

Teil 1 Allgemeines

I Organisatorisches

I.1 Impfungen

Ein wichtiger Schritt in der Reisevorbereitung sind die Impfungen. So nutzte ich eine Beratungsstunde beim Tropeninstitut in München um mich über notwendige Neuimpfungen bzw. Auffrischungen zu informieren. Zusammen mit dem beratenden Arzt erstellten wir einen Plan ab den bisher bestehenden Impfungen: Hepatitis A und B, Gelbfieber Typhus und Tollwut.

Es ist hierbei wichtig zu erwähnen, dass sich einige Impfungen über mehrere Monate erstrecken und somit ausreichend Zeit im Voraus eingeplant werden muss.

I.2 Visum

Um in Kolumbien einreisen zu können braucht jeder ein Einreisevisum. Ein Visum ist jedoch recht unkompliziert zu bekommen. Außer der "Carta de Aceptación" des Praktikums benötigte ich vorab keine weiteren universitären Dokumente. Direkt bei der Einreise am Flughafen erhielt ich problemlos ein 90 –tägiges Touristenvisum. Da das Praktikum nicht länger als diese 90 Tage dauerte, musste ich dieses auch nicht verlängern. Die Universität informiert dennoch regelmäßig über notwendige Visaverlängerung. Das erstmalige Touristenvisum war kostenlos, eine Verlängerung würde ca. € 25 kosten.

I.3 Wohnen

Bei der Wohnungssuche wurde ich schon vorab von der Universität unterstützt. In einem Informationsformular ließen sich Präferenzen zu Gastfamilien oder Wohngemeinschaft mit anderen Austauschstudenten angeben.

Da ich vorab erst ein Anfängerkurs in Spanisch belegt hatte und ich das Leben innerhalb einer kolumbianischen Familie kennenlernen wollte, entschied ich mich für eine Gastfamilie. Trotz meiner späten Ankunft in Barranquilla wurde ich vom Flughafen abgeholt. Bei meiner unglaublich netten Gastfamilie erwartete mich dann "spät" nachts ein herzlicher Empfang.

Ich teilte ein Doppelzimmer mit einem mexikanischen Austauschstudent und zahlte inklusive Verpflegung € 266 im Monat. An die Zeit innerhalb der Gastfamilie erinnere ich mich gerne zurück.

Über meine Arbeitskollegen der Universität lernte ich nach kurzer Zeit zahlreiche kolumbianische Studenten kennen. Innerhalb des Freundeskreises unternahmen wir viel zusammen, so dass ich nach der Hälfte der Praktikumszeit bei meinen kolumbianischen Freunden einzog. Der dortige Stadtteil war weniger abgesichert, jedoch voller einheimischer Studenten und mit einem kolumbianischem Flair. Dementsprechend bezahlte ich in dem Vierbettzimmer ohne Verpflegung € 94 im Monat. Beide Wohnsituationen waren zwei komplett verschiedene und einzigartige Erfahrungen. Ich bin froh beide erlebt zu haben.

II Leben in Kolumbien

II.1 Universidad del Norte

Die Universidad del Norte ist eine Privatuniversität im amerikanischen Stil. Das Gelände wird von einem Sicherheitspersonal abgesichert und lässt sich nur mit Ausweis betreten. Die universitären Einrichtungen sind im landesweiten Vergleich exzellent :

Auf dem Campus gibt es verschiedenste Restaurant- und Imbissmöglichkeiten: Verteilt zwischen Hörsälen, Laboratorien und Bürogebäuden findet man kolumbianisches, mexikanisches, arabisches, amerikanisches oder auch italienisches Essen. Ein Mittagsmenü kostet zwischen zwei und fünf Euro.

Weiter verfügt die Universität über ein eigenes Krankenhaus. Grundleistungen bei Allgemein Ärzten, Zahnärzten oder Physiotherapeuten sind für alle Angestellten und Studenten kostenlos. An gewissen Wochentagen kommen Spezialisten auf das Unigelände. Diese Untersuchungen werden nicht von der Universität oder des Staates übernommen und müssen vor der Behandlung des Patienten bezahlt werden.

Das internationale Büro ist ganztägig geöffnet und unterstützt bei jeglichen organisatorischen Angelegenheiten. Es bietet preiswerte Exkursionen und Tagesausflüge in Museen und zu landesweiten Attraktionen an. Zusammen mit dem internationalen Büro organisieren wir, Austauschstudenten, eine internationale Studentenmesse und informieren unsere kolumbianischen Kommilitonen über Austauschprogramme der Partneruniversitäten. Weiter versendet das internationale Büro per Email eine Art Wochenzeitung zu Sonderattraktionen innerhalb der Universität oder zu anderen kulturellen Events in Barranquilla.

Das Sprachzentrum bietet allen Austauschstudenten einen vier wochenstündigen Spanischkurs an. Eine Niveaueinstufung und Kurszuteilung erfolgte schon aus Deutschland anhand eines Onlinetests. Ein Kurswechsel innerhalb der ersten Semesterwoche wäre jedoch kein Problem.

Der Unterricht gestaltete sich sehr interaktiv. In Kleingruppen stand neben Vokabular vor allem Konversation im Fokus. Im Kontakt mit einheimischen Studenten lernte ich wichtige Redewendungen kennen und verbesserte mich weiter.

Auch Sport- und Kulturangebote der Universität war sehr breit aufgestellt: Da ich erst in der zweiten Semesterwoche mein Praktikum begann, versäumte ich zunächst die offizielle Anmeldung. Nach kurzem Nachfragen konnte ich mich jedoch nachträglich für meine Wunschaktivitäten anmelden. Ich belegte drei verschiedene Tanzkurse (kolumbianischer, arabischer und brasilianischer Volkstanz) und war Teil des universitären Schwimmteams. Über das Kulturangebot lernte ich viele Studenten kennen.

II.2 Praktikum

Alle Probenpräparationen absolvierte ich im Labor des Departements für angewandte Physik. Die Räumlichkeiten sind exzellent ausgestattet und ermöglichen innovative Forschung. Während meiner Untersuchungen besprach ich meine Experimente zunächst mit meinem betreuenden Professor vor, um sie anschließend selbstständig durchzuführen. Bei offenen Fragen konnte ich mich an andere Laboranten bzw. an Herrn Doc. Rada direkt wenden. Die Dokumentation, Auswertung und Diskussion meiner Ergebnisse präsentierte ich in einem wissenschaftlichen Protokoll. Ein Auszug aus diesem ist im fachlichen Teil aufgeführt.

II.3 Land und Leute: Barranquilla

Direkt am karibischen Meer liegend ist das Klima in Barranquilla tropisch heiß. Im September und Oktober ist Regenzeit. Dies zeichnete sich in starken Regenfällen aus, wobei sich Straßen in Flüsse verwandeln. Scheint die Sonne bei 35 Grad und hoher Luftfeuchtigkeit sind die universitären Klimaanlagen Fluch und Segen zugleich: Sie ermöglichten einerseits ein angenehmes Arbeitsklima andererseits erkältete ich mich durch den ständigen Temperaturwechsel mehrmals.

Die Costeños, wie man die Kolumbianer an der Karibikküste bezeichnet, leben eine sehr offene und herzliche Kultur. Sie zeichnet Freundlichkeit und Lebensfreude aus und treten gerne in Kontakt mit Ausländern. Ein wichtiger Lebensteil in Barranquilla ist der Karneval im Februar. Ganzjährig finden Vorbereitungen und Proben innerhalb der Stadt statt. Die Volkstänze werden von klein auf gelehrt und erlernt. Wer nicht tanzt, ist kein Costeño. Während meiner Zeit in Kolumbien konnte ich zahlreiche neue Bekanntschaften und Freunde finden.

Barranquilla ist außerhalb der Karnevalszeit nicht gerade eine touristische Stadt: Ich lernte ich dennoch das Lebensgefühl der Stadt sehr zu schätzen. Schließlich konnte ich durch meine kolumbianischen Freunde viele kulturelle Events abseits von Tourismuszentren kennen lernen. Für Wochenendausflüge in den Nationalpark Sierra Nevada oder Tayrona, nach Minca, Santa Marta oder Cartagena ist Barranquilla stets ein idealer Ausgangspunkt.

Das Thema Sicherheit ist in Kolumbien immer wieder von Bedeutung:

Die Sicherheitslage hat sich in Kolumbien in den letzten Jahren stark verbessert. Gerade zum Zeitpunkt meines Aufenthaltes fand jedoch ein umstrittenes Referendum zum Friedensvertrag zwischen der FARK (Rebellen) und der Regierung statt. Politisch höchst interessant wurde es mit einer knappen Mehrheit abgelehnt. In den internationalen Medien verbreitete sich in der Folge eine Ungewissheit zur nationalen Sicherheitslage aus. Ich selbst konnte nach dem Referendum keinerlei Veränderungen im alltäglichen Leben wahrnehmen.

Die Universität, wie auch meine beiden Unterkünfte, liegen im nördlichen, sicheren Stadtteil. Das Zentrum und den Süden sollte man ab späten Nachmittag meiden. Busse fahren überall hin und verkehren tagesüber bis ca. 21:00. Für spätere Uhrzeiten, ist die etwas teurere Taxifahrt die sichere Option.

Die Orientierung in Barranquilla wird durch ein gerastertes Straßennetz in carrera und calle sehr erleichtert. Ein Basiswissen in Spanisch ist sehr empfehlenswert, da man außerhalb der Universität nicht auf große Englisch Kenntnisse trifft. Dennoch kommt man meist mit wenig Vokabular und viel Engagement ziemlich gut zum Ziel.

Die kolumbianische Kultur ist wahrlich sehr hilfsbereit.

Teil 2 Fachliches – Dye-Sensitized Solar Cells

Table of Contents

Abstract	5
1 Introduction	6
2 Dye-Sensitized Solar Cells	7
2.1 Operational principles	7
2.2 Parameters	8
2.2.1 Open circuit voltage (V_{oc}) and Short circuit current (I_{sc})	8
2.2.2 Incident Photon to Current Conversion Efficiency (IPCE)	8
2.2.3 Current-Voltage (I-V) characteristics	9
3 Preparation and Measurement	11
3.1 Transparent and conductive oxide substrate (TCO)	11
3.2 TiO_2	11
3.3 The natural dyes	13
3.3.1 Achioté	13
3.3.2 Agraz	13
3.3.3 Corozo	13
3.3.4 Mora	13
3.3.5 Remolacha	13
3.4 Platinum coated cathode	14
3.5 Assembling the Solar Cells	14
3.6 Measurement	15
5 Resumé	16
References	18

Abstract

The Caribbean Coast holds a high potential for solar energy. So far the silicon-dominated solar industry mostly sells expensive solar power plants, making it difficult for Colombia to move towards cleaner energy production. The rising Dye-Sensitized Solar Cells (DSSC) hold a profound alternative.

They offer low-cost fabrication and good environment aspects. In contrast to traditional silicon-based solar cells, the semiconductor is solely used for charge transport whereas the photoelectrons are provided from a separate photosensitive dye. In this study, native dyes were extracted from five native Caribbean fruits and plants: Achioté, Agraz, Corozo, Mora and Remolacha.

The objective of this study was to analyse and optimize the DSSCs' performance depending on their preparation and lighting condition. The dye type unfolded as an important distinction determining the cell's performance potential. Top values originated from an Achioté DSSC achieving under sunlight $\eta = 0.21\%$ and a fill factor $FF = 56.2\%$.

When measured under a halogen lamp, the efficiencies averaged about half of the sunlight values. Top-performers, dyes ranked by efficiency, scored as the following: Achioté 0.0733%, Mora 0.0151%, Corozo 0.0148%, Agraz 0.0082% and Remolacha 0.0005%. The impact of different semiconductor surfaces and power inputs was to be examined. In the following different methods surveying the DSSC's longevity were developed and applied yielding optimizations. Recommendations on further improvements completed the investigation.

The DAAD RISE scholarship foundation enabled this research project, carried out at the Universidad del Norte in Barranquilla, Colombia.

1 Introduction

In sustainable civilisation energy supply sourced in renewable resources is fundamental. Solar energy offers a huge potential to manage this global demand: Being a decentralized and unlimited natural resource, the amount of energy reaching the surface of the earth in one hour $4.3 * 10^{20} J$ is more than all energy consumed by humans in an entire year $4.1 * 10^{20} J$. [1]

The sun emits light in a broad spectrum of wavelengths, reaching from the ultraviolet to the infrared. As the light is travelling through the atmosphere, various light sections are absorbed and do not reach earth's surface. In addition to this total absorption, about 15% of the sunlight will be scattered by molecules and particles before coming to earth. This is referred to as diffuse light, whose ratio increases in higher latitudes and covered sky conditions. For high solar-to-electrical energy conversion efficiencies the absorption spectra of solar cells has to be adapted to the characteristic sunlight.

The so far dominant and primarily operating solar cells have been Silicon-based, making them complex and costly in production. Dye-Sensitized Solar Cells (DSSC) are amongst the next generation of solar cells: They promise the prospect of low-cost production and show enhanced performance under diffuse light conditions, when compared to other solar cell technologies. Environmentally beneficial DSSCs imply design opportunities in their shape, colour and transparency. This key concept of "diversity", researching thousand of different dyes yields DSSDs' greatest capacity for future improvements.

Basic characteristics and conceptual models were developed by O'Regan and Grätzel in 1991. The following years the DSSCs' efficiencies have continued to increase, with a confirmed record of 14%. Based on previous research done at the Physics department of the Universidad del Norte in Barranquilla, the aim of this study was to build, test and optimize DSSCs out of Colombian native fruits and plants. [2, 3]

2 Dye-Sensitized Solar Cells

2.1 Operational principles

The DSSCs are based on a transparent conducting glass electrode, which is coated with a nanocrystalline semiconductor TiO_2 . Dye molecules are attached to semiconductor's surface and an electrolyte containing a reduction-oxidation couple was injected into the DSSCs. At the illumination, the cell produces voltage over and current through an external load connected to the electrodes.

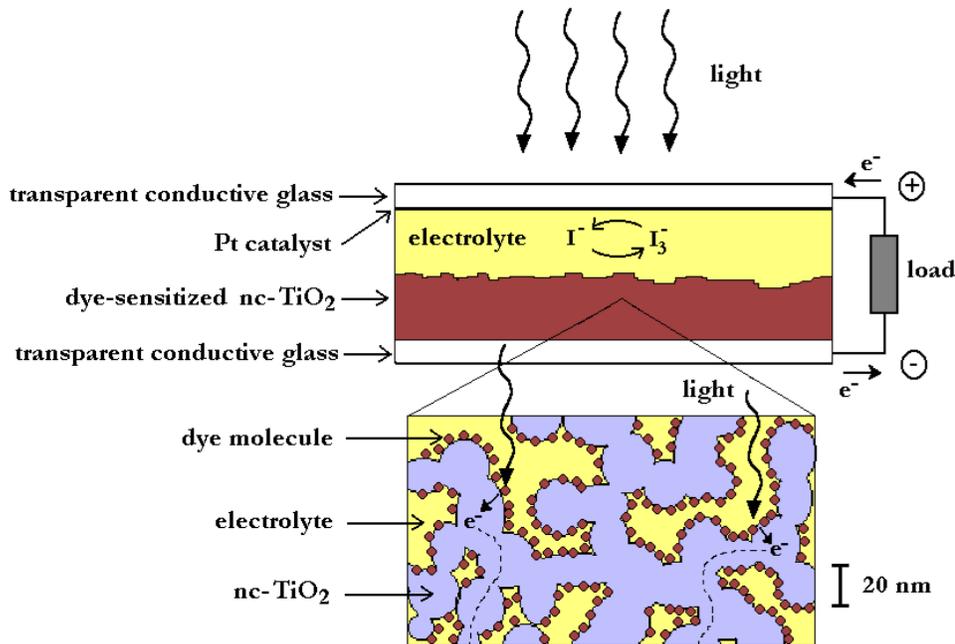


Figure 1: Structure and components of Dye-Sensitized Solar Cells [4]

At the core of each DSSC is a mesoporous oxide layer composed of a network of TiO_2 nanoparticles. The TiO_2 has been sintered together onto conducting glass to build up electronic conduction. Attached to the surface of the mesoporous film is a monolayer of charge-transfer dye. Through photon absorption of the dye, electron excitation occurs (1) and results in the release of a free electron into the conduction band of TiO_2 (2). Linked to the dye is an electrolyte, which subsequently restores the dye's ground state (5). The electrolyte regeneration itself consists of a redox couple (4) and results in an electron migration through the external load (3). The difference between the electrochemical potential of the electrolyte and the Fermi level of TiO_2 determines the reachable voltage under irradiation. The resulting power output is directly proportional to this potential gap.

Overall, the cell converts light into electric power without any permanent alteration. [4, 5, 6]

An overview on the described principle of operation is given through Figure 2, the numbers (in brackets) in the text below link text and figure.

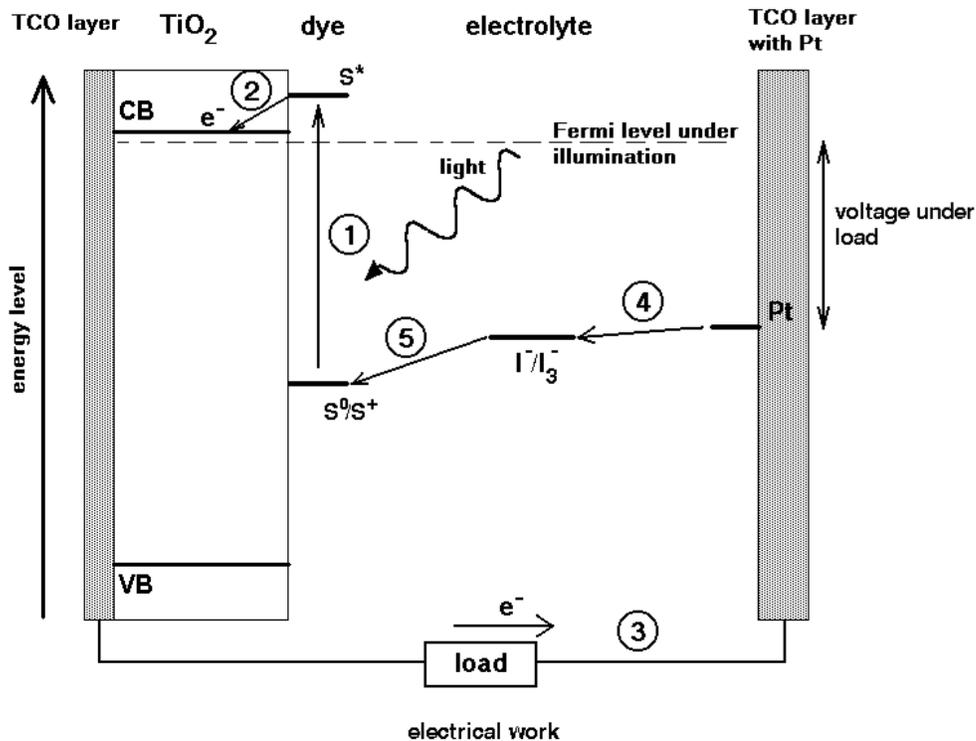


Figure 2: Working principle of Dye-Sensitized Solar Cells [4]

2.2 Parameters

A DSSC is characterized by a variety of experimental parameters, such as the photocurrent I and photopotentials V which are measured under different conditions, in open and closed circuit (index oc and sc): I_{oc} , V_{oc} , I_{sc} , and V_{sc} . [7]

2.2.1 Open circuit voltage (V_{oc}) and Short circuit current (I_{sc})

The open circuit voltage, V_{oc} , is the difference in potential between the cell's terminals under light illumination when the circuit is open. It is dependent on the gap between the Fermi level of the semiconductor and the redox potential of the electrolyte.

The short circuit current, I_{sc} , is the photocurrent, measured when the illuminated cell is short circuited. Light intensity, light absorption, injection efficiency and the regeneration of the oxidized dye are all factors determining I_{sc} . There is no electric power at short- and open-circuit operation of a solar cell, as either voltage or current vanishes at these points. For the sake of completeness, open circuit current I_{oc} and short-circuit voltage V_{sc} are enlisted. In following analysis they are rather circumstantial, as they do not influence other parameters. [8]

2.2.2 Incident Photon to Current Conversion Efficiency (IPCE)

One of the fundamental measurements of the performance of a solar cell is the Incident Photon to Current Conversion Efficiency (IPCE). It describes how efficiently the light of a specific wavelength is converted to current and is customary measured under short-circuit conditions.

IPCE can be interpreted as the ratio of the total outgoing electrons per time and surface to total incoming photons per time and surface: [6]

$$IPCE(\lambda) = \frac{\frac{N_{electrons}}{\Delta t * \Delta A}}{\frac{N_{photons}}{\Delta t * \Delta A}}$$

(N: number of, Δt : time interval, ΔA : surface element)

The amount of outgoing electrons per time and surface is equal to the change in electron surface charge density: $\frac{N_{electrons}}{\Delta t * \Delta A} = \dot{\sigma}_{electrons}$

As well as the amount of incoming photons per time and surface equals the incident photon flux: $\frac{N_{photons}}{\Delta t * \Delta A} = \phi_{photons}$

So that:

$$IPCE(\lambda) = \frac{\frac{N_{electrons}}{\Delta t * \Delta A}}{\frac{N_{photons}}{\Delta t * \Delta A}} = \frac{\dot{\sigma}_{electrons}}{\phi_{photons}}$$

Writing it with the incoming power P_{in} and the energy of a single photon $W_{single\ photon}(\lambda)$ follows:

$$\phi_{photons} = \frac{P_{in}}{W_{single\ photon}(\lambda)} = \frac{P_{in}}{\frac{hc}{\lambda}}$$

Introducing the short circuit current density J_{sc} one can write:

$$\dot{\sigma}_{electrons} = \frac{J_{sc}}{Q_{single\ electron}} = \frac{J_{sc}}{e}$$

It follows:

$$IPCE(\lambda) = \frac{\frac{N_{electrons}}{\Delta t * \Delta A}}{\frac{N_{photons}}{\Delta t * \Delta A}} = \frac{\dot{\sigma}_{electrons}}{\phi_{photons}} = \frac{hc}{e} * \frac{J_{sc}}{P_{in} * \lambda}$$

2.2.3 Current-Voltage (I-V) characteristics

The Current-Voltage (I-V) characteristics of a solar cell under illumination are used to determine the Incident Photon to Current Conversion Efficiency η :

The I-V curves can be obtained by applying a potential scan, from zero voltage (short-circuit conditions) to the open-circuit potential, under constant illumination. They are plots of all possible working points in the considered range. Due to their high capacity, dye-sensitized solar cells have a relatively slow electrical response. For this reason, the voltage scan should be performed sufficiently slowly. From the I-V curve, I_{sc} is determined at the zero voltage measurement point, while V_{oc} is found at the zero current measurement point. The maximum output power of a solar cell is obtained when the product of $|V * I|$

reaches a maximum. At this characteristic point the slope of the I-V curve is highlighted in the following chart, figure 3.

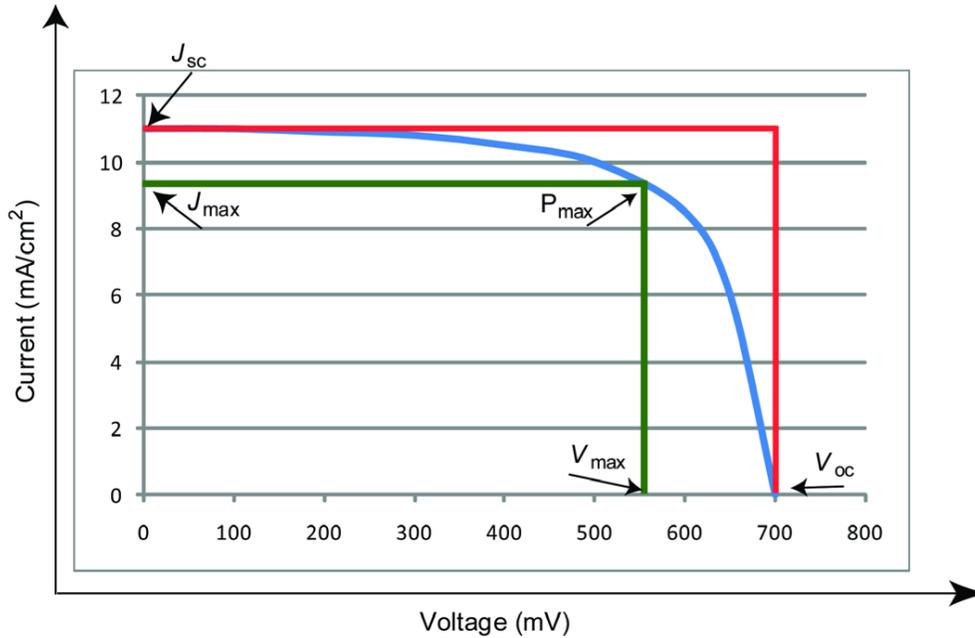


Figure 3: Current-voltage characteristics for solar cells. *Blue line:* measured current-voltage curve. *Red line:* area of $V_{oc} * I_{sc}$. *Green line:* area of $V_{max} * I_{max}$. [8]

The overall sunlight to electric power conversion efficiency η of DSSC is given by:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{|V * I|_{max}}{P_{in}} = \frac{V_{oc} * I_{sc} * FF}{P_{in}}$$

Whereas P_{in} refers to the solar power input and FF is defined as the fill factor:

$$FF = \frac{V_{max} * I_{max}}{V_{oc} * I_{sc}}$$

The fill factor is a value between zero and less than one and describes the shape of the I-V curve. A high value indicates a more preferable rectangular shape. A low value indicates high electrical and electrochemical losses of the solar cell, so that the fill factor measures the ideality of the device.

In summary, I_{sc} , V_{oc} , IPCE, FF and η are the key performance parameters of the solar cell. [6, 7, 8]

3 Preparation and Measurement

All solar cell preparations and measurements were carried out at the physics laboratories of the Universidad del Norte in Barranquilla, Colombia:

3.1 Transparent and conductive oxide substrate (TCO)

The building process of the DSSCs starts with the substrate, which forms the basis of the cell. The company Solaronix provides a variety of conductive substrates suitable for Dye Solar Cells in particular TC030-8. This transparent and conductive oxide substrate (TCO) will be the glass of choice for the fabrication of all DSSCs. It comes at 2.2mm and 3.0mm thickness and shows a resistivity of 8 ohm/sq. TC030-8 is made out of sodalime glass and is one-sidedly coated with fluorine-doped (FTO) tin oxide, forming the conductive layer. The Coating ensures optimal adhesion of the TiO_2 , an important requirement for the electrode fabrication. [10]

The standard glass size is 10cm x 10cm, which in the following had to be cropped to the desired size of 2cm x 2cm for a more appropriate and efficient handling. For the cutting, a paper template of the requested 2cm x 2cm grid was laid underneath the glass substrate. Subsequently, with a glass cutter the grid was scratched onto the non-conducting side, inducing breaking points onto the glass surface. A multimeter set to measure resistance was used to identify the conductive side. The glass was then carefully broken into the desired sizes by bending the plate from both sides of the line.

Half of the glass panes were set apart for the anode, whereas the other half were appropriated for the cathode. For the later injection of the electrolyte into the cell, two holes running through the cathode substrate were required. The holes were drilled using Dremel 300 fine drill and carbide burs SSW FG-700. Running the drill at mid-speed and constant cooling, through distilled water, prevented overheating. This step was very critical but difficult to be executed properly: Any slight tilt of the drill might have led to a breaking of the glass or the drill bit itself. It can be very time consuming. During the preparation processes it was found out, that the thinner substrates (2.2 mm) were significantly easier to drill without breaking the tool or the glass. Furthermore it was discovered, that glass splintering at the bottom could simply be prevented by exerting pressure onto the cell during its drilling.

For a faultlessly application of the printed layers later on, a supremely clean glass surface was fundamental. Hence the glass planes underwent an ample cleaning process:

At first all rough dust or other particles were sub ducted in soap water using a tough brush. Secondly an Ultrasonic cleaning was conducted. The pre-cleaned samples were put into glass jars filled with distilled water and the device Elmasonic S 30 H was set to a ten minute clean at 35°C. Afterwards, the procedure was operated for a second time using ethanol as the cleaning agent. Finally all cleaned samples were stored in plastic containers, if not utilised immediately.

3.2 TiO_2

As explained above, the photo-anode consisted of mesoporous layers of titanium dioxide nano-particles on top of the cut and cleaned substrates described above. All layers were stained with Ti-Nanoxide D/SP from Solaronix. It is a diffusing active layer obtained from a mixed titania particle paste. The mixing of large and small nano-particles ensured both very high surface area and light diffusion. [10]

TiO₂ was deposited at two different superficial contents: 0.5cm x 0.5cm and 1.0cm x 1.0cm. Even for the greater surface, this left enough room for the adhesive area and allowed proper assembling and measurement.

The application process for all samples is called slot-coating or doctor blade: The intended shape and thickness of the layer was predefined by the recess of an overlying tape and obtained through an evenly spread of the substance. Therefore the projected quadrate with lateral lengths of 0.5cm and 1.0cm were printed onto paper and a microscope slide had been laid over top. Scotch Ruban Magic Tape from 3M was disposed to the slide. The mould was cut out with a sharp knife while aiming at the underlying quadrate. The tape was then carefully detached from the slide conserving the clear cut quadrate and thereafter reattached onto the conductive side of a sample substrate. Using a second microscope slide the titanium paste was finally spread across the mould and smoothly levelled out until a reasonable homogeneous layer was achieved. Ultimately the tape was entirely removed from the glass.

The Scotch tape had been designed to residue-freely detach from the surface and adhere equally successfully for several following times. As some TiO₂ remainders stuck to the tape and might have slipped across the surface during a second sampling, the tape was not reused and the blueprint fabricated each time.

Once the TiO₂ printing is completed, the samples need to be sintered at a temperature of 450°C for 30 minutes. This requirement was met in using a furnace with programmable temperature control. All printed samples, put into high temperature resistant glass containers, were heated up at a rate of 5.0°C per minute to the final temperature of 450°C, which was then put on hold for the desired half an hour. The cooling-down was controlled to the same degree as the heating: -5.0°C per minute to the output temperature of 50°C. This slow-in-change temperature curve was used to ensure an even and steady calefaction of the glass preventing glass fractures. A Ney Vulcan Furnace Model 3-550 by Gesswein features all required characteristics and was operated in the sintering of all samples.

To control the TiO₂ thickness several prints can be stacked. In prior studies at the laboratory, three layers were found out to be optimal. Once the first layer had been sintered, the second and third prints were applied in identical manners as described above.

For tracking, analysis and assignment purposes all solar cells needed to be referred to by a unique number: Picking up the running laboratory number, the first cell started at 300. Each number was scratched onto the anode's non-conductive surface at one the corner of the cell, so that the light transmission wouldn't be hindered. This was done using a stylus (Scriber from RedLine Professional) made of tungsten steel and designed for marking glass objects. Scribing on the glass surface had been found out by the laboratory in previous studies to be the most enduring way to mark the cells. All anodes were marked before applying the third layer.

Having completed their last furnace sintering, the TiO₂ quality of each anode surface was checked and defects recorded. Sometimes the TiO₂ did not sinter properly and parts of the layer peeled off leaving a non-integral surface. This defect can lead to power losses later on. As long as the defect remained a local imperfection, the anode surface was still used and built up to an entire cell.

3.3 The natural dyes

The last step in the preparation of the anode is the subsidence of the TiO₂ layer into the natural dyes:

In the course of this study five different kinds of fruit and vegetables were used in the building of solar cells: *Bixa orellana* (Achiote), *Vaccinium meridionale* (Agraz), *Bactris guineensis* (Corozo), Blackberry (Mora) and Beet Root (Remolacha). In the following they will be referred to by their native Colombian names, marked in parentheses.

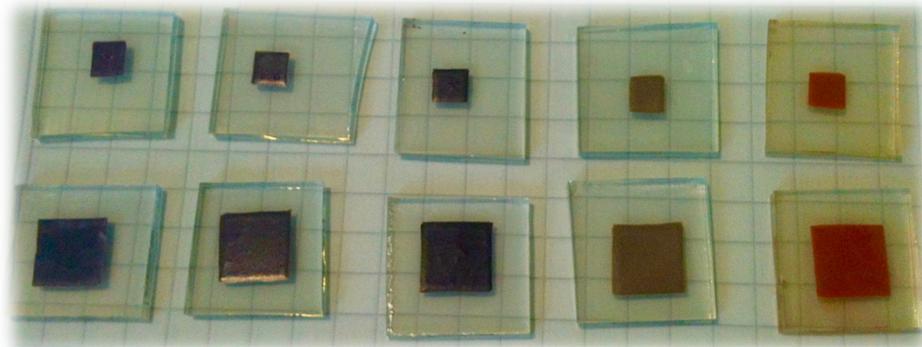


Figure 7: DSSCs soaked into (from left to right) Mora, Corozo, Agraz, Remolacha, Achiote

3.3.1 Achiote

Achiote is a shrub native to tropical areas of America and mainly known for being the source of the Annatto seeds, containing the carotenoid Bixin. Carotenoids are organic pigments naturally occurring in photosynthetic organisms and are in charge of the blue light absorption in those plants and vegetables. As the seeds are pretty dense and hard to be scrunched, they were soaked in ethanol over night. The reason why the colorant was extracted in ethanol is that the dye is not soluble in water. [11]

3.3.2 Agraz

Agraz is a promising fruit of the family Ericaceae growing in the Andean highland forests of Colombia. It is known for its high content of anti-oxidant properties and anthocyanin. Anthocyanins are water-soluble pigments, absorbing blue-green and ultraviolet light and thereby naturally protecting the fruit tissues from photo damage. The Agraz was boiled in water to receive the pigments. [12]

3.3.3 Corozo

Corozo is a wild tropical fruit, promising a source of natural pigments due to its high content of anthocyanins. Anthocyanin, characterized above, was extracted by boiling the fruit in water. The received juice was used for dyeing the samples. [13]

3.3.4 Mora

Mora or Blackberries contain a strongly light-absorbing dye molecule called anthocyanin, which occurs in many types of fruits and berries. It's the compound that gives Mora their colour. Anthocyanin is characterized above. A mortar crushed the fruit and if needed some distilled water was added to further liquidate the juice. [14]

3.3.5 Remolacha

The red color of beet roots comes from betalain pigments. Betalains are a class of red and yellow indole-derived pigments found in plants, where they replace anthocyanin pigments.

For this plant, the juice was received in two different ways. The root got rasped into flesh and was then either cooked with added water or squeezed to extract its natural juice. In the following a comparison of both techniques “cook or squeeze” was done. [15]

Once the dyes are prepared, the anodes could be soaked into them:

Having completed the third layer of TiO_2 and coming out of the furnace the glass substrates exhibited a temperature of 50°C and were immediately immersed into the dyes. For Corozo and Achiote samples the dye was liquid enough, that the colorants would simply diffuse into the TiO_2 layer, as soon as the anodes were deposited face-up. As the resulting Mora juice was more viscous, still containing pulp, the samples were laid on the surface facing downwards. To ensure a decent staining, the samples were soaked in the dyes overnight for at least 12 hours. During this process, they were kept covered and cooled inside the fridge.

Provided that the anodes were stained sufficiently, any remaining juice on the non- TiO_2 glass surface was sub ducted and dried. This completed the anode’s preparation before the assembling process.

3.4 Platinum coated cathode

To enhance the electron transfer rate between the cathode and the electrolyte, the cathodes were coated with platinum. This elevated the charge density of the solar cell and helped yielding higher photo-currents.

Solaronix offered a Platinum Catalyst Paste for DSSCs called Platisol T/SP, which in the following was applied to achieve catalytic platinum layers on the cathodes. It was a viscous paste containing a precursor of platinum and got activated as a coating after heat treatment at 450°C .

Platisol T/SP was deposited onto the cathodes’ conductive side after the substrates had been drilled and cleaned appropriately. Using a regular paintbrush and the slot-coating technique (described above), a thin and evenly spread layer was ensured.

Next this wet layer had to be fired, in order to remove the organic vehicle. The heat treatment was executed in similar manners as the TiO_2 sintering. The New Vulcan Furnace at a rate of 5.0°C per minute heated the samples up to a maximum temperature of 450°C , held the heat for 10 minutes and slowly cooled down at 5.0°C per minute to 50°C . After the firing all cathodes were coated with an activated layer of platinum and ready for assembly. [10]

3.5 Assembling the Solar Cells

The two electrodes, conductive sides facing each other, were laminated together using the hot melt sealing film Meltonix. A rectangular, slightly bigger than surface of TiO_2 frame was cut out of a sheet of Meltonix. To prevent the electrolyte from leaking, it is important that the Meltonix frame is a complete ring and has no notches. The frame was then put onto the anode surrounding the stained TiO_2 . Next the counter-electrode, conductive side facing down, was laid overtop and positioned correctly. A small side shift of the electrodes generated enough space at both ends for the measurement pins.

The cell was the put onto a hotplate at 120°C for less than a minute. A slight pressure applied onto the cells’ top helped forming a good adhesion and prevented pockets within the gasket.

Once the cell was cooled back down to room temperature, the electrolyte was injected through one of the holes in the counter electrode using a pipette. It was made sure that the

whole TiO₂ surface was soaked in fully. An immediate sealing of both holes with Scotch Magic Tape limits evaporation to a minimum. This completes the cell preparation.

3.6 Measurement

The method of choice for determining the efficiency η and the fill factor FF of a cell was running a current-voltage characteristic:

In following, the solar cell performance was measured under a halogen lamp and in the sun. Under both conditions a measurement pin was attached to each conducting surface of anode and cathode. Between those pins a Keithley 2400 SourceMeter applied an external voltage onto the cell. The input source was set to voltage and the current safety limit to 10mA. No sample ever exceeded this limit when tested.

A solar power meter was used to determine the light input.

To encounter the maximum power the cell's performance has to be analysed within its working interval. For this purpose a voltage sweep was carried out from – 40mV to 600mV. A linear staircase increase with a power-measurement delay of 0.5s and a step width of 5mV was configured and the resulting cell currents stored for later analysis. The delay between applied voltage and measured current prevented inductive or inertial effects from adulterating the performance analysis. This ensured independent measurement points. The short circuit current could be read out at the zero-voltage-point whereas the open-circuit voltage was retained once the current hit zero Ampere. A Solar Power Meter from Ambient Weather measured the incoming luminance in W/m² and the received data was recorded in the lab book. This represented the standard sequence for analysing the cell's performance. They recorded data was entered and analysed in Microsoft Excel using the equations addressed in the theoretic part.

As some samples comprised preparation defects, a full current-voltage scan was not carried out and the performance only characterized through their I_{sc} and V_{oc} values, obtained through a multimeter. I_{sc} and V_{oc} both implied a limit to the maximum power and were efficiently measurable.

In following the cell's performance was analysed depending on the different dyes and TiO₂ surfaces, dye preparation, light sources and power input. Optimizations were developed as well as the DSSCs' longevity was tested.

5 Resumé

In the current economic, environmental and social climate, creating a revolutionary low-cost photovoltaic system suitable for large-scale power generation is of utmost urgency. Dye-sensitized solar cells are receiving considerable academic and industrial attention for this purpose, since they promise to convert solar to electrical energy at a fraction of the cost of traditional semiconductor-based photovoltaics.

In the course of this study a variety of different DSSCs were built and tested. The combination of modifying the cells themselves and changing the light input enabled major analysis. The significance and correlation of performance parameters could be monitored under alternant circumstances.

Achiote was found out to be the most powerful dye. It achieved maximum efficiencies of all dyes, both under halogen and sunlight. With a halogen efficiency of 0.0733% Achiote lead group of dyes. Mora 0.0151%, Corozo 0.0148%, Agraz 0.0082% and Remolacha 0.0005% followed accordingly. For these top performers a higher efficiency came along with a greater fill factor. Taking samples from Mora, Corozo and Agraz into the sun, their efficiencies more than doubled. Achiote and Remolacha offered even greater improvements: 0.21% efficiency for Achiote and twelve times higher efficiency under sun than halogen light for Remolacha.

The larger 1.00 cm² TiO₂ surface area was found out to yield slightly bigger efficiencies than 0.25 cm². This trend is likely to dissolve once surfaces are further enlarged. The non-correlation of surface area and efficiency marked a crucial necessity for large-scale application.

Efficiency and fill factor were accounted as the two key parameters. For 40% to 60% fill factors a linear correlation between efficiency and fill factor was discovered. At top performances deviations from this rule of thumb accumulated. Varying the illumination power, the scans showed clearly, that the output was not linear to its input. A halogen lightening between 400 and 500 W/m² yielded the greatest efficiencies.

Under blocked light conditions, the cell efficiency slowly decreased over the course of a week. Corozo, in particular showed a very pleasing stability after two days. The lack of sufficient electrolyte was found out to contribute to the efficiency loss. Better sealing improved stability. Next, a basic characteristic of solar cells, the I_{sc} , had been tracked under constant illumination. A slow decline could be noticed which offered an interesting question: How does the cell operate at its maximum power point over time? Once an approximate method was developed, the output power and the total energy could be evaluated. The DSSCs were doing their job.

Even though a lot of improvements have been developed, further optimizations still remain to be made:

Studying the absorption spectra of the different dyes helped explaining the dyes' output differences. Further spectroscopic analysis of the assembled DSSCs as a whole would be including possible red-shifting effects from TiO₂. Alongside with a solar simulator discrepancies of artificial and outdoor circumstances could be further diminished.

As the dyes' efficiency varied differently with incoming power, a combination of different dyes might be beneficial. It was started in earlier studies and further investigations should

be continued. Enlarging the scope of surface area or building a grid of various cells also appears as promising field of studying.

The longevity monitoring revealed a need for better sealing. So far dyes' chemical analysis has not been carried out. It would be beneficial for analysing the decomposing of the dyes over time. New chemical key parameters for longevity testing could be evolved.

I hold high hopes that organic dye-sensitized solar cells will receive further optimizations and attention. For Colombia this is a unique chance to build solar cells and finally tapping its resources for clean energy.

Special thanks to my supervising professor Dr. Tomás José Rada Crepo, who excellently guided my investigations. It was a grate privilege researching for the Universidad del Norte in Barranquilla Colombia.

References

- [1] Lewis N.S., Crabtree G. Basic Research Needs for Solar Energy Utilization. Office of Science, U.S. Department of Energy, Washington, DC, USA, 2005.
- [2] O'Regan B., Grätzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. in: *Nature*, 1991, 353, 737-740.
- [3] GCell Power. Dye Sensitized Solar Cells. 05.10.2016. www.gcell.com/dye-sensitized-solar-cells.
- [4] Halme, J. Dye-sensitized nanostructured and organic photovoltaic cells: technical review and preliminary tests. Lecture, Helsinki University of Technology, Helsinki, Finland, 2002.
- [5] Grätzel, M. Dye-sensitized solar cells. in: *Journal of Photochemistry and Photobiology C-photochemistry Reviews*, 2003, 4:145–153.
- [6] Hagfeldt A., Boschloo G., Sun L., Kloo L., Petterson H. Dye-Sensitized Solar Cells. *Chemical Review*, Department of Physical and Analytical Chemistry, Uppsala University, Uppsala, Sweden, 2009.
- [7] Friedrich D. A study of charge transfer kinetics in dye-sensitized surface conductivity solar cells. PhD thesis, Helmholtz Zentrum Berlin, Germany, 2011.
- [8] Karlsson K. M. Design, Synthesis and Properties of Organic Sensitizers for Dye Sensitized Solar Cells. PhD thesis, KTH, Stockholm, Sweden, 2011.
- [9] Dittrich T. *Materials Concepts for Solar Cells*. Imperial College Press, Helmholtz Center Berlin for Materials and Energy, 2015.
- [10] Solaronix - Supplier of specialty chemicals and materials. Materials specification. Aubonne, Switzerland, 2013.
- [11] Medina-Flores D., Ulloa-Urizar G., Camere-Colarossi R., Caballero-García S., Mayta-Tovalino F., del Valle-Mendoza J. Antibacterial activity of *Bixa orellana* L. (achiote) against *Streptococcus mutans* and *Streptococcus sanguinis*. in: *Science Direct - Hainan Medical University*, 2016, 400-403.
- [12] Hernandez Perez M. I., Lobo Arias M., Medina Cano, C.I., Cartagena Valenzuela, J.R. Andean blueberry (*vaccinium meridionale swartz*) seed storage behavior characterization under low temperature conservation. in: *Revista Facultad Nacional de Agronomía, Medellín*, 2012, volume 65, 6627-6635.
- [13] Osorio C., Carriazo J.G., Almanza, O. Antioxidant activity of corozo (*Bactris guineensis*) fruit by electron paramagnetic resonance (EPR) spectroscopy. In: *European Food Research and Technology*, 2011, volume 233, 103-108.
- [14] Young, C. *Organic Solar Energy and Berries. Laboratory Guidelines*. National Science Foundation GK-12 and Research Experience for Teachers (RET) Programs, University of Houston, Houston USA, 2013.
- [15] Zhang D., Lanier S., Downing J., Avent J. Betalain pigments for dye-sensitized solar cells. in: *Journal of Photochemistry and Photobiology A-chemistry*, 2008.