are discussed in §5.1. Their high hole conductivity, chemical versatility, and easy deposition make them suitable candidates for use in nanostructured heterojunctions solar cells. However, many challenges have yet to be conquered in order to come to commercial applications. Bi-layer devices of sexithiophene (the hexamer of thiophene) and TiO$_2$ have been prepared (§5.2). These devices show a pronounced photovoltaic effect, but applying a bias voltage did not yield an effect on size of the active interface region. Sexithiophene is subject to reduction under forward bias in the dark and to oxidation under reverse bias and UV-illumination. Nanostructured blends of poly(3-octylthiophene) (a soluble polymer of thiophene) and TiO$_2$ are synthesized with co-deposition using spray pyrolysis (§5.3). Under illumination, a clear photoconducting behaviour is found, but only a limited photovoltaic effect. Premixing of poly(3-octylthiophene) and TiO$_2$
nanoparticles, followed by uniaxial pressing, leads to cells with a small photovoltaic effect. For both systems more research is needed to assess whether efficient solar cells can be obtained.

In Chapter 6 thin films of nanosized anatase titanium dioxide (TiO$_2$) particles are deposited using an aerosol technique, in which ultrasonically formed droplets of titanium isopropoxide are pyrolysed. The size of the particles and the morphology of the films depend on the deposition parameters, i.e., reaction temperature, concentration of the precursor, and gas flow. Under optimal conditions, films can be deposited consisting of stoichiometric anatase TiO$_2$ particles with a diameter of 50 to 300 nanometer. At higher concentrations and carrier gas flows agglomeration occurs and the particle sizes and dispersion thereof increase. Spincoating poly(3-octylthiophene) on top of these TiO$_2$ films leads to solar cells, which show efficiencies 20 times higher than cells with “flat” TiO$_2$, while the optical density for both systems is comparable. Devices for which P$_3$OT is added during TiO$_2$ deposition show similar efficiencies, indicating that the penetration of the P$_3$OT into the porous TiO$_2$ network is quite effective. We have found that the maximum penetration depth of P$_3$OT inside the nanoporous TiO$_2$ is around 1 μm. Larger pore sizes facilitate penetration of P$_3$OT, but due to the small exciton diffusion length more recombination occurs. Interpenetrating solar cells with polymers and TiO$_2$ will be a trade-off between pore-filling ability and recombination losses.

In Chapter 7 another approach to form nanostructured heterojunction solar cells is described. Thin films of 2,2'-bithiophene (2T) and 2,2'-5',2'-terthiophene (3T) are polymerized by UV irradiation. Radicals of these oligothiophenes, formed as a result of the irradiation, merge and form an oligomer twice as long as the starting compound. The polymerization process can be observed by UV-VIS and photoluminescence spectroscopy. If 2T is used as starting material, predominantly 4T (quarterthiophene) is formed, while 6T (sexithiophene) is formed if 3T is used as starting material. This polymerization reaction can also take place in solutions of 2T or 3T in
chloroform or toluene, or in a film of nanocrystalline titanium dioxide (nc-TiO₂), soaked with a 2T or 3T solution. In the latter case the pores are (partly) filled with 4T or 6T, which acts as hole conductor. A photovoltaic response is observed if nc-TiO₂/4T or nc-TiO₂/6T interpenetrating structures are irradiated with visible light. The increase of oligomer length from 2T to 3T and the corresponding decrease in orientational freedom of the molecules strongly affects the ease of polymerisation and the structural order of the compounds formed. The reason for the limited photocurrent in these systems requires more research.

In Chapter 8 a new concept of forming ordered nanoporous TiO₂ networks is employed to fabricate solar cells. Thin films of highly ordered latex spheres are formed using a confinement method. These so-called photonic films are deposited using self-organisation of latex spheres. By infiltration of a TiO₂ precursor solution in the voids between the spheres and subsequent calcination, a highly organized porous structure is formed. These inverse opals of TiO₂ are sensitized with a Ru-535 dye, which yields solar cells with a power conversion efficiency of 0.6% under simulated solar light. The efficiency is primarily limited by the small area of the ordered structure. If the TiO₂ photonic crystalline area is enlarged, higher efficiencies will result, as we have observed that by ordering the TiO₂ nanoporous network, the photovoltaic response improves significantly. These cells may be promising for future applications, provided that improved fabrication techniques will enable an enlargement of the ordered area.

In conclusion, in this thesis some issues concerning the bottlenecks of hybrid solar cells are discussed (see also §1.3.5). For bi-layer devices a new mechanism for photocurrent decay is described, which is a result of unwanted doping of phthalocyanine films by oxygen (Chapter 4). Ohmic losses are discussed for TiO₂ thin films in combination with ZnPc (§3.2). Stability issues are, amongst others, addressed for sexithiophene thin films (§5.2). Several new approaches to produce nanostructured heterojunction solar cells are tested to see whether they are suitable or not. It turns out to be very complicated to infiltrate semiconducting polymers into nanoporous
TiO$_2$ (Chapters 6 and 8), while the pores are either too small for dyes to penetrate or too big, yielding too much bulk recombination. This problem could be solved by increasing the exciton diffusion length inside the organic phase, either by improved stacking or by the development of new materials. Using small thiophene oligomers as a starting point is convenient as they can easily fill the TiO$_2$ pores. We have succeeded to dimerize these oligothiophenes with UV light. Making blends of TiO$_2$ and dyes in one step leads to the formation of non-percolating or non-connecting networks ($\S$3.3, $\S$5.3). In conclusion, there is still a lot of work to be done to come to efficient nanostructured heterojunction solar cells. A big step forwards could be achieved by the use of highly-ordered materials, either produced with advanced techniques or by self-assembly.
Samenvatting


Het gebruik van fossiele brandstoffen (olie, kolen, gas) leidt tot milieuproblemen, doordat de uitstoot van CO₂ mede het broeikaseffect veroorzaakt. Nieuwe, schone technologieën zijn nodig om electriciteit te produceren. De Nederlandse regering wil het percentage duurzame energie laten toenemen van de huidige 1% naar ongeveer 12% in 2010 als uitvloeisel van het Kyoto akkoord. Wind, water, geothermische, biomassa en zonne-energie zullen op grote schaal ontwikkeld moeten worden om dit doel te bereiken. Verder zijn er technologieën nodig voor opslag van energie, zoals bijvoorbeeld herlaadbare batterijen en waterstof.

Zonne-energie is schoon, onuitputtelijk, heeft een groot potentieel en kan op vele plaatsen, op vele manieren en op vele schalen toegepast worden. In dit proefschrift concentreren we ons op fotovoltaïsche zonne-energie: zonlicht wordt direct omgezet in electriciteit. Er zijn verschillende typen zonnecellen; sommige al commercieel toegepast, anderen nog in de onderzoeksfase. Commercieel verkrijgbare zonnecellen voor aardse toepassingen zijn meestal op silicium gebaseerd. Enkel- en polykristallijne Si cellen hebben een goede efficiëntie (12-15% voor panelen), maar hun hoge prijs is een nadeel. Nieuwe ontwikkelingen (zoals multi-junctie cellen en verbeterde produktiemethoden) zullen hopelijk de efficiëntie verhogen en/of de produktiekosten verlagen. In tegenstelling tot deze zogenaamde "eerste generatie zonnecellen" wordt er ook gekozen naar goedkope, veel voorkomende halfgeleiders, die minder eisen stellen aan zuiverheid. Titanium dioxide (TiO₂) is een veelbelovende kandidaat, omdat het in grote hoeveelheden wordt gebruikt als wit pigment in verven, plastics en papier, alsmede in cosmetica. Door zijn eigenschappen is TiO₂ zeer geschikt voor gebruik in zonnecellen, maar omdat alleen absorbtie in het ultraviolette deel van het zonnespectrum optreedt, is een zichtbare kleurstof nodig om een hybride zonnecel te kunnen vormen.
Achtergrondinformatie betreffende halfgeleiders en de werking van zonnecel len vindt u in paragraaf 1.3.

De eigenschappen van TiO₂ en onderzoek aan dunne en nanogestructureerde TiO₂ films worden beschreven in Hoofdstuk 2. Titaandioxide is eenvoudig aan te brengen als dunne film door gebruik te maken van gasfase technieken als Chemische Vorming uit Damp (CVD), Elektronenbundel Deposietie en Sproei Pyrolyse Deposietie (SPD). Gebruiksgemak, filmkwaliteit en defectconcentratie van deze drie technieken zijn onderzocht en met elkaar vergeleken.

In Hoofdstuk 3 wordt de groep der ftalocyanines besproken. Deze klasse van moleculaire p-type halfgeleiders wordt regelmatig gebruikt als kleurstof in hybride zonnecellen. Hun eigenschappen staan besproken in §3.1. Dunne films van zinkftalocyanine (ZnPc) kunnen worden gedeporteerd door middel van thermische verdamping en bestaan uit kleine kristallieten (100-200 nm). De werkwijze en bandbuiging zijn bepaald met behulp van Kelvin probe metingen en de waarden komen goed overeen met de literatuur. Deze ZnPc films zijn gebruikt om bi-laag zonnecellen te vormen met TiO₂. De fotovoltaïsche karakteristieken hangen sterk af van de dikte van de TiO₂ film en de warmtebehandeling van diezelfde film vóór depositie van ZnPc. De fotostroom daalt bij toenemende TiO₂ laagdikte als gevolg van de weerstandstoename. Een warmtebehandeling in lucht leidt tot lagere stromen, terwijl een warmtebehandeling in vacuüm de fotostroom met een factor 4 vergroot. Langere behandelingen vergroten het effect, terwijl dit groter lijkt te zijn voor dunnere TiO₂ films. Het effect van de warmtebehandeling op de fotostroom wordt waarschijnlijk veroorzaakt door de veranderingen in donordichtheid in de TiO₂ films. Sublimatie van ZnPc leidt tot films die bestaan uit lange, dunne draden, die met elkaar verbonden zijn tot een poreus netwerk. Het is mogelijk, dat deze draden een nieuw polymorf van ZnPc vormen. Pogingen om dit netwerk met TiO₂ op te vullen door middel van gasfase-technieken leiden helaas niet tot werkende zonnecellen. De draden worden ingekapseld tijdens de TiO₂ depositie en zijn niet meer onderling verbonden. Er wordt geen fotovoltaïsch effect, maar wel
fotogeleiding waargenomen. Co-depositie van ZnPc en TiO₂ in een CVD reactor leidt tot een netwerk zonder percolatie van de ZnPc fase. Voor beide technieken is meer onderzoek nodig naar de toepasbaarheid voor het fabriceren van nanogestructureerde heterojunctie zonnecellen.

Gedurende het onderzoek naar bi-lagen van TiO₂ en ZnPc werd ontdekt dat de fotostroom afneemt in de tijd als er gemeten wordt in lucht. Deze afname in fotostroom is in detail onderzocht in Hoofdstuk 4 en blijkt veroorzaakt te worden door de gecombineerde aanwezigheid van zuurstof, licht en een elektrisch veld, terwijl het effect geheel reversibel is. Als licht en zuurstof beide aanwezig zijn, worden zuurstofradicalen gevormd, die mobiel zijn en naar het grensvlak tussen TiO₂ en ZnPc gedreven worden door het extern aangelegde elektrische veld. Daar aangekomen accumuleren ze en doven ("to quench") de singulet excitonen uit die in de ftalocyanine films gegenereerd zijn, waardoor de fotostroom significant verkleind wordt. De curves van de afname in fotostroom kunnen gefit worden aan een tweede-orde exponentiële functie. Het "snelle" deel is onafhankelijk van aangelegde potentiaal en lichtintensiteit en het "langzame" deel is afhankelijk van de potentiaal, maar niet van de lichtintensiteit. De afname van de fotostroom wordt bepaald door de belichtingsintensiteit. De karakteristieke tijd wordt bepaald door het elektrisch veld aan het grensvlak. Onder belichting stijgt de zuurstofradicaalconcentratie naar $6 \times 10^4$ cm$^{-3}$, wat twee ordes van grootte meer is dan de literatuurwaarde voor dezelfde concentratie in de donker. Het De Gouy-Chapman-Stern model is gebruikt om de ophoping van lading aan het grensvlak tussen TiO₂ en ZnPc te kwantificeren.

Thiofenen worden behandeld in Hoofdstuk 5. De eigenschappen van deze organische halfgeleiders worden besproken in §5.1. Hun goede gatengeleiding, chemische veelzijdigheid en eenvoudige depositie maakt hen geschikte kandidaten voor gebruik in zonnecellen. Echter, er zijn nog vele uitdagingen te overwinnen, voordat gedacht kan worden aan commerciële toepassingen. Bi-laag structuren van sexithiofeen (de hexameer van thiofeen) en TiO₂ vertonen een duidelijk fotovoltaiïsch effect (§5.2), maar een extern elektrische veld heeft geen effect op de grootte van het actieve gebied. Sexithiofeen wordt gereduceerd onder "forward bias" (in doorlaatrichting
geschakeld) in het donker en geoxideerd onder "reverse bias" (in sperrichting geschakeld) en UV-belichting. Nanogestructureerde mengsels van poly(3-octylthiofeen) (P3OT, een oplosbaar polymer van thiofeen) en TiO₂ zijn gesynthetiseerd met behulp van SPD (§5.2). Onder belichting is duidelijke fotogeleiding waarneembaar, maar slechts een klein fotovoltaïsch effect. Voormengen van P3OT en TiO₂ nanodeeltjes, gevolgd door persen leidt tot cellen met een klein fotovoltaïsch effect. Voor beide laatstgenoemde technieken is meer onderzoek nodig om te kunnen vaststellen of deze wel of niet geschikt zijn voor het fabriceren van efficiënte zonnecellen.

In Hoofdstuk 6 worden dunne films van nanogestructureerde anataas TiO₂ deeltjes gedeponeerd, gebruikmakend van een aerosol techniek. Ultrasoon gevormde druppels van titaanisopropoxide worden gepyrolyseerd en slaan neer op een substraat. De grootte van de gevormde deeltjes en de morfologie van de films hangt af van depositieparameters, zoals reactietemperatuur, precursorconcentratie en gasstroom. Onder optimale condities kunnen films gemaakt worden, die bestaan uit stoechiometrische deeltjes anataas TiO₂ met een diameter van 50 tot 300 nm. Hogere precursorconcentraties en/of hogere gasstromen leiden tot grotere deeltjes en een bredere deeltjesgrootedistributie. Het spincoaten van P3OT bovenop deze films leidt tot zonnecellen die een 20 keer hogere efficiëntie hebben dan cellen die gemaakt zijn met vlak TiO₂, terwijl de hoeveelheid kleurstof voor beide gelijk is. Cellen, die gemaakt zijn door het toevoegen van P3OT tijdens de TiO₂ depositie (in tegenstelling tot na afloop) leveren vergelijkbare resultaten op, wat duidt op een efficiënte penetratie van het polymer in het TiO₂ netwerk. We hebben kunnen bepalen dat de maximale doordringdiepte van het polymer in dit poreuze TiO₂ ongeveer 1 micrometer bedraagt. Grotere porieën vergemakkelijken het binnendringen van P3OT, maar gezien de kleine exciton diffusielengte treedt er meer recombinatie op. Om interpenetrerende zonnecellen van TiO₂ en polymer te maken, zal een evenwicht gezocht moeten worden tussen porievulling en recombinatieverliezen.
In Hoofdstuk 7 wordt een andere benadering voor het maken van nanogestructureerde heterojunctie zonnecellen gevolgd. Dunne films van 2,2'-bithiofeen (2T) en 2,2'-5',2''-terthiofeen (3T) worden gepolymeriseerd door UV-straling. Er worden radicalen van deze oligothiofeenen gevormd, die samen een oligomeer vormen dat twee keer zo lang is als de uitgangsstof. Dit polymerisatieprocess kan worden gevolgd door UV-VIS en fotoluminescentiespectroscopie. Als 2T wordt gebruikt als uitgangsmateriaal, dan wordt voornamelijk 4T (quaterthiofeen) gevormd, terwijl 6T (sexthiofeen) wordt gevormd als uitgegaan wordt van 3T. Deze polymerisatiereactie kan ook plaatsvinden in oplossingen van 2T of 3T in chloroform of toluene, of in een film van nanoporeus TiO₂ doordrenkt met een 2T of 3T oplossing. In dit laatste geval worden de poriën gedeeltelijk gevuld met 4T of 6T, dat een gatenleider is en zichtbaar licht kan absorberen. Een fotovoltaïsch effect wordt waargenomen als deze TiO₂/4T of TiO₂/6T structuren worden belicht. De toename van de oligomeerlengte van 2T naar 3T en de corresponderende daling van de orientatievrijheid van de moleculen beïnvloedt het polymerisatieschema en de ordening van de reactieprodukten sterk. Een antwoord op de vraag waarom het fotovoltaïsch effect zo klein is vereist meer onderzoek.

In Hoofdstuk 8, tenslotte, wordt een nieuw concept toegepast om geordende nanoporeuze TiO₂ netwerken voor zonnecellen te vormen. Dunne, zeer geordende films van latex bolletjes worden gevormd door middel van een "opsluit"-methode. Deze zogenaamde fotonische films vormen zich door middel van zelf-organisatie. Door infiltratie van een TiO₂ precursor in de poriën en een daaropvolgende calcinatiestap wordt een geordende poreuze structuur verkregen. Deze inverse opalen van TiO₂ zijn gekleurd met een Ru-535 kleurstof en zonnecellen zijn verkregen met een efficiëntie van 0.6% onder gesimuleerd zonlicht. De efficiëntie wordt voornamelijk beperkt door het kleine geordende oppervlak. Als dit oppervlak wordt vergroot zullen hogere efficiënties worden behaald, omdat dat waargenomen dat het fotovoltaïsch effect veel sterker is voor geordende dan voor niet-geordende oppervlakken. Dit type cel zal mogelijk veelbelovend zijn voor toekomstige toepassingen, mits verbeterde technieken het geordende oppervlak vergroten.
Concluderend bevat dit proefschrift een aantal onderwerpen, die samenhangen met de knelpunten bij de ontwikkeling van hybride zonnecellen (zie ook §1.3.5). Voor bi-laag cellen is een nieuw mechanisme ontdekt, dat de fotostrook laat afnemen als een gevolg van ongewenste dotering van ftalocyanine films door zuurstof (Hoofdstuk 4). Ohmse verliezen worden waargenomen voor titaandioxide films in combinatie met ZnPc (§3.2). Stabiliteitsproblemen worden onder andere besproken voor sexinthiofeen films (§3.2). Een aantal nieuwe benaderingen om nanogestructureerde heterojunctie zonnecellen te produceren wordt bediscussieerd om te beoordelen of ze geschikt zijn of niet. Het blijkt erg lastig te zijn om halfgeleidend polymeren in nanoporeuze TiO₂ netwerken te penetreren (Hoofdstuk 6 en 8), omdat de poriën ofwel te klein zijn om binnen te dringen, ofwel te groot zijn, wat leidt tot recombinatieverliezen. Dit probleem zou op te lossen zijn als de exciton diffusielengte van de gebruikte organische fase drastisch vergroot zou kunnen worden door verbeterde stapeling of door de ontwikkeling van nieuwe materialen. Het gebruik van kleine, oplosbare thiofeenoligomeren als startpunt is handig omdat deze gemakkelijk in TiO₂ poriën doordringen. UV-belichting leidt tot dimerisatie van deze oligomeren. Het maken van mengsels van TiO₂ en kleurstoffen in één stap leidt tot de vorming van netwerken waarin geen percolatie optreedt, of waarin geen onderling contact is (§3.3, §5.3). Als conclusie kunnen we stellen dat er nog veel werk te verrichten valt om nanogestructureerde heterojunctiezonnecellen te ontwikkelen. Een grote stap voorwaarts zou gemaakt kunnen worden door het gebruik van geordende materialen, ofwel gevormd door geavanceerde technieken, ofwel door gebruik te maken van zelf-organisatie.
Publications


Huisman, Carolien L.; Goossens, Albert; Schoonman, Joop. “Aerosol synthesis of anatase titanium dioxide nanoparticles for hybrid solar cells”. *Chemistry of Materials* in press. (Chapter 6).

Huisman, Carolien L.; Huijser, Annemarie; Donker, Harry; Goossens, Albert; Schoonman, Joop. “UV-polymerization of oligothiophenes and their application in nanostructured heterojunction solar cells”. Submitted to *Macromolecules*. (Chapter 7).


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Dankwoord

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Curriculum Vitae


Maar voor een toverspreuk van kwaliteit
ben je zomaar duizend gulden kwijt
en naar een beetje toverboek
ben je toch wel vijftig jaar op zoek
en de hele cursus tovenaar
duurt honderd vijfentwintig jaar.
Dat brengt hij allemaal niet op.
Ik denk dat hij voor 't begin al stopt
want zelfs de oma van z'n oma
had nooit een tovenaarsdiploma.

Uit: Toveren, Herman van Veen