Master’s Thesis

Solar cells based on synthesized nanocrystalline ZnO thin films sensitized by chlorophyll a and photopigments isolated from spinach

Kristian Nygren
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Dye-sensitized solar cell, thin film, Au cathode, nanocrystals, mesoporous, ZnO, chlorophyll, spinach, photopigments, XRD
Abstract

The principles of dye-sensitized solar cells were studied and are outlined in this thesis. An overview of the basic steps needed to create a DSC is followed by detailed experimental information on how to assemble the solar cells that were fabricated in this project. They were based on synthesized nanocrystalline ZnO thin films sensitized by chlorophyll a as well as isolated photopigments from spinach leaves. The nanocrystals were studied using XRD, and it was confirmed that three different methods of synthesis resulted in ZnO crystals of a few nanometers. The solar cells were assembled with Au electrodes in a sandwich configuration and their photovoltaic properties were measured. Overall light-to-electricity conversion was low with the highest efficiency being 0.21%. An astonishingly low efficiency of 0.0003% was noted for a thin film which was not thermally treated, and it is suggested that heat-treatment is of great importance. It was also found that photopigments from spinach can be extracted easily and used as molecular sensitizer without any demanding purification steps.
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This master’s thesis has been a great and challenging project to work with. The contents of chemistry, biotechnology, physics and practical implementation were a perfect combination for my undergraduate program in engineering biology. The project has in its entirety been carried out at The Department of Physics, Chemistry and Biology (IFM) at the Institute of Technology at Linköping University.

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I would also like to thank all the nice people I have met at IFM during my time here.
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>DSC(s)</td>
<td>Dye-sensitized solar cells</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray powder diffraction</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent conducting oxide</td>
</tr>
<tr>
<td>NC(s)</td>
<td>Nanocrystal(s)</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>Ru</td>
<td>Ruthenium</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
<tr>
<td>Au</td>
<td>Gold</td>
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<tr>
<td>ZnO</td>
<td>Zinc oxide</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Titanium dioxide</td>
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<tr>
<td>J-V curve</td>
<td>Current density vs. voltage plot</td>
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<tr>
<td>I$^-$</td>
<td>Iodide</td>
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<tr>
<td>I$_3^-$</td>
<td>Triiodide</td>
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1. Background

1.1. The purpose

During the past 20 years a lot of articles have been published regarding solar cells. Considering the world’s increasing demand for clean and renewable energy, it is no wonder that a lot of effort is being put into this field. Still most photovoltaic devices are expensive and/or lack effectiveness for a true breakthrough.

The purpose of this project is, however, not to solve the world’s energy crisis, but to gain knowledge and insight into a special type of solar cells called dye-sensitized solar cells, or just DSC for short. Back in 2004 an article about a functional solar cell, based on the energy conversion of light into electricity occurring naturally in plants, was published by a team from Italy [1]. The absolute aim was to get a working photovoltaic device based on the same principle. Another goal was to study what affected the results and if any improvements could be made.

1.2. History

The photoelectric effect was first discovered by Edmond Becquerel in 1839 [2]. His early experiments had more to do with photography than solar cells [3]. Although these studies were done in liquids and not solid-state devices, it was discovered that aspects of photography could be studied using photo electrochemical cells [4]. Early photographic films were insensitive to red light, which is now known to be because of the band gap of the silver halide grains used [3]. With the addition of different dyes the photosensitivity could be enhanced to longer wavelengths.

After the global oil crisis in the 1970s, various alternative energy sources were intensively studied [2]. This really laid the foundation for the evolvement of solar cells, with the number of publications reaching several tens of thousands by today.

1.3. The sun as an energy source

It is common knowledge that we are very likely to deplete the available resources of fossil fuels in a not too distant future. Even with improvements in extraction techniques [2], such fuels will not be able to sustain our demand for energy indefinitely. The only source of energy that will last forever, seen from our human perspective, is the sun. Recent data suggests that the sun will continue to support life on Earth for another 1 billion years. At that point the sun will have become so hot that presence of liquid water on the surface of the Earth will be impossible [5]. Meanwhile, the sun continues to output an overwhelming amount of energy. Every year $3 \times 10^{24}$ J of energy hit the surface of the Earth, exceeding 10,000 times our current demand for energy [3]. Covering 0.1 % of the Earth’s surface with solar cells with an efficiency of 10 % would meet our current energy demands. Although an efficiency of 10 % is achievable with today’s technology, the area required would be in the order of 100,000 km$^2$, i.e. something between on fifth and one quarter of the land mass of Sweden.

1.3.1. Solar insolation

The solar constant is the amount of electromagnetic radiation per unit area reaching the Earth, measured just above the atmosphere. Its value is 1,367 W/m$^2$ and it includes all wavelengths, not just the visible light [6]. The actual sunlight hitting the surface varies, depending on the angle of incidence
and gases and particles in the atmosphere. In the southern part of Sweden an annual average of 3758 MJ/m² has been reported [7], which translates into about 1000 kWh/m². Cloud cover affects the solar irradiance dramatically, with clear skies resulting in values of about 900 W/m², light cloud cover in 250-500 W/m² and heavy cloud cover in less than 100 W/m² [8].

Figure 1. This image illustrates the yearly sum of solar irradiation per square meter at an optimally-inclined plane for the European countries. Most Nordic countries can receive about 1000 kWh/m². Image source: PVGIS © European Communities, 2001-2008 [9]. Used with permission.
Figure 2. This image illustrates the yearly sum of solar irradiation per square meter at an optimally-inclined plane for Africa. In terms of solar irradiation, the Sahara desert is one of the most suited locations for solar power with yearly irradiation reaching over 2,500 kWh/m². Image source: PVGIS © European Communities, 2001-2008 [10]. Used with permission.
1.4. The photovoltaic effect

Photovoltaic devices operate on the principle that photons falling on a material can excite electrons. However, these electrons will only remain at this higher energy state for a very short period of time before returning to their original energy level. To collect these electrons, and allow for generation of electric current, semiconductors are used to allow current to travel in only one direction [11].

Traditionally, solar cells are made from p and n-type doped silicon [12]. The n-type has free extra electrons and the p-type has extra holes. When these two materials are placed in contact with each other, a p-n junction is created. Some of the electrons from the n-type will flow into the p-type to fill the holes. This will lead to charge separation across the junction, and the resulting electric field will eventually stop the electrons from flowing. Right in the middle of the junction there will be no mobile charge carriers left, and this is called the depletion region [13,14].

As photons fall on the semiconductor, they can excite electrons to the conduction band. When an electron is excited a hole is also created, commonly known as an electron-hole pair. If an external load exists, the electron will flow from the n-type across the external circuit and lose potential. Eventually it will end up at the p-side of the junction, filling up a hole it left behind [11,14].

If the excited electron does not reach the p-n-junction, recombination occurs and the electron returns to its original state eliminating the hole created before. The electron-hole pairs that recombine do not produce any external electricity. The ratio between the number of collected electron-hole pairs and the number of incident photons is known as quantum efficiency (QE), and is often measured as a function of wavelength. The QE is also known as Incident-Photon-to-Electron Conversion Efficiency (IPCE) [15].

1.4.1. Band gap

A photon’s energy $E$ is inversely proportional to its wavelength $\lambda$ according to

$$E = h\nu = \frac{hc}{\lambda}$$

where $h$ is Planck’s constant and $c$ the speed of light [14]. If the energy exceeds the band gap of the semiconductor, the photon can be absorbed and an electron will be excited from the valence band to the conduction band. Electrons in the conduction band can move, which allows for electric current. The difference between the photon energy and the band gap will end up as heat. However, it has been documented that a high energy photon can give rise to multiple electron-hole pairs in certain materials, and this could possibly be used to reduce heat loss in solar cells [16].

Figure 3. The band gap is the difference in energy between the valence band and the conduction band [14].
1.5. Silicon solar cells

Most commercial solar cells today are made of mono- or polycrystalline Si [16]. The major drawback of these devices is the requirement of high-grade Si. An increase in demand and an expensive manufacturing process makes these solar cells troublesome from an economic point of view. The narrow band gap of Si, 1.14 eV [6], also results in large parts of the energy in the visible region is lost as heat. Other materials based on the same principle include, among others, amorphous Si, CuInSe₂, CuInGaSe₂, CdTe and Ga-As [3]. These are known as first and second generation solar cells [16].

1.6. Dye-sensitized solar cells (DSC)

Much cheaper alternatives to Si are TiO₂ and ZnO, both of which are metal oxide semiconductors. These feature a wider band gap of about 3.2 eV and are as a consequence more chemically stable [3]. The downside is that their band gap practically means that only the UV range of the solar irradiation is absorbed. The solution to this problem was the functional separation of light absorption and charge transport, which was suggested by Grätzel in 1991 [17]. A photosensitive dye was used to capture the incoming light, and then transfer the charge carriers to a wide band gap semiconductor. These cells are commonly called Grätzel cells. As of 2009, DSCs had a verified record efficiency of 11.1 % with life expectancies reaching 10 years of stable operation [18].

1.6.1. Efficiency limitations

A traditional solid-state p-n device has an upper theoretical limit of 33 % power conversion efficiency from light to electricity [16]. The thermodynamic limit for this process in general is 93 %, and it is believed that this can be approached by stacking thin films of different properties on top of each other or by inventing fundamentally new concepts.

1.6.2. Concept

The concept of the DSC is outlined in Figure 4. A thin layer (10 µm) of interconnected, mesoporous (2-50 nm) semiconducting material, such as ZnO or TiO₂, covers a transparent conducting oxide glass substrate (TCO). Light enters the sandwich construction through the glass and excites a dye molecule adsorbed on or bonded to the semiconductor. The electron is injected into the conduction band of the metal oxide, in which it travels according to a random-walk model to reach the anode [19]. The oxidized dye is regenerated by reductive species in the electrolyte [20]. If an external load is applied, the electrons will flow from the anode to the cathode to close the circuit. The cell is then said to be working in a regenerative mode, with no overall change in chemical environment [21].

The major advantage of the mesoporous structure, compared to that of a flat surface, is the enormous increase in available surface area for dye absorption [3]. Using nanosized crystals the increase in volume-to-surface ratio reaches 1,000 times, and this will be shown later theoretically. Only the first monolayer of a dye will provide efficient electron injection into the semiconductor, so this structure enhances light absorption significantly [22].
Figure 4. This illustrates the basic design of a DSC. The distance between the two electrodes is less than 20 µm and the size of the metal oxide crystals is about 10-25 nm [23]. Iodide is oxidized to triiodide at the anode, with the corresponding reduction occurring at the cathode. The overall reactions taking place are: \( 3I^- \rightarrow I_3^- + 2e^- \) (anode) and \( I_3^- + 2e^- \rightarrow 3I^- \) (cathode) [21]. It was recently observed, using nanosecond laser spectroscopy, that an intermediate reaction involving a diiodide radical is responsible for regeneration of the dye [18].

1.6.3. The semiconductor-electrolyte interface

The semiconductor-electrolyte junction results in a photoelectrochemical system that has different properties than the traditional solid-state photovoltaic devices. Because of the nanosized particles, no depletion layer can be formed in the solid [3]. The photocurrent instead depends upon kinetics of different charge carriers in the system. When transfer of holes to the electrolyte is faster than the transfer of electrons, anodic current will flow and the semiconductor can be considered n-type. The redox couple in the electrolyte, together with the semiconductor and its properties, highly determines the kinetics of these processes. Photoexcitation and injecting an electron into the valence band are in the range of 0.05 – 150 ps, where as recombination (to the dye or the redox mediator) takes about 0.1 – 1 ms for a TiO\(_2\)/Ru/I\(_3^-\)/I\(^-\) system [18]. This means the process of electron injection into the semiconductor is kinetically favored (under these circumstances). Actually, using a different redox couple or by altering the surface of the semiconductor, the process can be reversed, rendering it p-type to produce cathodic current instead [24].
1.6.4. Diffusion

As will be discussed later, the electrolyte is often based on the I\textsubscript{3}/I\textsuperscript{-} redox couple. Due to the kinetic processes, there must sufficiently high local concentrations of iodide near the dye for good regeneration [18]. After the oxidization of iodide, the triiodide needs to be transported to the cathode for reduction. This motion is based upon diffusion [25]. If the solvent is too viscous or if the concentration of triiodide is low, depletion may occur at the cathode, resulting in an over potential which lowers the voltage of the cell [18]. The size of the pores in the semiconducting layer also affects the diffusion, and although a smaller pore size increases the surface area, the more compact layer may impact the diffusion processes negatively [26]. Under high illumination and high current densities, the transfer of I\textsubscript{3}\textsuperscript{-} ions to the cathode is a limiting factor [25].

1.6.5. The cathode-electrolyte interface

The counter electrode should be chosen with respect to the redox couple to catalyze the cathodic reaction [27]. In this case Pt electrodes have been widely used as they facilitate the reduction of triiodide [25]. Iodine is chemisorbed on Pt surfaces, and this process reduces the high activation energy needed to break the I-I bond [19]. This leads to rapid electron transfer from the cathode to the oxidized electrolyte species. Other cathodic materials that have been used with varying success are graphite, activated carbon, carbon nanotubes, PEDOT, polypyrrole and carbon-black (amorphous carbon) coated stainless steel [28].

1.6.6. Voltage

The reason a DSC works is favorable kinetics overall. Under illumination in open circuit mode the injection of electrons from the dye must eventually be balanced by back routes (dark current), and three such pathways can be identified [19]. Electrons can be transferred from the oxide to the oxidized electrolyte (I\textsubscript{3}\textsuperscript{-}), from the oxide to the oxidized dye (D\textsuperscript{*}) and from the backend TCO layer on the anode to I\textsubscript{3}\textsuperscript{-} (shunting). It is stated that under high intensities and open-circuit operation, the rate of reverse transfer of electrons to I\textsubscript{3}\textsuperscript{-} is what limits the voltage.

Charge injection from the dye results in an increase of the electron concentration in semiconductor, and this is the reason for the observed photovoltage [29]. The maximum achievable voltage, in theory, is the difference between the redox potential of the electrolyte and the bottom of the conduction band in the semiconductor (Figure 5) [30].

It should be pointed out that this is by no means the complete picture. The true workings behind the DSC, including quantum effects such as electron traps in the oxide and tunneling between the oxide and TCO interface, are still not fully understood [31], and a lot of the physical chemistry involved goes beyond the scope of this thesis.
Figure 5. This figure illustrates the different potentials in a DSC. D, D* and D+ represent a dye molecule in the standard state, the photoexcited state and the cation state. The maximum voltage is the difference between the bottom of the conduction band and the redox potential. The scale on the left is for guidance only and actual values depend upon the materials. It should however be noted that the potential drop involved in the regeneration of the dye, $E_0(D^+/D) - E_0(Ox/Red)$, is often significant, but the redox couple must also be chosen to provide favorable kinetics to the solar cell [18]. The image was inspired by Grätzel [3].

1.6.7. Dye

The purpose of the dye is to absorb as much light as possible and inject the photo-excited electrons into the conduction band of the semiconductor. It must function in a wide thermal range and maintain photo stability for long-term use [32].

Ruthenium sensitizers

The state of the art sensitizers are ruthenium-based and can result in DSCs having an efficiency of about 11% [3]. They feature broad light-absorption and also great long-term stability, attributed to the fact only the oxidation state of the ruthenium center is changed upon electron injection, instead of the dye molecule becoming a cation radical [22]. These Ru-dyes are common but remain expensive due to rareness of the ruthenium metal, and cheaper alternatives are under investigation [32, 33].
Chlorophylls are the main pigments involved in the photosynthesis, absorbing most of the blue and red light, while accessory pigments known as carotenoids and phycobilins can serve to enhance the absorption in the blue-green and yellow part of the spectrum [35]. In nature, carotenoids also act as energy transfer molecules for chlorophyll and prevent degradation of the molecules by quenching certain energy states, thus acting as photoprotectors [36]. Another interesting feature found in nature is the stacking of the thylakoid membranes (containing the chlorophyll) to enhance light absorption [26]. Such stacking has similarities with the structure of the mesoporous network in a DSC. These properties make photosynthetic pigments attractive to use as sensitizers in solar cells [1]. As mentioned before, these molecules become cation radicals and are susceptible to undesirable side reactions before being reduced by the electrolytic species [22].
Figure 7. Chlorophyll a (left) and chlorophyll b (right). They only differ by one functional group. Images are public domain and were verified by textbooks [35].
1.7. Characterizing performance of solar cells

Regardless of the type of solar cell, they can be compared in terms of how well they perform. Four different parameters are typically listed: Open-circuit voltage, short circuit current, fill factor and efficiency. A fifth definition, maximum power point, is also used in some of the parameters.

Open-circuit voltage refers to the potential difference between the two electrodes when there is no external circuit to allow for current. Short circuit current is the current flowing between the two electrodes when they are connected externally without any resistance. The maximum power point ($mp$) is where the voltage $V$ and the current density $J$ of a solar cell are such that their product $P_{\text{max}}$ is maximized [11].

$$P_{\text{max}} = V_{mp} \times J_{mp}$$

Fill factor is defined as the maximum achievable power divided by the theoretical power at short-circuit current and open-circuit voltage [19]. As the quality of the solar cell goes up, this value approaches 1.

$$FF = \frac{P_{\text{max}}}{I_{sc} \times V_{oc}}$$

The power conversion efficiency $\eta$ of a solar cell is the ratio between output electric power density and input light power density [11]. $P_{\text{max}}$ and $E$ are usually given in mW/cm$^2$ for laboratory purposes.

$$\eta = \frac{P_{\text{max}}}{E}$$
Figure 9. This is a J-V curve of a hypothetical DSC. The maximum power point is where the DSC has its highest power density. As the external resistance increases, the current density will drop. For an infinitely large resistance, the open-circuit voltage $V_{oc}$ is reached.
2. Overview of used methods and materials

All DSCs were constructed using ZnO as semiconducting material. Previous experiments with regards to the synthesis of nanosized ZnO had been carried out at the institution. Commercially available chlorophyll a and photopigments extracted from spinach were used as sensitizers.

![Diagram of DSC structure](image)

Figure 10. The basic structure of the DSCs created. The two electrodes were aligned with an overlap to allow for electric contact to be made. This illustration is not to scale and the liquid electrolyte does not easily leak out of the cell even without sealing.

2.1. Construction

2.1.1. ZnO

ZnO has a wide band gap of 3.3 eV at room temperature [37], which makes it insensitive to visible light with absorption only in the UV range [38]. Most ZnO has n-type characteristics [39]. Other inorganic electron receptors that have been used previously in DSCs include, among others, TiO₂, SnO₂ and CdSe [1,40--42]. Only ZnO was used in this project.

Nanoparticle synthesis

There are different ways to synthesize NC ZnO. By choosing method and altering concentrations, times and temperatures, it is possible to control the size of the final crystals at the nanoscale [38,43,44]. Three methods were used and the synthesized products were verified in this project.

The basis of crystal growth is a process known as Ostwald ripening [44]. At the starting point, a solution will contain only small particles, which are more soluble than larger particles due to higher surface energy. These small particles will nucleate into larger particles, which are thermodynamically favored. The atomic ordering inside a crystal represents a lower energy state than that of the surface, and larger crystals have a smaller surface to volume ratio. The rate of the nucleation process decreases as the particles grow, due to the fact that the entropy is small for an ordered structure [45].

2.1.2. Approximation of surface area

To approximate the amount of “chlorophyll dye” needed to cover the mesoporous ZnO structure, a mathematical model was created. The mass of ZnO in an electrode was estimated to be...
m = pVF (1)

where $p$ is the density of ZnO (5.606 g/cm$^3$), $V$ is the volume of a solid layer 1 cm x 1 cm x 10 µm in size and $f$ is a porosity factor. This mass was estimated to be 2 mg. The total surface area of N spheres with an average radius $r$ is given by:

\[ A(N, r) = 4N\pi r^2 \] (2).

A crystal in the thin film must be in contact with one or more crystal(s) reducing the total available surface area. To account for this, a constant $k$ defining mean available surface was introduced:

\[ A_{\text{eff}}(N, r) = 4N\pi r^2 k \] (3).

The total mass of N crystals is given by

\[ m = Np \times \frac{4\pi r^3}{3} \] (4).

Solving this equation for $N$ results in

\[ N = \frac{3m}{4\pi r^3} \] (5).

Combining (5) and (3) gives a formula for calculation of the surface area as a function of the total mass and radius of the particles.

\[ A_{\text{eff}}(m, r) = \frac{3mk}{pr} \] (6)

The density $p$ and the introduced parameter $k$ are assumed to be constant. If a chlorophyll a molecule has an area of $A_c$ and is always adsorbed to the ZnO in a flat manner, the mass of all chlorophyll a can be estimated to be

\[ m_c = \frac{A_{\text{eff}}(m, r) \times M_c}{A_c N_A} \] (7)

where $M_c$ is 893.43 g/mol and $N_A$ is the Avogadro constant. Assuming $m = 2$ mg, $r = 5$ nm, $k = 0.5$ and $A_c = 10 \times 10$ Å$^2$, the total surface area of ZnO is 0.10 m$^2$ and the amount of chlorophyll a needed to cover it is 0.14 mg. Although this is a very simple model, it illustrates the huge 1,000-fold increase in available surface area compared to that of a solid bulk electrode. These values correspond well with values stated elsewhere [3].

### 2.1.3. Deposition of ZnO to the anode

Typically a thin layer of ZnO in the order of 10 µm is deposited on a transparent conductive glass [3]. Layer thickness affects the efficiency of the DSC [27]. A thin layer has high quantum efficiency, but its total surface area is smaller than that of a thicker one. Thicker layers suffer from higher rates of recombination due to the increased particle to electrode distance [24]. Therefore a thickness exists where the energy conversion efficiency is maximized.
Various methods of depositing inorganic compounds such as TiO$_2$ and ZnO for the purpose of making dye-sensitized solar cells have been described in the literature [1,15,27,46]. These methods include spin-coating, casting, sol-gel, spraying and a method using a viscous paste of the compound which is pressed onto the surface. The latter approach [46] was primarily used in this project. It is well known that the morphology of the film greatly affects the photovoltaic performance [21], so different fabrication techniques and even small variations in the preparation of the films may result in substantially different properties.

2.1.4. Annealing the anode

In order to create an interconnected mesoporous semiconducting network, and also remove organic surfactants, atmospheric water and other adsorbents from the ZnO, the film should be heated to 400°C for 30 minutes [47]. This also improves the porosity of the layer as the nanocrystals increase in size during annealing, which has been shown by XRD.

2.1.5. Handling chlorophyll

Chlorophyll a is highly susceptible to degradation during processing and storage [48]. The recommended storage stated by the manufacturer (Sigma-Aldrich) is inert gas, darkness and -20°C. Petrella et al. [1] reported storing photo-synthetic pigments including chlorophyll a in the dark, in wet n-pentane, at -80°C under an N$_2$ atmosphere.

2.1.6. Extracting photopigments from spinach leaves

The chlorophylls and the different accessory pigments can be extracted from plants or algae using solvent based methods, and later separated and purified with column chromatography [49]. Pigments have been isolated from algae and used as sensitizers in solar cells previously [1]. It was decided to try out the first steps of an extraction method based on methanol and dioxane [50], but to skip any further chromatographic steps [51] since that would probably require too much time. Chlorophyll and dioxane precipitate in microcrystalline structures, allowing for simple isolation [49].

2.1.7. Coating the ITO electrode with chlorophyll

A method of adsorbing a sensitizer to the oxide layer is by dipping the electrode in a solution of the dye [1]. This is the typical approach and it has been used in many experiments [15,40,52,53]. Concentrations of the sensitizer solution are in the order of 10$^{-5}$ M and incubation times range from 1 to 24 h.

It has been shown that chlorophyll a does not adsorb efficiently on TiO$_2$ surfaces from polar solvents such as ethanol or acetone [22]. This is because of weak interaction between the carbonyl groups and the hydrophilic oxide surface. By choosing a less polar solvent, such as pentane, the adsorption can be increased. It was assumed that the same might hold for ZnO.

2.1.8. Electrolyte

An electrolyte based on I$^-$/I$_3^-$, which is commonly used in DSCs, was chosen for this work [22,53]. Overall, it features acceptable light properties, suitable redox potential and a high reduction rate of oxidized dye, and most importantly very slow kinetics regarding the recombination rate of electrons between the semiconductor (TiO$_2$) and the triiodide [18]. Although the latter study implied the use of TiO$_2$, no major difference was expected for ZnO.

A disadvantage of the I$^-$/I$_3^-$ redox couple is that it is highly corrosive and attacks metals. It has been reported that vapor-deposited Pt, for the purpose of catalytic electrodes in DSCs, was not chemi-
cally stable when used together with an electrolyte containing I$_2$ [54]. Thermally platinized (450 °C, 30 min) TCO glass seems to be stable for long term use though [18,55].

2.1.9. Cathode

Silica plates sputtered with Au were used as counter electrodes in all solar cells. It was assumed that Au instead of Pt would work, but with lower efficiency.

2.2. Characterization

2.2.1. X-ray powder diffraction (XRD)

XRD is a technique that uses the scattering of x-rays to determine the structure of crystalline powders. The monochromatic x-ray beam hits the crystals and scatters in many different directions, and by measuring the angles and intensities it is possible to obtain information about the unit cell and atomic ordering. In a powdered sample, every single crystal rotation is ideally represented. This rotational averaging projects the three-dimensional reciprocal space (that is normally studied in crystallography) onto a single dimension. The relationship between the lattice interplanar spacing, $d_{hkl}$, the diffraction angle $\Theta$, and the wavelength of the x-rays used is given by the Bragg law,

$$2d_{hkl}sin\theta = \lambda.$$  

An X-ray diffractogram is a plot of the observed intensities, $I_{hkl}$, vs. $2\theta$. Because every crystal has a unique diffraction pattern, it is possible to use powder XRD diffractograms as fingerprint identifiers of crystalline phases. From the broadness of the diffraction peaks, the crystal sizes can be estimated.

The size of the particles can be calculated from the FWHM of a peak in a diffractogram using the Debye-Scherrer equation [56],

$$d = \frac{K\lambda}{Bcos\theta'},$$

where $d$ is the crystal size (Å), $K$ is a shape factor (k=0.9), $\lambda$ is the x-ray wavelength (Å), $B$ is the FWHM in radians and $\Theta$ is the half the observed scattering angle [57].
3. Experimental

3.1. Syntheses of nanocrystalline ZnO

3.1.1. Materials

Zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O), ethanol, ethyl acetate, hexane, sodium hydroxide (NaOH), 2-propanol and oleic acid were provided by IFM. Anhydrous zinc acetate (Zn(CH₃COO)₂), tert-butyl phosphonic acid (TBPA), hexadecylamine (HDA, 90%), tetra-methyl ammonium hydroxide (TMAH) and dimethyl sulphoxide (DMSO) were purchased from Sigma-Aldrich. Unless otherwise stated, all substances were of reagent grade.

3.1.2. Preparation

**NaOH (0.02 M) in 2-propanol.** 80 ml of 2-propanol was added to a 100 ml volumetric flask and immersed in a water bath at 65°C. 0.08g NaOH was dissolved in the 2-propanol under vigorous stirring. The heat source was removed and 2-propanol was added up to the mark.

**Oleic acid (0.06 M) in 2-propanol.** 0.4 ml oleic acid was added to 19.6 ml 2-propanol.

**Zn(Ac)₂·2H₂O in DMSO (0.1 M).** 2.5 mmol Zn(Ac)₂·2H₂O was dissolved in 15 ml of DMSO in a 25 ml volumetric flask. Additional DMSO was added up to the mark.

**TMAH in ethanol (0.55 M).** 5.5 mmol TMAH was dissolved in 5 ml of ethanol in a 10 ml volumetric flask. Additional ethanol was added up to the mark.

3.1.3. Method A

This synthesis is based on a method described by Hale et al. [44]. 0.2 mmol Zn(OAc)₂·2H₂O was dissolved in 16 ml 2-propanol under vigorous stirring at 65°C. The solution was diluted with 168 ml cold 2-propanol and chilled to 0°C. 16 ml 0.02M NaOH in 2-propanol at 0°C was added over 1 minute under constant stirring. The suspension was immersed in a water bath at 65°C. After 5 minutes at 65°C the heat source was removed and 5 ml 0.06M oleic acid in 2-propanol was added to stop crystal growth. The precipitate was allowed to fall to the bottom. Most of the solvent was decanted and both ethanol and isopropanol were added. The colloid was centrifuged at 3000 rpm for 2 minutes and washed once again with ethanol and isopropanol.

3.1.4. Method B

This synthesis is based on a method described by Pereira et al. [58]. 8 ml 0.55M TMAH in ethanol was added dropwise to 24 ml of 0.1M Zn(CH₃COO)₂·2H₂O in DMSO. The solution was stirred for 1 hour. 66 ml ethyl acetate was added to precipitate the nanocrystals. Once a sediment layer had formed most of the solvent was carefully discarded. Ethyl acetate and ethanol were added in a 3:1 volume ratio and the mixture was centrifuged at 3000 rpm for 2 minutes. The washing process was repeated and the nanocrystals were stored in ethyl acetate until further use.

3.1.5. Method C – Slow Heating Method

This synthesis is based on a method described by Cozzoli et al. [43] and requires the use of air-free techniques. 7 g of HDA and 0.2 mmol of TBPA were added to a three-way flask. The flask was immersed in an oil bath at 80°C and 1 mmol anhydrous ZnAc₂ was dissolved in the mixture. The contents were degassed under vacuum for 1 hour under vigorous stirring. Nitrogen flow was introduced to
the flask and the reaction vessel was then heated at a rate of 10°C/min to induce decomposition of the ZnAc₂. A temperature of 240°C was maintained for 5 minutes after which the heat source was removed and the flask was rapidly cooled to about 100°C, well above the melting point of HDA. The nanocrystals were extracted by adding ethanol at 50°C and then isolated by centrifugation at 3000 rpm for 2 minutes. The precipitate was washed twice with ethanol and re-dispersed in hexane.

### 3.1.6. Powder for further use

The extracted precipitate was washed repeatedly with appropriate solvent depending on the method of synthesis. All solvent was then evaporated under vacuum or left to dry.

### 3.2. Dyes

#### 3.2.1. Chlorophyll a

Chlorophyll a was purchased from Sigma-Aldrich. 1 mg of chlorophyll a was stored in 0.5 ml n-pentane in the dark at -80 °C. The concentration was 2.2×10⁻³ M.

#### 3.2.2. Extraction of photopigments from spinach

Photopigments were extracted from fresh spinach leaves bought at a local store. The method was based on a concept described previously [50]. Although the authors carried out their experiments at 5°C in total darkness or dim green light, in this work the procedure was carried out at normal room temperature and no special lighting. 10 g of fresh spinach leaves were mixed in a blender with 50 ml of MeOH. The suspension was filtered through a cotton pad and all of the debris was discarded. The solution was centrifuged for 5 minutes at 3000 rpm and the resulting deep green supernatant was mixed with 7 ml of dioxane. About 10 ml of distilled water was added drop-wise under stirring, followed by a 1-hour long sedimentation in an ice box. The top portion was quickly and carefully decanted and the lower thick, dark green mass was centrifuged for 5 min at 5000 rpm. Again the top portion was decanted and pentane was added to the supernatant. This resulted in a phase separation in which the yellow colored part was removed. The remaining green solution was finally centrifuged for 5 min at 5000 rpm and the green core was mixed with a very small amount of pentane and stored at -80°C in the dark. The extracted photopigments were characterized by absorbance measurements.

### 3.3. Deposition of ZnO onto TCO glass

A voltmeter was used to identify the conductive side of the TCO glass. It was cleaned with ethanol and acetone, followed by drying in air. NC ZnO powder was grinded with a glass rod while a few drops of acetic acid (pH = 3) were added to create a paste [42,46]. A rectangular mold, roughly 5 x 5 mm in size, was created on the surface by masking off the edges with tape. The paste was pressed into the mold, left to dry for a couple of minutes after which the tape was removed. This resulted in a thin film of ZnO and clear areas to allow for electric contact. Other deposition techniques tried included direct application of as-synthesized material immediately after centrifugation, replacing acetic acid by ethyl acetate and casting with ethanol as solvent.

### 3.4. Sensitization of anode with chlorophyll

The following procedure was carried out swiftly in standard laboratory atmosphere and lightning. The ZnO coated ITO glass was annealed in an oven at 400 °C for 30 minutes after which it was al-
allowed to cool down to room temperature. 5-10 µl 2.2 mM chlorophyll in n-pentane and 5 µl ethanol were added from the same micropipette to 1 ml n-pentane. The electrode was put in a small glass container and covered by the chlorophyll solution (1.1-2.2×10^{-5} M). It was stored in an air-tight seal in the dark for 1-4 hours. Once sensitized, the electrode was dried in air and immediately assembled to the final device. The sensitization process resulted in a distinct green color of the electrode.

3.5. Electrolyte

The redox electrolyte consisted of 0.5 M KI and 40 mM I\(_2\) in 80% ethylene carbonate and 20% propylene carbonate v/v [52]. The ethylene carbonate was liquefied in a water bath at 50°C before use. For practical reasons a total of 100 ml was made, however, only very small amounts (less than 0.1 ml) are required to fill the micrometer sized gap between the electrodes. The desired I\(_3^-\) ion is a result of the equilibrium I\(_2 + \Gamma \rightleftharpoons I_3^-\) [18].

3.6. Assembly of anode and cathode

A sensitized anode was clamped together tightly to a counter-electrode made of sputtered gold using a single alligator clip. It is of great importance that the pressure is even so the distance between the two electrodes is the same. The two electrodes were aligned to allow an overlap on each side for electrical contact. A few drops of electrolyte were placed on the edges between the two electrodes, which resulted in wetting of the micrometer-sized interstitial space by capillary forces. Any excess electrolyte was wiped off. If the cell voltage under illumination was zero, the pressure point of the clip was carefully altered to avoid short-circuiting.

3.7. Light source

The primary light source used for illumination of the cells was a standard 60 W tungsten light bulb with a reflector dish kept at 30 cm from the surface of the anode. With a similar setup (35 W light bulb at 15 cm), a light intensity of 40 µW/cm\(^2\) was used by Liu et al. [42]. If the light intensity is projected onto a circular area, then area is proportional to the square of the distance to the lamp. Thus, if the distance is doubled the light intensity per surface area unit is reduced by a factor of four. The light intensity was estimated to be 20 µW/cm\(^2\) at the electrode:

\[
\frac{35 \text{ W}}{k(15 \text{ cm})^2} = 40 \mu\text{W/cm}^2
\]

\[
k = \frac{35}{40 \times 10^{-6} \times 15^2} = 3890
\]

\[
\frac{60 \text{ W}}{k(30 \text{ cm})^2} = 17.1 \mu\text{W/cm}^2 \approx 20 \mu\text{W/cm}^2
\]
4. Results

4.1. Characterization of NC ZnO using XRD

Products of the three different syntheses were measured with a Philips PW 1820 powder diffractometer using CuKα radiation (λ = 1.5418 Å). All diffractograms were recorded using a scan mode of Θ/2Θ, a current of 40 mA, a voltage of 40 kV, a divergence slit of ½° and a receiving slit of 0.2°. The samples were placed on glass substrates by repeatedly dripping a solution of ZnO and letting the solvent evaporate or by pressing a powder form of the sample onto an adhesive tape attached to the glass.

Figure 11. XRD diffractograms of the different methods used to synthesize nanocrystalline ZnO.

All diffractograms in Figure 11 show the characteristic wurtzite phase of ZnO [43,53]. By using the Debye-Scherrer equation on the (100) peak [58], the average particle size was estimated to be 5 nm. One sample was fired at 400°C for 30 minutes prior to XRD measurement, resulting in an increase of the average particle size to 16 nm.
4.2. Spectrophotometric analysis of photopigments

Measurements of the absorbance of the photopigments were carried out using a Hitachi U-2010 UV-Vis spectrophotometer. The results indicate that chlorophyll a was present in both of the samples with distinct maxima at 440 and 660 nm (Figure 12). The additional peak at 460 nm and the slight broadening at 660 nm suggested the extract also contained chlorophyll b and, possibly, carotenoids. By comparing the absorbance and using the Lambert-Beer law, the purified extract from spinach had an estimated concentration of $10^{-3}$ M. This information was used further on when coating the solar cells with dye.

![Absorption spectra of chlorophyll in ethanol](image)

Figure 12. This shows the absorption spectra of chlorophyll a (lower line) and an extract of pigments from spinach (upper line). The solvent used was ethanol.
4.3. Photoelectric results of the DSCs

Voltage was measured using a digital voltmeter, while current was measured as the voltage-drop over a known resistance [52]. Short-circuit currents were measured using an ammeter. Some data are missing because initially it was problematic to measure the small currents involved.

All of the DSCs responded rapidly to any changes in light intensity, and both the open-circuit voltage ($V_{oc}$) and short circuit current density ($J_{sc}$) were affected. The reported values in Table 1 were stable under standard illumination, but higher values could be reached by increasing the light intensity. In particular, device G was pushed to $V_{oc}$ 188 mV and $J_{sc}$ 4.04 µA/cm$^2$, but these values were not stable and dropped at rate seemingly proportional to the intensity. Interestingly, the same values could be achieved again if the cell was placed in the dark for some time. The effect was observed for all the cells tested.

The sensitized cells responded even to very weak light intensities with an output of a few mV caused by ambient (diffuse) lightning. No voltage our current could be detected when the DSCs were placed in total darkness. It was possible to revive cells stored in the dark for several days by reapplying electrolyte, but such cells did not regain their initial electric potential.

<table>
<thead>
<tr>
<th>ID</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (µA/cm$^2$)</th>
<th>FF (%)</th>
<th>η (%)</th>
<th>Area (cm$^2$)</th>
<th>ZnO</th>
<th>Annealed</th>
<th>Deposition</th>
<th>Sensitizer</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Yes</td>
<td>See explanation*</td>
<td>Chl a</td>
<td>Died after realignment</td>
</tr>
<tr>
<td>B</td>
<td>70</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Yes</td>
<td>Paste</td>
<td>Chl a</td>
<td>Gold dissolved</td>
</tr>
<tr>
<td>C</td>
<td>250?</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Yes</td>
<td>See explanation **</td>
<td>Chl a</td>
<td>Died due to accident</td>
</tr>
<tr>
<td>D</td>
<td>66</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Yes</td>
<td>See explanation ***</td>
<td>Chl a</td>
<td>Gold dissolved, dark reactions observed</td>
</tr>
<tr>
<td>E</td>
<td>7.5</td>
<td>0.4</td>
<td>36.5</td>
<td>0.005</td>
<td>0.70</td>
<td>B</td>
<td>Yes</td>
<td>Paste</td>
<td>Chl a</td>
<td>Very responsive</td>
</tr>
<tr>
<td>F</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.50</td>
<td>B</td>
<td>Yes</td>
<td>Paste</td>
<td>None</td>
<td>Control</td>
</tr>
<tr>
<td>G</td>
<td>64.5</td>
<td>2.9</td>
<td>22.7</td>
<td>0.21</td>
<td>0.50</td>
<td>B</td>
<td>Yes</td>
<td>Paste</td>
<td>Spinach</td>
<td>Strong green color</td>
</tr>
<tr>
<td>H</td>
<td>46.6</td>
<td>2.86</td>
<td>22.7</td>
<td>0.15</td>
<td>0.30</td>
<td>B</td>
<td>Yes</td>
<td>Paste</td>
<td>Chl a</td>
<td>Strong green color</td>
</tr>
<tr>
<td>I</td>
<td>0.7</td>
<td>0.25</td>
<td>36.2</td>
<td>0.0003</td>
<td>0.20</td>
<td>B</td>
<td>No</td>
<td>Paste</td>
<td>Chl a</td>
<td>Slightly weaker green color than G and H</td>
</tr>
</tbody>
</table>

$V_{oc}$ is the open-circuit voltage, $J_{sc}$ is the short circuit current density, FF is the fill factor and η is the light-to-electric power conversion efficiency. * The ZnO was applied directly after centrifugation (see Experimental chapter). ** Paste with ethyl acetate as solvent. *** Casting of a colloid solution with ethanol as solvent.

The best devices fully measured were G and H. These thin films, along with I, were sensitized with twice the concentration of photopigments compared to the other ones, resulting in a very distinct green color. The sensitization with pigments from spinach (G) increased the efficiency by a 40 % compared to that of pure chlorophyll a (H). The thin film I was not thermally treated and the cell showed a much lower response, with an efficiency about 700 times lower than the highest achieved in this study. High stability and very fast response times were noted for device E, and a stability test was performed (Figure 13). On the other hand it featured lower overall output compared to the similar cell H. A reference cell without any sensitizing dye (F) showed no measurable photoactivity.

Chemical instability was detected on cell D as the Au electrode dissolved. A negative potential of -27 mV was noted under dark conditions. This potential could be overcome by illuminating the device, but eventually the adverse reaction lead to a complete malfunction with major loss of the Au surface. Cell B also had problems with cathodic degradation, but in that case the cell promptly died and no dark reactions were noted. J-V curves for E, G, H and I can be seen in Figure 14 - Figure 17. A higher fill factor seemed to be associated with lower current density.
Figure 13. A stability test was run with assumed constant illumination for 20 minutes and the current density dropped by 2\%.
The light was switched on at $t = 0$ s, and the current density was stable in $t < 3$ s. The DSC was made of NC ZnO synthesized according to method B (See 3.1.4) sensitized by chlorophyll a.
Figure 14. J-V curve of device E. The sensitizer was chlorophyll a. The power density peaked at a voltage of 3.7 mV. The external resistance was varied and the current density dropped as the resistance increased.
Figure 15. J-V curve of device G. The sensitizer was photopigments from spinach. The power density peaked at a voltage of 33.5 mV.

Figure 16. J-V curve of device H. The sensitizer was chlorophyll a. The power density peaked at a voltage of 21.6 mV.
Figure 17. J-V curve of device I. The sensitizer was chlorophyll a, but the thin film was not thermally treated. The power density peaked at a voltage of 0.31 mV.
5. Discussion

5.1. Performance

The current densities were of the same level as reported by the authors of the paper used as a starting point in this project [1,53], but the light intensities used by them are unknown. For similar DSC constructions based on chlorophyll and TiO₂ [42], the open-circuit voltages and current densities were about 5-10 times lower in this study. As a consequence, the overall efficiencies were low and can probably not be explained by a single factor, but rather by a combination of issues. It is however very interesting to see that the DSC sensitized with pigments from spinach outperformed the cell sensitized by pure chlorophyll a by 40% in terms of efficiency. Although improvements using mixtures of chlorophyll a and carotenoids have been reported [1,42], it was surprising to see this result considering the minimal purification of the pigments that were made.

As will be discussed later, the ZnO films were probably thicker than desired. That would lead to higher rates of recombination and contribute to the low efficiencies. A thick layer would also pose more restrictions on the diffusion processes. The photovoltaic performance dropping under high intensities can be explained by mass transfer limitations of the electrolyte. Since the cells were able to recover their initial characteristics after some time in darkness, it must be concluded they were not irreversibly degraded. If the reductive electrolytic species near the dye become depleted, the oxidized dye can only receive electrons through recombination reactions. As this will reduce the concentration of electrons in the conduction band of the semiconductor, voltage must as a consequence drop. The stable operation voltage and current are thus established when the overall rate of injection into the semiconductor can be matched by the diffusion of holes in the electrolyte. It has been found that increasing the temperature affects the fill factor positively for high viscosity electrolytes containing propylene carbonate [21], with the obvious reason being improved mass transfer. The lower fill factors in Table 1 are associated with higher current densities, suggesting that the cells are indeed limited by diffusion.

Another contributing factor is the Au cathode. It has been shown theoretically that cathodes made of less catalytic materials than Pt will render large potential losses due the increased amount of energy needed to drive the reduction of I³⁻ [19]. Under open-circuit conditions no current flows, so the open-circuit voltage should remain unaffected, but the fill factor will drop.

The poor photovoltaic properties of the non-sintered DSC (device I) are not surprising. Without the thermal treatment the layer is likely to be much less porous and a lot of organic residue should remain on the particles. Although the ZnO crystals were nanosized, the layer may have had a closer resemblance to that of a compact bulk, considering the efficiency was lowered by a magnitude which corresponds to the difference in surface area between a flat and nanostructured surface. The same reasoning can be applied to device A, which had a ZnO paste applied to the TCO glass right after a centrifugation step. The particles in the paste were probably aggregated into larger clusters with remains of the organic solvents accounting for the viscosity.

The thin film of device C was created using a different solvent (ethyl acetate), and this device showed remarkably high open-circuit voltage compared to the other cells. Unfortunately the clamps holding the electrodes together fell off after a few seconds, and no further measurements could be made. The question mark in Table 1 indicates this value may not be accurate for longer exposures, but this can certainly be taken as an indication that ethyl acetate may provide good performance as a deposition solvent for hydrolytically prepared NC ZnO.

If device E and H are compared, they feature the same construction properties but still differ greatly in terms of performance. The reasons for this might be that they were not constructed at the same
time, they did not use the same batch of hydrolytic ZnO and the application procedure seemed to render slightly different layers. Naturally this aspect must be considered for all the other DSCs, but at least G/H/I were created from the same batch and treated in a very consistent manner.

Nothing can be said about how the different nanosyntheses affect the solar cells’ output from the data gathered, but the different methods and their implications are discussed in 5.3.

5.2. Chlorophyll

The extraction of chlorophyll from spinach was a simple method to get photoactive pigments of acceptable purity. The process is fairly straightforward but also provides the opportunity to stop at an early stage to get a broader collection of pigments, such as carotenoids. In this case, most of them were likely removed due to the addition of pentane which resulted in a two-phase system where the yellow part was discarded. If chlorophyll a of higher purity is required, column chromatography can be used [51]. Further experiments regarding the purification of chlorophyll from spinach has been done by Khalyfa et al. [49], including ion-exchange chromatography, size-exclusion chromatography and HPLC.

It was probably a wise choice to store the photopigments in the same environment as described by Petrella et al. [1]. The photoactive properties were conserved throughout the entire project. Although they were stored at -80 °C, it should be noted that pentane has a melting point of -130 °C. The manufacturer stated a storage temperature of -20 °C, which is probably sufficient though.

The solubility of chlorophyll in pentane seemed to be low, so during experiments small additions of ethanol were made to facilitate handling, especially when working with pipettes where the chlorophyll seemed to get stuck.

5.3. Nanosynthesis of ZnO

All of the three methods used yielded nanocrystals of ZnO, as confirmed by XRD. They do differ a lot though when it comes to ease of use and how much product is synthesized.

Method A resulted in a small amount of ZnO in large amounts of solvent, which makes it a less practical choice. It is not easily scalable. The particle size can be varied by choosing how long the suspension is immersed in the water bath. A time of 5 minutes was chosen resulting in particles of about 4 nm in size. This was estimated using cut-off wavelengths from an absorption spectra given by Hale et al. [44] and the effective-mass model [59]. A MATLAB script was constructed to facilitate calculations and it is given in Appendix A.

Method B was simple, reproducible and fast, and it also comes out on top as the most scalable. By varying the ratio of base to metal cations, the size of the particles can be adjusted [58].

Method C was the most complicated synthesis of the three tested. It required high temperatures and vacuum, which led to a more sophisticated laboratory setup. This method was the only non-hydrolytic approach tested. Although not proven in this project, the NCs synthesized by this method have been shown to provide a higher photocurrent than hydrolytic ZnO NCs [38]. It is stated this is because hydrolytic ZnO NCs have acetate- and hydroxyl groups at their surfaces which negatively affect the charge transfer. Non-hydrolytic synthesis does not result in the same problematic surface chemistry. This difference was first noted by me while experimenting. Hydrolytic NCs dissolved completely into a colloid in ethanol, where as the non-hydrolytic NCs were precipitated by ethanol. Despite not knowing exactly what was going on, the surfaces were likely covered with some organic layer.
Regardless of the method used, centrifugation can be used to precipitate the ZnO crystals. Typically higher rotation speeds provided a better separation, but the chosen speeds were sufficient.

5.4. Deposition of ZnO

Although the concept described works, the small amounts of synthesized ZnO is not very practical to handle using the paste method. When creating a paste of ZnO, it tends to stick to the equipment used. I must recommend scaling up the synthesis to get larger quantities of NC oxide.

A major flaw was that the thickness of any layer was never verified. It remains unknown if the thin films were of the desired size and structure. This could be studied using TEM or SEM. Although XRD verified the size of the nanocrystals, aggregation does occur and it may reduce the performance of the photovoltaic device. It has been reported that TiO2 films having a thickness less than 10 µm are transparent [52] or possibly translucent [22]. Most of the films created in this project were opaque or lightly translucent, and this gives me reason to believe most of them were thicker than desired. A deposition method which can be controlled systematically or mechanically, and depend less upon the person, would give more control.

5.5. Annealing

Annealing was shown to improve performance dramatically, so this step should always be included. Further investigation is necessary to determine optimum values. It has been reported that solar cells constructed with hydrolytical ZnO may benefit from a lower temperature of 150 °C, but non-hydrolytical ZnO yielded better performance if treated at 350 °C [38]. The significance of this difference was not shown and the lower temperature was not tested in this project. Although the different surface chemistry likely accounts for this effect, I believe that it also impacts how nucleation occurs and that the size distributions of the synthesized NCs not necessarily correlate well.

5.6. Degradation

Some of the devices exhibited chemical instability on the counter electrode. It is known that the chosen redox couple is highly corrosive, especially in the presence of oxygen and water [60]. As the cells were not sealed, it is likely this is the cause of the gold going into solution. One of the problematic devices also generated a reverse potential (low mV range), suggesting one or more secondary redox processes were present in those systems. The reduction potentials of gold and iodine in the given electrolyte are unknown to me, but these problems may have been initiated by mistake. By putting the voltmeter in resistance mode, a forced potential is introduced between the nodes, and it is not impossible that this assisted some unknown redox reaction. For whatever reason the gold was dissolved, bare silica was presented and this may also have contributed to the adverse reactions noted for device D.

Considering the negative effect storage had on the DSCs, it would probably have been better to seal them with glue. Even if new electrolyte was applied, the performance was lower. The most obvious reason for this would be degradation of the chlorophyll dye by oxygen in the atmosphere [22].

5.7. Statistics

The results obtained in this study lack statistical significance, but many of the observations have been strengthened by theoretical reasoning and references. I believe some of them are strong enough to justify conclusions, where others can only serve as indications.
6. Conclusions

Photovoltaic cells based on semiconducting NC ZnO using chlorophyll as a sensitizer have been shown to work, and the devices remain stable for hours of continuous use. Although the obtained voltages and currents in this project were low, further studies of how the molecules of photosynthesis convert light into electrons may give rise to new ideas on how to improve DSCs. Not only is it important to cover the largest possible portion of the visible light spectra, improving the charge transport in every step of the process is essential.

Chlorophyll of reasonably good quality and purity can be extracted from spinach using simple solvents. The method can provide adequate amounts of photoactive pigments at an affordable cost and time. Commercially available high-grade chlorophyll a is more expensive. It was shown that isolated photopigments from spinach yielded better photovoltaic performance than pure chlorophyll a, and that there is potential use for these mixtures in DSCs.

This study also showed that Au can be used as material for counter electrodes. Although no comparison between Au and Pt cathodes was made, it is likely that the latter would have had a beneficial effect on the performance due to its catalytic abilities. Unfortunately, both Au and Pt are expensive metals and for large scale applications cheaper substitutes must be developed. Further, chemical instability between Au plates and the iodine-based electrolyte may be a problem too. Au cathodes is not a viable alternative for high quality solar cells.

The heat-treatment procedure turned out to be crucial for the output of the cell. In fact, growth of the nanocrystals occur, resulting in an interconnected network, and the increase in particle size can be estimated with good accuracy by XRD.

In order to improve the long term stability, devices should be sealed once wetted with electrolyte and not taken apart. If not sealed, fresh electrolyte can be applied to make the DSC regain its function, but the performance is likely to be less good than initially.

The approaches used in this project can serve as starting points for studying the properties of DSCs, but as shown, the previously reported efficiencies are not easily attained.
7. Future work

I feel that more attention is required to other deposition techniques and to study the morphology of the resulting thin films. At the same time, if your primary interest is biology, the process of extracting photopigments from different plants may also be investigated. The method used in this project can be repeated to improve purity or it can be halted at an early stage to include lots of different molecules, such as carotenoids and phycobilins. Different sensitizers are also of interest, perhaps in conjunction with others, to improve the absorption spectrum. Another idea is to heat a dye-covered electrode, manufactured the standard way, at low temperature. This would perhaps allow for even better distribution and absorption of the dye without damaging it, thus possibly increasing the efficiency of the solar cell.

The nanosynthesis can also be studied more extensively, and may include altering concentrations, reactions times and temperatures to get NCs of different size and distribution. Any change at the nanolevel will definitely affect the final photovoltaic properties. Using the non-hydrolytic approach as a standard should, according to theory and previous reports, give promising results.

The most important thing to point out here is to study only one property at a time. It has been shown that several factors affect the final outcome, and without strong consistency and reproducibility, the end result may not prove or disprove any hypothesis. There are many different fields involved in the area of DSCs, ranging from inorganic and organic chemistry, biotechnology, physical chemistry, electrochemistry to quantum physics, that in the end, personal preference may decide what comes next.

If I were to suggest hypothetic improvements, they would include non-hydrolytic NCs of slightly larger size, spin-coating, a Pt catalyst, an electrolyte with lower viscosity, and sealing between the electrodes.
References


Appendix A

MATLAB script to calculate cut-off wavelength

```matlab
function [ l_c ] = emm_lc(r)
% emm_lc(r) return the desired cut-off wavelength
% input: r [nm]
% effective mass model
% Brus, L.E., Nanostructured Materials 1, 71 (1992)
% Hale, S., Growth Kinetics and Modeling of ZnO Nanoparticles

r = r/10^9;

E_gbulk = 5.4470*10^-19;     % bulk band gap for ZnO
h = 6.6261*10^-34;           % Planck's constant
h_bar = h/(2*pi);            % reduced Planck's constant
m_e_e = 0.24;                 % effective mass of electrons
m_h_e = 0.45;                 % effective mass of holes
eps = 3.7;                    % relative permittivity
eps_0 = 8.8540*10^-12;       % permittivity of free space
c = 299792458;               % speed of light
m_0 = 9.1090*10^-31;         % free electron mass
e = 1.602*10^-19;            % electron charge

E_g = E_gbulk + (h_bar^2*pi^2)/(2*r^2)*(1/(m_e_e*m_0) + 1/(m_e_e*m_0)) - 1.8*e^2/(4*pi*eps*eps_0*r) - 0.124*e^4/(h^2*(4*pi*eps*eps_0)^2)*(1/(m_e_e*m_0)+1/(m_h_e*m_0))^-1;
l_c = h*c/E_g * 10^9;
end
```