IMPROVED EFFICIENCY OF BETANIN-BASED DYE-SENSITIZED SOLAR CELLS AND A METHOD OF MEASURING RAMAN SPECTROSCOPY OF BETANIN THROUGH QUENCHING OF FLUORESCENCE WITH TiO₂ COLLOIDAL NANOPARTICLES

By

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Master of Science in Chemistry

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The members of the Committee appointed to examine the thesis of Cody S. Sandquist find it satisfactory and recommend that it be accepted.

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IMPROVED EFFICIENCY OF BETANIN-BASED DYE-SENSITIZED SOLAR CELLS AND A METHOD OF MEASURING RAMAN SPECTROSCOPY OF BETANIN THROUGH QUENCHING OF FLUORESCENCE WITH TiO$_2$ COLLOIDAL NANOPARTICLES

Abstract

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Dye-sensitized solar cells (DSSC) are emerging as a possible and less expensive alternative to silicon solar cells. Their advancement is presently limited by the capabilities of the sensitizing dyes used in terms of cost effectiveness, conversion efficiency, and lifetime. Betanin is an abundant and inexpensive natural dye obtained from beets for this study. Results at this point indicate that betanin-based DSSCs are the most efficient cells to use a natural plant pigment as a sensitizer, with conversion efficiencies as high as 2.7%. The improvement in conversion efficiency ($\eta$) is the result of a purification technique involving medium pressure liquid chromatography and efforts to reduce charge recombination with a TiCl$_4$ post-treatment of TiO$_2$ electrodes or by incorporating a blocking layer into the design of the DSSC. A method of quenching the fluorescence of betanin with colloidal TiO$_2$ is also described. Doing so allows for the measurement of a Raman spectrum of betanin, reported here for the first time. Also discussed are the ways to further improve $\eta$ by increasing the open-circuit voltage and preliminary results for the lifetime of a betanin-DSSC under illumination are presented.
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DEDICATION

I have to dedicate my master’s thesis to my parents, Harold and Dee, who have always supported the major decisions I have made in life and sacrificed for my well-being. My thesis is also dedicated to the other special people in my life; my brother Rob, little sister Christa, who have also shown encouragement and generosity. And of course, to Grandma Doris, for all of her prayers and the things in life that only grandma’s can provide. I cannot list all of the other relatives this is dedicated to, who live in Iowa and throughout the county. This is also dedicated to my girlfriend Kim, who made graduate school worthwhile. Furthermore, this is dedicated to Kim’s wiener dogs, Buddy and Bella, even though Bella tries to suffocate me when she’s hungry. Lastly, my thesis is dedicated to all the boys of Oscar ’07 and the many friends I have made in graduate school.
ATTRIBUTES

Much of Chapter Four was written with the assistance of Dr. Jeanne McHale for a journal article with the same title as the chapter. The journal article is not yet published at the time of printing this thesis. The contents of Chapter Four are similar to the journal article but not identical, as additional experimental detail is included in this thesis. The diffuse reflectance data appearing in Fig. 2 of Chapter Four was measured by Candy Mercado of the McHale lab and Enamul Khan of Dr. Tom Dickenson’s lab.
Chapter One
Introduction

Goals of Dye Sensitized Solar Cell Research

The sun provides a plentiful, renewable, and clean source of energy that can be harvested with solar cells to supplement our increasing needs for electricity generation. However, the cost of solar energy is a major hindrance to its large scale implementation into the power grid. The solar cells on the market today are based on the semiconductor material silicon, made of two layers that are doped to be either electron rich or deficient.\(^1\) Absorbed light excites electrons in the crystal to form electron-hole pairs. These charged particles collect at a p-n junction, where charge separation creates an electric field. A small external voltage applied to the electric field will allow current to flow. Marketable Si-based solar cells are considered to be highly efficient with conversion efficiencies around 15\%, but this comes at the expense of high temperature processing of extremely pure and defect free Si in clean rooms. Although the prices of Si solar cells are trending downwards, they remain out of reach for most people, businesses, and developing countries. Dye sensitized solar cells (DSSCs) have been an attractive alternative to Si solar cells since their inception by Michael Grätzel in 1991.\(^2\) While Si solar cells are currently more efficient, DSSCs may have an advantage in producing a greater amount of watts per unit cost by using TiO\(_2\) as a less expensive wide band gap material combined with a simpler and less energy intensive manufacturing process. The overall objective of researching DSSCs is to produce a low cost alternative to Si solar cells, thus making solar
energy conversion into electricity an economically viable means of meeting the world’s electrical energy needs.

**How DSSCs Work**

DSSCs are unique amongst photovoltaic devices in that they are composed of both inorganic and organic materials, and both solid and liquid phases. Fig. 1a provides general diagram of the composition of a DSSC. A typical DSSC is made by coating conductive fluorine doped tin oxide (FTO) glass with a TiO$_2$ layer, and chemically adsorbing a dye onto this layer. An electrolyte solution consisting of a redox couple is sandwiched between the TiO$_2$ layer and a counter electrode made from FTO glass and coated with a Pt catalyst. The I/I$_3^-$ redox couple is most commonly used as the electrolyte and graphite catalysts$^1$ have also been used as low cost alternatives to Pt. The process of electron transfer and transport are outlined in Fig. 1b. An adsorbed dye molecule is considered to be ‘sensitized’ when photons are absorbed, exciting the molecule to a higher energy state greater than that of the conduction band of TiO$_2$. The excited state dye now has sufficient energy to inject an electron into the conduction band and is transported through the TiO$_2$ layer to the FTO glass anode, where charge is collected. A circuit connects the anode and cathode of the cell. The negative charge at the cathode is mediated by the electrolyte solution back to the oxidized dye molecule to regenerate it. While DSSCs can potentially be a cost-effective means of producing electricity, they are currently limited by the cost and capabilities of the sensitizing dye. Factors including the cost of synthesizing a dye, low efficiencies, and a tendency to decay over time, all contribute to deferring the advancement of DSSC technology.
Types of Sensitizing Dyes

Numerous dyes have been incorporated into DSSC designs with varying success. The basic categories of sensitizing dyes include metal-centered organo-metallic complexes, and organic dyes. The best performing and longest lasting sensitizing dyes have tended to be metal-centered complexes, the best performing being ruthenium-based with conversion efficiencies over 10%, and have been illuminated for up to 1000
hours with little decline in efficiency.\(^6\) Despite the impressive performance of the Ru dyes, such as N3, N719, and N621; Ru is a rare metal and therefore any commercial application would be inherently limited by availability and cost. Additionally, Ru is a heavy metal so exhausted DSSCs would present environmental risks from Ru’s toxicity if discarded improperly. Because of the expense and toxicity associated with metal-centered dyes, many organic dyes have been developed as alternatives. Whereas metal-centered dyes rely on metal-to-ligand charge transfer (MLCT) to inject an electron into the TiO\(_2\) conduction band,\(^7\) organic sensitizing dyes contain links of conjugated double bonds contributing to their strong \(\pi-\pi^*\) charge transfer.\(^8\) Some of the synthetic organic dyes are approaching efficiencies and illumination duration of the better performing Ru-based dyes. Some organic dyes have reached efficiency values of 8-9\%\(^9,10,11\) with the dye in Ref. 9 enduring illumination for 1000 hours with comparable results to the fore mentioned Ru-centered dyes.

The lure of natural dyes however, is that they are the least expensive and readily obtainable sensitizing dyes. While extraction of natural dyes from plants is requisite, synthesis is not. There are four classifications of natural plant pigments: chlorophyll, carotenoids, anthocyanins, and betalains; all of which have been used in DSSCs to varying degrees. Chlorophyll and anthocyanin pigments are by far the most well studied, despite low efficiencies, typically below 1\%.\(^12,13,14,15\) Carotenoids have not been studied as sensitizers to the same degree as chlorophylls and anthocyanins but have also yielded low conversion efficiencies.\(^16\) Apart from carotenoids, betalain pigments have been the most understudied sensitizers, appearing in literature for the first time in a 2008 report by Zhang et. al. in Ref. 17, which used the betalain pigment betanin extracted from beets to
make DSSCs. Since 2008, betanin DSSCs have been attempted by at least one other research group, and improved upon by the McHale group (not yet published) to reach conversion efficiencies up to 2.7%, exceeding all other natural dye sensitizers.

**Objectives of Research**

The overall purpose of this study can be divided into three primary objectives: one, to improve the efficiency of betanin DSSCs; two, quenching the fluorescence of betanin so that a Raman spectrum can be obtained; and three, to determine the limits of betanin DSSCs over extended periods of illumination and operation.

The first reported betanin DSSC study by the McHale group only achieved a conversion efficiency of 0.67%. Given that most natural dye sensitizers also afford low efficiencies, with a maximum of only 1.5% prior to this study, there was great interest in optimizing the performance of betanin as a sensitizer. Improvement in efficiency was sought after by two main methods: increasing dye loading through an improved dye extraction method, and reducing charge recombination from the TiO$_2$ conduction band to the electrolyte or oxidized dye molecule.

The dye extraction process from plant material is an important step affecting the production of current in a DSSC. Betanin is found in common plants such as beets, the prickly pear, and the bougainvillea flower. These plants also contain a yellow co-pigment known as indicaxanthin. One of the conclusions from Ref. 17 was that dye loading of betanin on TiO$_2$ is limited because of preferential adsorption by indicaxanthin, and therefore, obtaining a greater purity solution of betanin is desirable. More recent experiments are in agreement that a higher purity betanin increases dye loading, but for
an unknown reason, as indicaxanthin does not appear to adhere to TiO$_2$ in easily detected quantities.

In addition to obtaining high purity yields of separated betanin, it is also necessary to acquire appreciable amounts for sensitizing films. The method used to “purify” betanin in this study is reverse-phase medium pressure liquid chromatography (MPLC) with a partially polar C-18 bonded silica gel column. The new method has created higher purity yields of betanin than the previous McHale group study$^{17}$ and is considered a major contributing factor to the improved performance of the betanin DSSCs.

The performance of a DSSC can also be improved by minimizing the occurrence of charge recombination between the conduction band and the electrolyte or oxidized dye. Reducing charge recombination was pursued by using two common methods: post-treatment of the TiO$_2$ electrode with aqueous TiCl$_4$, or the incorporation of a blocking layer between the conductive glass and TiO$_2$ layer. Post-treatment of the TiO$_2$ anode with TiCl$_4$ is one of the most common and simple methods used to gain small increases in efficiency. TiCl$_4$ hydrolyzes in water to produce HCl(g) and amorphous TiO$_2$ nanoparticles that insert themselves into the nanocrystalline film. One potential benefit of introducing additional TiO$_2$ nanoparticles into film, is that there are more pathways available for electrons to follow to the conductive glass, increasing the overall rate of electron transport,$^{20, 21}$ although the validity of this assertion has been disputed.$^{22}$ A more tenable explanation for the effectiveness of a TiCl$_4$ post-treatment is that the newly created TiO$_2$ nanoparticles fill in defect sites where charge recombination likely occurs at high rates.$^{23}$ Oxygen vacancies are prevalent in an unmodified TiO$_2$ electrode, and are locations where either the dye or electrolyte can interact to cause charge recombination.
Inserting TiO$_2$ nanoparticles into the defect sites limits the effects of charge recombination. Incorporating a blocking layer into the design of the cell can also improve the conversion efficiency of the DSSC by preventing charge recombination at the glass anode.\textsuperscript{24} There is a possibility that a liquid electrolyte can permeate all the way through a porous TiO$_2$ film and come into direct contact with the glass substrate. When this interface is formed, back-electrons from the conductive glass can easily recombine with the electrolyte. A blocking layer is a physical barrier capable of conducting electrons in one direction to the glass anode by severing any potential contact between the glass and electrolyte solution.

The second primary goal of the study was to obtain a Raman spectrum of betanin, which can later be used to design experiments to analyze the molecule in the excited state. Obtaining a Raman spectrum of betanin presents a challenge arising from fluorescent interference. Some of the fluorescence can be attributed to small quantities of indicaxanthin remaining in a “purified” betanin solution, but betanin also happens to be fluorescent, despite a report to the contrary.\textsuperscript{25} Consequently, the fluorescence of betanin needs to be quenched in order to measure a Raman spectrum of betanin. Quenching betanin’s fluorescence can be accomplished by bonding it to aqueous TiO$_2$ nanoparticles, and varying the concentration of TiO$_2$ can also be used to determine the efficiency of electron injection.

The third and final goal of this study is to evaluate the lifetime of a continuously illuminated betanin DSSC connected in a closed circuit. DSSCs using any type of sensitizing dye will remain impractical if they cannot withstand multiple years of exposure to the light and heat stress expected outside. At this point, only preliminary
experiments into the duration of betanin-based DSSCs have been conducted. Unsealed cells exposed to artificial light have lasted up to 8 hours, but with significant losses in efficiency. Gradual decline in the efficiency of DSSCs functioning over long time periods is a major obstacle in DSSC research. DSSCs are usually constructed with liquid electrolytes, acetonitrile (ACN) and methoxypropionitrile (MPN) being common examples. However, the high volatility of liquid organic solvents like ACN and even the low volatility of MPN decreases dye stability and makes cells susceptible to leakage and evaporation if the sealant is not air tight. Attempts by researchers to minimize losses in efficiency over time focused on replacing volatile electrolytes more than any other method. Nonvolatile solids or gel electrolytes, or negligibly volatile ionic liquids have been successful at minimizing declines in efficiency when compared to liquid organic electrolyte solutions over long periods of operation.
References


Chapter Two

Betalain Plant Pigments

Overview

In the plant world, pigments play vital roles in the survivability of species. Pigments have properties enabling them to power photosynthesis, protect from oxidative stress, or attract pollinators with their color. These pigments vary not only in color, but structure and function; there are four types of natural plants pigments: chlorophyll, carotenoids, anthocyanins, and betalains.\(^1\) Chlorophyll is active in photosynthesis, collecting yellow and blue light and facilitating the transfer of energy from sunlight to a plant.\(^2\) Carotenoids often act as an accessory pigment to chlorophyll in the fruit or roots of plants, capable of both participating in photosynthesis and dissipating excess energy from the sun through oxidation.\(^3\) Neither anthocyanics nor betalains are involved in photosynthesis but do serve as antioxidants and protect the leaves, petals, stems and berries from excess irradiation.\(^4\) Despite the similarities in function between anthocyanins and betalains, it is interesting that the two have never been found in any of the same plants.\(^5,6\)

Chlorophyll and anthocyanin dyes have been the most extensively researched natural dye sensitizers for DSSCs, with conversion efficiencies (\(\eta\)) typically below 1%.\(^7,8,9,10\) Carotenoid DSSCs have been attempted but also with low \(\eta\)’s.\(^11\) Despite the similarity in properties between anthocyanins and betalains, there have been comparatively few attempts at producing betalain-based DSSCs; Ref.’s 12 and 13 are the only two appearing in literature at present. Betalains are found in a biological order of
flowering plants known as Caryophyllales but have also been found in some higher fungi. Several cultivated crops such as beets, the prickly pear, the bougainvillea flower, and amaranth all contain betalain pigments; meaning that betalains are abundant, available, and inexpensive. Other than their beneficial role in human health as powerful antioxidants, betalains are also known for their intensity in color in low concentrations, which is exploited by the food industry and used as natural food colorants.

The building block for all betalains is betalamic acid which is biosynthesized starting with the amino acid tyrosine. With the addition of a hydroxyl group, tyrosine is converted into dihydroxyphenylalanine (Dopa), which then undergoes an enzymatic conversion to betalamic acid. The basic biosynthesis of betalamic acid and selected betalain pigments is depicted in Fig. 1. There are two categories of betalains that are divided by structure and color. General structures are given in Fig. 2. Betaxanthins are ammonium conjugates of betalamic acid and an amino acid or amine, appearing yellow or orange in color. Betacyanins consist of betalamic acid and a Dopa group, and are red or purple in color. Betacyanins can be further divided into four structural types: betanin, gomphrenin, amaranthin, and bougainvillein. These four structures differ by the attachment of glucose groups to either of the oxygen atoms in the ortho position on cyclo-Dopa moiety. The betanin-type betacyanin structure has a hydroxyl group on the C2 carbon and a glucose group on the C1 carbon. The gomphrenin structure is just the opposite of betanin, with a glucose group on the C2 carbon and hydroxyl group on the C1 carbon. Amaranthins, whose name derives from the amaranth plant native to South America, differs from the betanin structure in that it has two contiguous glucose groups attached to the C1 carbon. The bougainvillean structure is also referred to as 2-
descarboxy-betanin-type betacyanin by Strack. This structure differs from the others in that there is no carboxylic acid group at the C8 carbon. A glucose group on C1 is a descarboxy-betanin, while two ortho hydroxyl groups at the C1 and C2 carbons comprise the structure of betanidin. In all, there are over 20 known betaxanthin and 50 betacyanin pigments.

The properties that make betalains desired sensitizers for DSSCs include the possession of anchoring groups to chemically attach the molecule to TiO$_2$, strong absorption in the visible region of the solar spectrum, and structures with extensive $\pi$-conjugated bonds. All betalains also possess at least two carboxylic acid groups on the betalamic acid moiety, and many often have a third carboxylic acid that can be seen in Fig. 1 on the proline moiety of indicaxanthin and the cyclo-Dopa moiety of betacyanins. At least one or perhaps all three of the carboxylic acid groups chemically adsorb to TiO$_2$. The carboxylic acid groups serve as electron donors in sensitizing dyes while the central N1-atom connecting betalamic acid to the amino acid is capable of accepting electrons.

Because betacyanins and betaxanthins often co-exist in the same plant, it would be convenient to forego any separation of the two pigments and sensitize both onto TiO$_2$. However, betaxanthins have not been found to be worthy sensitizers at this point, but this is not to say that they will not work. While both types of betalain structures have conjugated double bond back bones ranging from the C18 atom to the central N1-atom, the cyclo-Dopa moiety also contains a conjugated aromatic ring directly attached to the N-atom which contributes to the overall strength of the $\pi$-$\pi^*$ charge transfer. Betaxanthins like indicaxanthin lack this extra $\pi$-stacking but miraxanthin does have a conjugated aromatic ring, although it is detached from the central N-atom. An example
of a betacyanin that is not a good sensitizer is betanindin. Betanidin has two hydroxyl groups in the ortho position on the aromatic ring. These hydroxyl groups will bind to TiO$_2$ and cause charge coupling so electrons transferred to the TiO$_2$ conduction band are transferred right back to the molecule via one of the hydroxyl groups. At this point, betalain based DSSCs have been reported by only the McHale group$^{12}$ and Calogero et. al.$^{13}$ and the best performing DSSCs have used betanin-type betacyanins obtained from beets. Calogera et. al. also reported DSSCs made with the betanin-type prickly pear and bougainvillein-type bougainvillea flowers. Betanin-type betacyanins were better performing and those made from beet extract were the best performing.

Betanin is currently the most efficient natural dye sensitizer but there are questions about exposure to the oxidative stress it would face in an outdoor DSSC. Betanin is used as a natural food colorant by the food industry and has been studied rigorously for its stability in an aqueous media.$^{22,23,24,25,26,27}$ The stressing factors that can influence the decay of betanin include, light, oxygen, pH, and elevated temperatures. Aqueous betanin is most stable in a pH range of 3.5 to 5,$^{21,22,23}$ and light exposure in this range does not contribute to betanin’s decay.$^{24}$ Betanin is even resistant to elevated temperatures with a pH of 3.5-5, but will succumb to decay though at a reduced rate.$^{22}$ A greater concentration of oxygen will also increase the decay rate of betanin.$^{25}$ The level of singlet oxygen ($^1$O$_2$) betanin is exposed to will also influence the rate of decay.$^{26}$ The most reactive form of molecular oxygen is $^1$O$_2$, which efficiently reacts with double bonds in biological molecules.$^{28,29}$ Aqueous betanin solutions containing the metal cations Fe(II-III) and Cu(II) have also been found to increase the decay rate,$^{23,26}$ but such experiments have not been carried out to determine if TiO$_2$ has a similar effect.
It is difficult to directly apply what is known about the stability of betanin in aqueous solutions used for food coloring to DSSCs. In the DSSCs that have been made, betanin is in a non-aqueous environment and bound to TiO$_2$. Although aqueous DSSCs based on natural dye have been produced,$^{29}$ such an option is not viable for betanin. Water has not proven to be as effective as other electrolyte solvents such as acetonitrile or methoxypropionitrile when used with other types of dyes.$^{30}$ Betanin has been regenerated in aqueous conditions$^{26}$ and timed photocurrent-photovoltage plot data also indicates that the molecule is being regenerated by virtue of producing current from 5-8 hrs connected in a closed circuit. The stability of betanin in DSSCs will most likely be a factor of complete absence of O$_2$ more than any other factor.
Figure 2: Structures of betaxanthins and betacyanins. Adapted from Cai and Strack, Ref.’s 18 and 30.
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Chapter Three

Extraction and Purification of Betanin from Beets

Introduction

Betanin, and betalains in general, are antioxidant and color intensive plant pigments that have long been used to benefit human health when included in a diet and when used as a natural food coloring. Another potential application of betanin arose when the first betanin-based dye-sensitized solar cells (DSSC) were developed and published by the McHale Group.1 One of the conclusions from this initial study was the need for a better purification method of betanin. Like most betalain pigment containing plants, beets have both betacyanin and betaxanthin present. The red-purple betacyanin pigment found in beets is betanin, while the yellow betaxanthin pigment is indicaxanthin. Ref. 1 concluded that indicaxanthin preferentially adsorbs to TiO₂, thereby limiting the amount of betanin capable of adsorbing. Recent experiments are in agreement with the assertion that indicaxanthin interferes with the dye loading of betanin but not because of preferential adsorption. Interestingly, indicaxanthin does not seem to adhere to TiO₂ films as strongly as previously believed but it is clear that adsorption of betanin is encumbered by its presence. Indicaxanthin’s effect in limiting the adsorption of betanin to TiO₂ is not understood but the necessity of separating the two pigments is well substantiated by absorbance data, as well as DSSC performance. In addition to obtaining a sufficiently pure solution of betanin, a second desirable condition is to provide an ample quantity of the purified dye to enable staining several TiO₂ films at a time for efficient DSSC fabrication.
HPLC is an effective chromatographic technique but was avoided due to its inability to produce high quantity yields of purified betanin. The method of separating betanin from indicaxanthin found in beet extract in Ref. 1 was by using a Sephadex G-25 gravity column. Sephadex is made of beads of dextran that attract betanin more strongly than indicaxanthin, allowing indicaxanthin to elute first. However, various issues arose as to the effectiveness of this chromatographic method. It was difficult to visually see a distinguishable separation of the yellow and pink pigments and reliance on a gravimetric column is not a time-efficient procedure.

The original purification process used by the McHale lab has been replaced with reverse-phase medium pressure liquid chromatography (MPLC). MPLC allows for separation of larger quantities of biological molecules in less time. The first attempts at using the MPLC lacked sufficient separation however. The column was packed with C-18 silica bonded gel particles obtained from Scientific Inc. (RTSI-533) and an eluent of 20-40% (v/v) MeOH in water was required for maximum separation. While this method was an improvement from the Sephadex column, the separation was not as acute as desired. The first eluted fraction was inter-mixed with yellow and pink pigments, and the last eluted fraction usually contained appreciable amounts of indicaxanthin, identified by UV-Vis spectroscopy.

The current method of separation utilizes the MPLC and Nacalai Tesque’s 75C18-OPN column packing. The unique characteristic of this packing when compared to other silica bonded gels is that the particles’ external surface is hydrophobic, and internal pores within the particle are hydrophilic. A stationary phase for reverse-phase chromatography is often purely hydrophobic. This packing is advertised to work using
only water for the mobile phase, an auspicious trait given that betalains are highly soluble in water. Using only water as the eluent, the indicaxanthin separates out first and the betanin second with visually distinguishable separation of colors. The only problem is that betanin tended to adhere to the stationary phase for 5 and up to 10 minutes before eluting out, resulting in a very dilute purified betanin sample. This is easily corrected for by adding a small amount of MeOH to the eluent to prevent betanin from adhering too strongly to the stationary phase. Overall, this method provides quick separation of the betanin and indicaxanthin dyes from beets, and in high concentrations.

**Experimental**

**Obtaining Beet Extract**

Beets were purchased from the farmers market in Moscow ID. The beets were first peeled, homogenized in a blender, and strained to remove large solids. Smaller solids not removed by straining were removed by centrifuging. To separate the pigments from large water soluble molecules such as peptides and starches, Millipore Centriprep Ultracell-3K filters were used with centrifugation. The beet extract after this point consists primarily of the two betalain pigments found in beets: betanin and indicaxanthin. The beet extract is frozen for storage.

**Reverse-Phase Chromatography**

The flow rate of the MPLC was 18 mL/min and Nacalai Tesque’s Cosmosil 75C18-OPN silica bonded gel was used as the column packing. Beet extract
was run through the MPLC with 10% (v/v) MeOH in water as the eluent for minimal indicaxanthin removal. A greater purity but less concentrated solution can be obtained by eluting with only water, and running the sample through the MPLC one to two times.

**Dye Loading**

Dye loading of purified betanin versus beet extract was evaluated in two different ways: one, by measuring betanin’s absorbance on thin TiO$_2$ films and two, by desorbing the dye from TiO$_2$ films and measuring absorbance. All films were made with Degussa P25 TiO$_2$ by making a paste with dry ethanol and HNO$_3$, as described in Ref 2. Thin, transparent films were made with a 1:12 (w/w) ratio of P25 TiO$_2$ to dry ethanol and thicker films with a 1:5 (w/w) ratio. The thicker films were approximately 10 µm thick. Both TiO$_2$ pastes were applied to fluorine-doped SnO$_2$ (FTO) glass substrates via the doctor blade technique.

For comparing absorbance of betanin on TiO$_2$ films, a single 25mm x 75 mm thin TiO$_2$ film (1:12 (w/w) TiO$_2$ to ethanol) cast on FTO glass was cut into three pieces. Two of the cut films were first treated in acidic ethanol made with 0.5 M HCl for one hour and then soaked in either purified betanin or un-separated beet extract. Dye solutions were adjusted to have the same betanin concentration before inundating the films. The third un-sensitized cut piece was used as a reference. Dye absorption on TiO$_2$ was measured with UV-Vis spectroscopy on a Shimadzu UV-2501 spectrometer. Indicaxanthin data was not included in this experiment because preliminary tests failed to detect its absorbance on TiO$_2$ films.
Comparing the relative amounts of betanin desorbed from TiO$_2$ films (1:5 (w/w) TiO$_2$ to ethanol) was carried out by using similarly sized films sensitized with either purified betanin (using 10% MeOH eluent with one run through the MPLC) or un-separated beet extract. The purified solution intentionally had a lower betanin concentration than the un-separated beet extract. Dye sensitization of the films was carried out in the manner described previously, and allowed to soak in the dye solutions for 1 hr. The dye was desorbed by soaking the films in 1 mM KOH, as betanin will dissociate from TiO$_2$ in basic conditions. Betanin’s peak absorbance wavelength ($\lambda_{\text{max}}$) shifts to 550 nm when deprotonated at basic pH, so an equivalent volume of 1 mM HCl was added to ensure $\lambda_{\text{max}}$ would be at 535 nm for absorbance measurements and quantification of dye loading. Water was used as a reference.
Results & Discussion

Effectiveness of separation by MPLC

![Normalized Absorbance vs Wavelength](image)

The amount of indicaxanthin separated with the MPLC can be quantified by comparing normalized absorbance spectra of the un-separated beet extract and that of separated betanin. Betanin’s $\lambda_{max}$ is at 535 nm with a high molar absorptivity of 65,000 $M^{-1} cm^{-1}$, while the $\lambda_{max}$ of indicaxanthin is at 482 nm with a molar absorptivity of 42,000 $M^{-1} cm^{-1}$. Beer’s Law is used to quantify betanin’s concentration in un-separated beet extract, but because indicaxanthin’s absorbance spectrum overlaps with that of betanin, an equation has been developed in Ref. 5 to quantify its concentration:
\[ [\text{In}] = 23.8A_{482} - 7.7A_{536} \]  

Eqn. 1 uses the absorbance (A) of a betanin/indicaxanthin spectrum at 482 nm and 536 nm. The concentration of indicaxanthin ([In]) is calculated in \( \mu \text{M} \). The molar ratio of indicaxanthin to betanin present in the un-separated beet extract is 0.59. After being run through the MPLC one time with a 10% MeOH (v/v) eluent, this ratio decreases to 0.18, or approximately by 70%; this represents a lower range of the amount of indicaxanthin that can be removed from beet extract. To deduce the upper limit of indicaxanthin removal, beet extract separated a first time with 10% (v/v) MeOH, and then a second time using only water (spectrum not shown in Fig 1). The final molar ratio of indicaxanthin to betanin using this method was 0.076, or the removal of about 87% of indicaxanthin.
Dye loading

The dye loading of betanin increases with the greater purity of the sensitizing solution. The TiO₂ film sensitized in purified betanin has a much greater absorbance maxima than did the film sensitized in un-separated beet extract. No absorbance of indicaxanthin was detected and therefore, is not included in Fig. 2. The presence of indicaxanthin clearly has an effect on the adsorption of betanin to TiO₂, but does not appear to adsorb in detectable quantities itself.

The effect of indicaxanthin removal was also confirmed by desorbing betanin from sensitized TiO₂ films. Fig. 3 further supports the statement the purifying betanin substantially improves dye loading. Two films of approximately the same surface area are compared in Fig. 3. The 3.37 cm² film is soaked in purified betanin, and the 3.40 cm² film is soaked in beet extract with a much higher betanin concentration. Although the
larger film was soaked in a solution with an overall greater concentration of betanin, much less betanin is desorbed from the film than from the smaller film soaked in purified betanin. The calculated betanin dye loading of the TiO₂ film soaked in purified betanin is $2.33 \times 10^{-8}$ mol/cm², compared to $8.39 \times 10^{-9}$ mol/cm² for the filmed soaked in un-separated beet extract.

![Absorbance vs Wavelength](image)

**Fig. 3.** Absorption of a 3.40 cm² TiO₂ film sensitized in a solution of un-separated beet extract (filled circles) and the betanin desorbed from that film (empty circles). Also, a 3.37 cm² TiO₂ film sensitized in a solution of purified betanin (filled squares) and the betanin desorbed from that film (empty squares).

**Conclusions**

The current method of reverse phase MPLC can remove approximately 70-90% of indicaxathin from beet extract depending on the eluting solvent and if the sample is run through the column once or twice. Greater purity yields of betanin significantly increase dye loading on TiO₂. A solvent mixture of 10% (v/v) MeOH in water as the mobile phase results in a lower purity of betanin, but higher concentration; this method is
recommend for fabricating DSSCs. Using only water as the mobile phase results in higher purity betanin but a more dilute solution; this method is recommended for fluorescence and Raman experiments.
References


Chapter Four

Improved Efficiency of Betanin-Based Dye-Sensitized Solar Cells

Abstract

An improved separation technique employing medium pressure liquid chromatography is used to purify betanin from beet root for use as a sensitizer in a TiO$_2$-based dye-sensitized solar cell. The use of a blocking layer and treatment by TiCl$_4$ were explored in order to optimize the performance of the solar cell, resulting in energy conversion efficiencies as high as 2.7%, the highest yet recorded for a natural dye sensitizer. The fluorescence spectrum of betanin in aqueous solution is reported as a function of added colloidal TiO$_2$, demonstrating efficient electron injection. Quenching of betanin’s fluorescence by TiO$_2$ permits the observation of its resonance Raman spectrum, reported here for the first time and discussed in light of recent theoretical work on the electronic structure of betanin. Solar cells sensitized by purified betanin were subjected to stability tests and methods to extend the lifetime of these solar cells are proposed.

Introduction

Since the first report of dye-sensitized solar cells (DSSCs) in 1991,$^1$ metal-centered dyes have been the best performing and most widely researched sensitizers, with energy conversion efficiencies as high as 11%.$^{2,3}$ Ruthenium-centered polypyridyl metalorganic complexes have been favored in DSSCs because of their strong absorption of visible light, favorable spatial separation of HOMO and LUMO (permitting rapid
electron injection and slower recombination), and because they can be repetitively oxidized and reduced without degradation. However, Ru is a rare metal making any future industrial application of Ru-based dyes resource limited and cost prohibitive. Additionally, the environmental and economic costs of using a heavy metal in the DSSC strongly mitigate their main potential advantages over conventional silicon solar cells. The efficiencies of DSSCs containing synthetic organic dyes have approached those incorporating metal centered dyes, but synthesis still contributes to the production costs. Ideally, natural plant pigments serving as sensitizers have the potential to improve the economic and environmental benefits of the DSSC, but so far natural dyes have not been able to compete with synthetic dyes in terms of efficiency. However, despite lower efficiencies, the benefits of natural dyes will be realized if a greater output of electricity per unit cost can be obtained.

Much of the research on natural sensitizers has focused on either chlorophyll or anthocyanin pigments. These have typically resulted in energy conversion efficiencies of less than 1%. Prior to this study, the highest conversion efficiency for a DSSC sensitized with a natural dye was the rhoeo spathacca (sw) stearn pigment (1.49%), whose molecular structure is based on the porphyrin ring of chlorophyll. Recently, 5.4% conversion efficiency has been obtained by co-adsorption of two synthetic dyes obtained from chlorophyll precursors which were extracted from plants and then altered to enhance their light-harvesting.

Another class of plant pigments with great potential for solar energy conversion are betalains, consisting of the red betacyanins and yellow betaxanthins. The reddish-purple pigment betanin (Fig. 1) is a betacyanin. Betanin obtained for example from beet
root, has a maximum absorbance at 535 nm with a molar absorptivity of 65,000 M$^{-1}$cm$^{-1}$. Betalains are thought to serve the same functions in plants as anthocyanins, acting as “sunscreen” and antioxidants.$^{14,15,16}$ We recently reported the first application of the betalain class of plant pigments in a DSSC, in which red beet root pigments containing betanin were employed to obtain a maximum energy conversion efficiency of 0.67%. In this work, an improved separation method and efforts to reduce charge recombination have resulted in betanin-based DSSCs displaying efficiencies as high as 2.7%. Improved separation of the pigment from the plant extract results in better dye adsorption to the TiO$_2$ film and hence improved light harvesting.

The reddish-purple pigment betanin Fig. 1 is commonly found in beets, bougainvillea flowers and the prickly pear; in most cases coexisting with another yellow or orange betaxanthin dye.$^{15,16}$ A recent calculation shows that the visible transition is well-described as a HOMO $\rightarrow$ LUMO excitation which moves electron density from the aromatic ring to the dihydropyridyl moiety.$^{18}$ The strong absorption of visible light associated with this transition is already taken advantage of by the food industry in the use of betanin from beets as a food coloring. (The pigment is “generally recognized as safe” by the US Food and Drug Administration.) In previous work, we found that yellow indicaxanthin adsorbs preferentially to the TiO$_2$ film, limiting the dye-loading of betanin, which has more favorable light-harvesting properties than the yellow pigment.$^{17}$ Dye loading of betanin was improved by acid treatment of the TiO$_2$ film to facilitate adsorption through the COO$^-$ groups on the molecule. In this work, we developed an improved chromatographic method for separating betanin from indicaxanthin and other
components of beet extract, resulting in an increased performance of betanin based DSSCs compared to our 2008 study.

Improved cell performance in this work can also be attributed to efforts to reduce charge recombination (CR) and improve electron transport (ET), which invariably relates to the overall efficiency of the cell. A typical nanoporous TiO$_2$ film contains numerous surface defects which permit CR to occur at the semiconductor/electrolyte interface.$^{21}$ One commonly used method to enhance ET and hinder CR is the post-treatment of TiO$_2$ films with aqueous TiCl$_4$.$^{19,20,21,22}$ The TiCl$_4$ undergoes hydrolysis to deposit nanoparticulate TiO$_2$ into the film which crystallizes upon sintering. This treatment eliminates defect sites$^{23}$ and results in better inter-particle connections and hence a greater rate of ET through the semiconductor.$^{24}$ The porosity of the film can also allow the electrolyte to permeate through it and directly come into contact with the fluorine-doped SnO$_2$ (FTO) glass anode, where CR is likely to occur. A common modification to prevent CR at this interface is the incorporation of a blocking layer,$^{25}$ in which a thin layer of TiO$_2$ is applied directly on the conductive glass substrate to establish a physical barrier between the substrate and the electrolyte. The importance of a blocking layer is speculated to be greater for comparatively smaller and more planar organic dyes than for the larger Ru-centered dyes.$^{26}$
It is reasonable to expect that betanin binds to TiO$_2$ through at one or more of the three carboxyl groups on the molecule’s structure. Given the above-mentioned theoretical interpretation of the visible transition, binding through the two carboxylate groups on the dihydropyridyl function would be especially favorable because this would place the LUMO relatively close to the TiO$_2$ surface and the HOMO farther away, favoring injection over geminate recombination. The resonance Raman spectrum of betanin, which has not been previously reported, has the potential to reveal how betanin binds to TiO$_2$. In addition, with the help of the analysis of vibrational modes and their reorganization energies from Ref. 18, the resonance Raman spectrum provides insight into the change in molecular geometry that accompanies electronic excitation. As shown
here, however, betanin’s fluorescence presents a serious obstacle to observing its resonance Raman spectrum. In this work, quenching the fluorescence of betanin not only makes it possible for a resonance Raman spectrum to be acquired, it also reveals the efficiency of electron injection from the dye to TiO₂.

Much is known about the stability of betanin in solution due to its use as a food colorant, but no previous research has focused on its long term stability under the conditions it would be exposed to in a DSSC. Factors that contribute to the degradation of betanin in solution include elevated temperatures, exposure to oxygen, light exposure, and pH sensitivity. Betanin is most stable at pH 3.5-5 in aqueous solution, a pH range in which it exhibits resilience to elevated temperature and light exposure. Thus while local pH of an acid-treated TiO₂ film is favorable to betanin stability, one must also be concerned with the ability of the molecule to withstand repeated oxidation and regeneration without degradation – a major concern with organic sensitizers. Cyclic voltammetry of aqueous betanin reveals three anodic waves at 404, 616, and 998 mV versus Ag⁺/AgCl with the shape of the voltammogram suggesting irreversible oxidation. Nevertheless, our previous studies of betanin-sensitized DSSCs suggested that the iodide ion in the electrolyte is capable of regenerating betanin in a working solar cell. Preliminary experiments reported here show that a sealed betanin-based DSSC can last up to four hours under continuous illumination with no loss of efficiency.

In this work, we present photocurrent-photovoltage (I-V) and photocurrent action spectra (IPCE) for DSSCs sensitized with purified betanin obtained from beet roots using medium pressure liquid chromatography (MPLC). Resonance Raman and fluorescence spectroscopy are presented and interpreted to gain insight into the excited electronic state
structure and efficiency of electron injection into TiO₂. We present the results of stability tests and provide evidence for the potential of betanin to serve as an economical and nontoxic alternative to Ru-centered dyes in DSSCs.

**Experimental**

**Dye extraction and purification**

Locally grown beets were purchased from the Farmers Market or the Moscow Food Co-op in Moscow, ID. The beets were peeled, sliced and homogenized in a blender with potassium phosphate buffer, pH 6. Approximately 50-100 mL of buffer solution was mixed with 2-4 beets and blended into a puree. Large solids were separated from liquids by straining the puree through cheesecloth. The juice from the beets was collected and centrifuged for an hour to remove additional solids. The remaining liquid was centrifuged again using Millipore Centriprep Ultracell-3K filters to concentrate the betanin and indicaxanthin pigments. The two pigments were separated using reverse-phase medium pressure liquid chromatography (MPLC) with Nacalai Tesque’s Cosmosil 75C₁₈-OPN as the stationary phase and a mobile phase of 90% water and 10% methanol by volume. Indicaxanthin elutes first and betanin tends to adhere strongly to the stationary phase unless some methanol is added to the eluent. As described below, pure water was used as the eluent to obtain more pure but more dilute solutions of betanin for fluorescence and resonance Raman experiments.
Fabrication of DSSCs

Surfactant-free TiO$_2$ films were made from a 1:5 ratio by mass of Degussa P25 TiO$_2$ in dry ethanol and applied to fluorine-doped SnO$_2$ (FTO) conductive glass (Hartford Glass) by the method described in Ref. 31. Following this procedure, the TiO$_2$ powder was first heated up to 450°C for 30 min and cooled to room temperature before immediately mixing with the dry ethanol. The paste was magnetically stirred between 1 and 21 days before being applied to the FTO glass substrate via the doctor blade technique. In this common casting method, scotch tape spacers are placed on the long edges (75 mm sides) of clean FTO glass. The paste is applied on one end and dispersed along the film using a straight edge. The tape is removed and the films are sintered at 450°C for 1 hour. Films made by this method without any additional procedure will be referred to as unmodified films and are approximately 10 µm thick. Two types of film modifications were evaluated. The first modification employed post-treatment of the TiO$_2$ electrode with aqueous TiCl$_4$ (Aldrich, 99.9% pure). In this procedure, TiCl$_4$ was added drop-wise to chilled water under stirring to make a solution with a final concentration of 0.1 M. Unmodified TiO$_2$ films were then soaked in this solution for 12 hours under refrigeration before being rinsed with ethanol and sintered at 450°C for 1 hour. The other modification employed in this study was the application of a blocking layer to FTO glass anode. The blocking layer was made by soaking the bare glass in a 0.1 M solution of TiCl$_4$ for 12 hours under refrigeration to deposit a thin TiO$_2$ layer on the glass surface. The film was then rinsed with ethanol and sintered for 30 minutes and allowed to cool back to room temperature. After this initial step, a layer of Degussa P25 TiO$_2$ paste was applied by the doctor blade technique and the film was then sintered at
450 °C for 1 hour. The counter electrode was made by drop casting 5 mM H$_2$PtCl$_6$ in isopropanol onto FTO conductive glass, evaporating the solvent at room temperature, and then sintering at 450 °C for 30 minutes. All electrolyte solutions consisted of 0.5 M I$_2$ and 0.05 M LiI dissolved in either dry 3-methoxypropionitrile (MPN) (Acros, 98% pure) or acetonitrile (ACN) (Acros, 99.9% pure) solvents. The TiO$_2$ films were sensitized by first being soaked in an acidic solution of 0.5 M HCl in dry ethanol for one hour before immediately being transferred into a solution of purified betanin for a minimum of one hour at room temperature or overnight under refrigeration. Films can be stored in this way for several days.

**Absorbance measurements**

A Shimadzu UV-2501 spectrometer was used for absorption studies, a water reference was used for spectra of solutions or an unsensitized TiO$_2$ film as a reference for transmission spectra of betanin on TiO$_2$. For measuring the absorption spectrum of sensitized films, a more dilute paste was made from a 1:12 (w/w) ratio of Degussa P25 TiO$_2$ to dry ethanol, in order to make thinner, more transparent films than those described above. The diluted paste was applied to a quartz substrate by the doctor blade technique. The 75 mm by 25 mm films were cut in half; one half was sensitized with betanin dye while the other half was used as a reference for absorption spectroscopy to attempt to subtract out the extinction due to scattering by TiO$_2$. Sensitized betanin was exposed to the air for no more than five minutes while the absorbance was being measured. The absorption of betanin on a film of regular thickness (~10 μm, using 1:5 (w/w) TiO$_2$ to ethanol) was also measured using a diffuse reflectance set-up on a PerkinElmer
Uv/Vis/NIR spectrometer with a Labsphere Teflon reference reflector (USRS-99-020) with a 99% reflectance factor. Reflectance (R) was converted to absorbance using \( \log(1/R) \). Using Eqn. 1, the absorbance of a unsensitized TiO\(_2\) film was subtracted from that of a betanin sensitized TiO\(_2\) film to account for scattering and accurately calculate the absorbance spectrum of betanin on a TiO\(_2\) film.

\[
\log\left(\frac{1}{R}_{\text{bet}}\right) = \log\left(\frac{1}{R}_{\text{bet/TiO}_2}\right) - \log\left(\frac{1}{R}_{\text{TiO}_2}\right) \quad (1)
\]

**Characterization of DSSCs**

Current-voltage measurements of DSSCs were made by illumination with 13 mW incident light from a 75 W Xenon Lamp. UV and IR filters were placed in front of the sample and the illumination area was 0.126 cm\(^2\). Current and voltage were measured using a Keithly 2400 source meter, and incident light power was measured using a Melles Griot bolometer. Reported power conversion efficiencies are based on the incident light and are not corrected for the absorption of the FTO glass. Energy conversion efficiencies (\(\eta\)) were calculated by:

\[
\eta = \frac{V_{\text{OC}}I_{\text{SC}}FF}{P_{\text{in}}} \quad (2)
\]

where \(V_{\text{OC}}\) is the open-circuit voltage (V), \(I_{\text{SC}}\) is short-circuit current density (A/cm\(^2\)), \(FF\) is the fill factor, and \(P_{\text{in}}\) is the incident light power density (mW/cm\(^2\))

DSSC longevity was preliminarily tested by continuous illumination to light in a closed circuit. Because the DSSCs were not sealed, MPN was used as the electrolyte solvent for its low volatility compared to ACN. More MPN was added when significant drops in \(\eta\) occurred.
Wavelength-dependent incident photon-to-current quantum efficiencies, IPCE(λ), were measured using a PTI Quanta Master fluorimeter with a 75 W Xenon arc lamp source. Light was filtered with the fluorimeter’s excitation monochromator with 1200 l/mm gratings. Following the procedure described in Ref. 17, $P_{in}$ was measured with a ThorLabs Optical Power Meter PM120 over an illuminated area of 0.126 cm$^2$, scanning from 800 to 400 nm and recording power readings for every 2 nm. The power meter was replaced with a DSSC and scanned across the same wavelengths, recording the $I_{SC}$ with the source meter. The power and photocurrent from the two scans were inputted into the following formula:

$$IPCE(\lambda) = \frac{1240.6I_{SC}}{P_{in}\lambda}$$

where $\lambda$ is the wavelength of the incident light in nm.

Fluorescence and resonance Raman studies

Fluorescence of betanin in aqueous solution was obtained using a PTI Quanta Master fluorimeter with a 5 nm slit bandpass. Betanin samples were purified as much as possible in MPLC using only water as an eluent, causing betanin to stick firmly to the stationary phase for a longer period of time to obtain a higher purity but more dilute solution. The betanin solution was run through the MPLC twice using only water as the eluting species, in each case collecting only the tail end of the separated betanin to ensure maximum purity.

Colloidal TiO$_2$ was added to betanin solutions to quench its fluorescence. The TiO$_2$ colloidal solution was made by adding TiCl$_4$ to chilled water drop-wise under stirring so that the final TiO$_2$ concentration reached the desired molar ratio of betanin to
TiO$_2$. Particle size was confirmed by evaporating a 9.145 mM colloidal TiO$_2$ solution on a quartz slide and analyzed with atomic force microscopy (AFM), revealing particles to be about 16 nm in diameter.

Fluorescence and resonance Raman (RR) studies of betanin-sensitized TiO$_2$ colloids were excited using a Lexel argon ion laser operating at 528.5 nm for fluorescence and 514.5 nm for resonance Raman, both at 10 mW. A slightly shorter wavelength was used for the RR measurement to minimize interference from the residual betanin fluorescence. Scattered light was reduced with a notch filter and emission was detected with a SPEC-10 single monochromator and CCD detection. The absorption spectrum of the purified betanin was measured to determine the concentration. Colloidal TiO$_2$ was added to the betanin solutions to obtain various molar ratios of betanin to TiO$_2$ as reported below. Fluorescence spectra were taken with a 1 s exposure time and one accumulation, using magnetically stirred solutions to minimize dye degradation. RR spectra were obtained using a backscattering light geometry and solutions with a maximum absorbance of $A \approx 1$ for a 1 cm path length cell. A molar ratio of 1:100 betanin to colloidal TiO$_2$ was used to obtain sufficient quenching of betanin fluorescence. The suspension of betanin-sensitized colloidal TiO$_2$ was flowed through a cuvette from a reservoir that was kept chilled in ice-water. Reported RR spectra were obtained by 10 accumulations of 30 s exposure time.
Results & Discussion

Absorbance spectra

Fig. 2 shows the absorption spectra of three betanin-sensitized films compared to that of aqueous betanin in the insert. The absorption spectrum of the solution phase dye peaks at about 535 nm. As in our previous work, the spectrum of the adsorbed dye is broader compared to betanin in solution, but in this work we observe a blue-shift in the spectrum of the adsorbed dye rather than the previously reported red-shift. While it is not clear what the origin of this difference is, we speculate that the less pure samples used in Ref. 17 might have resulted in blocking of potential betanin adsorption sites by
components of the extract which are not present in this work. Dye absorption on TiO$_2$ is probably quite inhomogeneous owing to a range of binding sites. Many sensitizers are red-shifted on adsorption on TiO$_2$, and the basis for this blue-shift is not readily apparent. Future work will explore the possible occurrence of dye aggregates on the surface as reported for example in a carotenoid-sensitized TiO$_2$ film as reported in Ref. 32.

Discrepancies in absorbance spectra of the thin betanin sensitized TiO$_2$ films measured in either ethanol or air arise from scattering. The peak absorbance of the film measured in ethanol is slightly blue shifted than when measured in air and is also narrower, owing to the refractive index of ethanol which reduces the effects of light scattering in TiO$_2$. Diffuse reflectance of a betanin sensitized film of the same thickness used to make DSSCs (~10 µm) was measured to better ascertain the true absorbance spectra of a betanin DSSC. The diffuse reflectance spectrum is similar to the $\lambda_{\text{max}}$ of the thin film in air, but overall exhibits a broader spectrum. In all cases, the $\lambda_{\text{max}}$ for betanin on TiO$_2$ is a broad peak between 492 and 500 nm.
Photocurrent and photovoltage measurements

Fig. 3. Comparison of photocurrent vs. photovoltage of betanin-sensitized DSSCs using the solvents MPN (left) and ACN (right). DSSCs were made from TiO$_2$ electrodes that were unmodified (squares), TiCl$_4$-treated (circles), and incorporating a blocking layer (triangle).

Photocurrent-photovoltage data for DSSCs containing unmodified, TiCl$_4$-treated, and blocking layer films are shown in Fig. 3 and summarized in Table 1. As in DSSCs using Ru-based dyes for sensitizers,$^{31}$ the best performing solar cells contain either MPN or ACN as electrolyte solvents. In this study, the cells using ACN routinely have a higher $\eta$ than their MPN counterparts but there is not a clear trend in the $I_{SC}$, $V_{OC}$, and $FF$ data to account for this. The highest $FF$ value of 0.61 was observed in the presence of MPN and a blocking layer, while the highest $I_{SC}$ was 13.9 mA/cm$^2$ for the blocking layer/ACN DSSC. These $I_{SC}$ values are comparable with those of Ru-based dyes, however, betanin-based DSSCs only have a maximum $V_{OC}$ of 0.44 V, compared to
around 0.7 to 0.8 V for the Ru-based dyes.\textsuperscript{33} Since recombination limits both the maximum current and the maximum voltage, higher values of $I_{SC}$ and $V_{OC}$ tend to go hand-in-hand. For example, the blocking layer/ACN cell had the highest $I_{SC}$, but one of the lower $V_{OC}$’s. Contrarily, the blocking layer/MPN cell had one of the lower $I_{SC}$’s, but a high $V_{OC}$. It is more than feasible to conjecture that a betanin DSSC can have a relatively high $I_{SC}$ and $V_{OC}$. This suggests that further gains in the efficiency of the betanin-sensitized solar cell could be realized if this recombination could be limited.

Focusing on increasing the $V_{OC}$ is also necessary to any future attempts to maximize $\eta$. Many methods have been employed with other dyes and are worth considering for betanin DSSCs.\textsuperscript{34,35,36,37,38}

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Film modifications</th>
<th>$I_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>$FF$</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
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<td>0.39</td>
<td>0.51</td>
<td>1.46</td>
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<tr>
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<td>TiCl$_4$</td>
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<td>0.36</td>
<td>0.55</td>
<td>1.93</td>
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<td>Blocking Layer</td>
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<td>0.44</td>
<td>0.61</td>
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Incident photon-to-electron conversion efficiencies

Fig. 4. IPCE(λ) for DSSCs with unmodified (squares) and TiCl$_4$ treated (circles) TiO$_2$ electrodes, and incorporating a blocking layer (triangles). Electrolyte solution contained I$^-$/I$_3^-$ in MPN for all samples.

Fig. 3 shows the photocurrent action spectra, IPCE(λ), for DSSCs containing MPN as electrolyte solvent. In all cases, the maximum IPCE(λ) of about 0.8 to 1 is obtained at the same wavelength, about 490-500 nm, as the peak in the absorption spectrum. The highest IPCE is obtained for the DSSC incorporating a blocking layer, and appears to slightly exceed 100%. Note that these values are not corrected for the absorption and reflection of incident light by the conductive glass, which should reduce the incident light power by as much as 20%. Indeed, in our hands, the maximum IPCE of an N3-based DSSC, which approaches 100% after correcting for absorption and reflection by the glass anode, is only about 60-70% owing in part to these loss factors. These considerations strongly suggest that betanin can inject more than one electron per photon, as betanin is capable of expending up to two electrons without being irreversibly
oxidized.\textsuperscript{30} Obtaining up to two electrons per photon absorbed would explain how recombination could limit the maximum obtainable photovoltages despite the high photocurrents obtained.

Fig. 5. Comparison of the absorption of a betanin sensitized TiO\textsubscript{2} film (empty squares) and the IPCE(\(\lambda\)) for a DSSC with an unmodified TiO\textsubscript{2} electrode. The IPCE(\(\lambda\)) is as it appears in Fig. 4. The absorption spectrum is of a betanin sensitized film measured with diffuse reflectance is taken from Fig. 2. Absorption spectra is fitted to the IPCE(\(\lambda\)) spectrum by setting the absorbance to an equivalent value of intensity at 500 nm and normalizing all other wavelengths accordingly.

Fig. 2 notes spectral discrepancies in the absorption spectra of betanin sensitized TiO\textsubscript{2} films based on thickness and light scattering. The IPCE(\(\lambda\)) of a DSSC should closely resemble its absorption spectrum. Fig. 5 compares the absorption spectrum of the betanin sensitized film measured by diffused reflectance (also appearing in Fig. 2), to the IPCE(\(\lambda\)) spectrum of a betanin DSSC with an unmodified TiO\textsubscript{2} electrode (also appearing in Fig. 4). The absorption spectrum obtained by diffuse reflectance, was fitted to the IPCE(\(\lambda\)) spectrum so that the absorbance and intensity are equal at 500 nm. The region between 500 and 700 nm for each of the spectra closely match one another. The spectra
are also similar between 400 and 460 nm, but offset marginally. The peak at 475 nm appearing in the IPCE(λ) spectrum does not match with the \( \lambda_{\text{max}} \) of the betanin sensitized TiO\(_2\) films. The IPCE(λ) peak at 475 nm is in fact an artifact arising due to an error at that wavelength in the calibration file of the power meter and is not an accurate representation of the true IPCE(λ) maximum. Due the similarities between absorption and IPCE(λ) at all other wavelengths, the true IPCE(λ) peak is expected to be a broad peak between 490 and 500 nm. The artifact is left intact because there was not a legitimate means of removing it.

**Fluorescence**

Despite a report that betanin itself does not fluoresce,\(^{39}\) our lab has found that it is fluorescent. Difficulties in obtaining fluorescence data for betanin by other researchers may be attributed to a residual betaxanthin pigment, depending on the pigment source and separation method. For this study, as much residual indicaxanthin was removed with the MPLC as possible before fluorescence was measured; this is not to say that indicaxanthin was completely removed, as small amounts are expected to be present. The peak emission of betanin is at 608 nm and the peak excitation is at 525 nm in Fig. 6. A completely pure sample of betanin would be expected to have an excitation peak closer to betanin’s maximum absorbance of 535 nm. Furthermore, the excitation peak does not remain at 525 nm at detection wavelengths that are not close to 610 nm. For example, detecting the excitation peak at 790 nm will result in the peak position red-shifting, a further indication that residual indicaxanthin is present, due to the limitations of the MPLC. Previously, our lab has obtained a fluorescent spectrum of betanin with an
excitation peak at 528 nm from beets specially breed to have high betanin content (data not shown).

Fig. 6. Fluorescence emission (empty squares) and excitation (filled squares) of betanin obtained from beets with residual indicaxanthin present. Samples were excited at 535 for the emission profile and detected at 610 nm to obtain the excitation profile.

Fig. 7 compares fluorescence profiles of purified indicaxanthin and betanin with residual indicaxanthin. The emission profile of betanin will not change with residual indicaxanthin, but the excitation peak will blue shift dramatically to more closely match that of indicaxanthin. The excitation peak of purified indicaxanthin is at 466 nm, with an emission peak of 508 nm. If a betanin sample has significant residual indicaxanthin present, the excitation peak more resembles that of the purified indicaxanthin with a peak at 472 nm when detected at 610 nm. The emission peak will still resemble that of betanin with a peak at 610 nm when excited at 535 nm.
The small Stokes shift of the fluorescence of betanin makes the measurement of its resonance Raman spectrum difficult. However, using colloidal TiO$_2$, this fluorescence can be quenched substantially as shown in Fig. 6. The weak peak at 645 nm is from the O-H stretch of water.

Fig. 7. a) Fluorescence emission (empty triangles) and excitation (filled triangles) of indicaxanthin. Sample was excited at 470 nm for the emission profile and detected at 510 nm for the excitation profile. b) Fluorescence emission (filled circles) and excitation (filled circles) of betanin with residual indicaxanthin. Sample was excited at 535 nm for the emission profile and detected at 610 nm for the excitation profile.
Fig. 8. Emission of varying molar ratios of betanin to colloidal TiO$_2$: dye only 0:1 (crosses), 1:5 (filled squares), 1:10 (filled circles), 1:25 (filled triangles), 1:100 (empty squares).
Resonant Raman measurements

Even after a large excess of TiO$_2$ is added to the betanin solution, the sample is still somewhat fluorescent so a background subtraction of the data is necessary. However, three peaks are more apparent and stand out even before the background subtraction. The peak at 1387, 1517, and 1603 cm$^{-1}$ in Fig. 9 are strong and representative of an aromatic ring on the molecule, and differ from those theoretically determined.$^{18}$ The other three smaller peaks at 1014, 1115 and 1157 cm$^{-1}$ are also indicative of another aromatic ring on the betanin structure. The peak at 562 cm$^{-1}$ is the lowest frequency and the only other consistent peak obtained. Ref. 18 suggests that other strong Raman peaks may be present between 0-500 cm$^{-1}$, a region which was not measureable with the method used.

Fig. 9. Resonance Raman spectrum of betanin with 1:100 molar ratio of betanin to TiO$_2$. Background subtracted from spectrum.
Fig. 10 shows the results of testing the stability of an unsealed solar cell. Unsealed solar cells were used to avoid the problems associated with hot-melt sealants which can degrade the dye. MPN was used as the electrolyte solvent because it is less volatile than ACN, nevertheless it was necessary to replenish the electrolyte periodically, as indicated by the X’s in Fig. 8. The efficiency and other parameters tended to rebound when solvent was added, but a general decline in the efficiency over time was observed. After about 8 ½ hours the conversion efficiency was decreased by 50%. The large dip in $\eta$ between 100-200 minutes results from solvent evaporation and leads to drops in $V_{OC}$. 
$FF$, and $I_{SC}$ that may be attributed to increased series resistance and decreased dye regeneration. This probably results in some irreversible dye degradation, reflected by the steady downward trend in $I_{SC}$ throughout the trial, decreasing at a greater rate than the conversion efficiency. As the $I_{SC}$ decreases, the $V_{OC}$ stays somewhat constant throughout the trial (when solvent is replenished) and the $FF$ tends to increase over time.

The amount of time the DSSC lasts indicates that the dye can withstand many oxidation-reduction cycles before its eventual decay. A calculation for the maximum amount of time a betanin DSSC could last without betanin’s regeneration is offered below.

$max\ electrons : 2.33 \times 10^{-8} \frac{mol}{cm^2} \times 0.126cm^2 \times 6.022 \times 10^{23} \frac{molec.}{mol} \times 3e^- \frac{molec.}{e^-} = 5.30 \times 10^{15} e^-$

electrons / second : $0.01 \frac{A}{cm^2} \times 0.126cm^2 \times \frac{6.242 \times 10^{18} e^- / s}{A} = 7.86 \times 10^{15} e^- / s$

$\text{time : electrons} \times (\text{electrons / second})^{-1} = 0.674s$

Assuming that the dye loading on the TiO$_2$ electrode is $2.33 \times 10^8$ mol/cm$^2$ (taken from Chapter Three), and the illuminated area is 0.126 cm$^2$, the total number of molecules in the illuminated area can be calculated using Avogadro’s number. If each molecule injects three electrons into the conduction band before the dye is completely and irreversibly oxidized, than a maximum of $5.30 \times 10^{15}$ electrons can be produced from the DSSC, assuming no recombination. If the initial $I_{SC}$ is 10 mA/cm$^2$, than $7.86 \times 10^{15}$ electrons are capable of flowing from the DSSC every second. Therefore, if the dye was not being reduced by the electrolyte, the DSSC would last at a maximum of 0.674 s. The
fact that a betanin DSSC can last for several hours strongly infers that the betanin molecule is undergoing repeated oxidation and reduction cycles, although eventually succumbing to decay. The ability to hermetically seal the solar cell will be an important step in future efforts to prolong the lifetime. Other ideas are discussed further in the next chapter.

Conclusions

Betanin sensitized solar cells have improved drastically from the previous experiment. With a current maximum 2.7% efficiency at this point, betanin is among the best performing natural dyes in terms of conversion efficiency. The next challenge lies in extending the lifetime of the DSSC’s, focusing in particular to the oxidative and regenerative properties of betanin of a TiO$_2$ surface. The method developed for taking a resonance Raman spectrum of betanin can be used to evaluate how the molecule binds to TiO$_2$ and ultimately the mechanism for electron injection into the TiO$_2$ conduction band.

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References


Chapter Five

Overall Conclusions

Overview

Prior to the work presented in this thesis, dye sensitized solar cells (DSSC) using natural dyes as sensitizers were characterized by low conversion efficiencies ($\eta$).\textsuperscript{1,2,3,4} Additionally, only one previous report used a betalain pigment as a sensitizer.\textsuperscript{5} While favorable results were obtained in regard to betanin-DSSC performance, there is still a great deal of challenges facing the practicability of not only betanin as a sensitizer, but for DSSCs in general. An ideal sensitizing dye has to be able to undergo oxidation and reduction cycles millions of times over and resist decay from stressing environmental factors such as temperature. In addition to relaying summarized experimental results, recommendations for future experiments and targeted areas of research are made. Summarizing the work presented is best relayed in five subtopics:

1) Using natural plant pigments and betanin as sensitizing dyes

2) The importance of purifying betanin and dye loading

3) Performance of betanin-DSSCs

4) Fluorescence and resonance Raman spectroscopy of betanin, applications for future experiments

5) Future work, improving DSSC performance and longevity

Subtopics 1-3 cover the important points and results for the complete DSSC research process, from purifying betanin to making an efficient DSSC. Subtopic 4 is not directly
applicable to improving DSSC performance, but presents a method that can be used to set up experiments that will probe electron transfer in the excited state betanin molecule into the TiO$_2$ conduction band. Lastly, subtopic five will discuss the most important issues facing the improvement of betanin-based DSSCs, and analogously all DSSCs made with sensitizers from natural plant pigments.

1) **Using natural plant pigments and betanin as sensitizing dyes**

   Natural plant pigments are undoubtedly the least expensive options for sensitizing dyes, but are currently characterized by low $\eta$’s. Of the four types of natural plant pigments, the most common types used in DSSCs are either chlorophylls or anthocyanins.$^{1,2,3,4,6}$ Before the work presented in this thesis was conducted, only one report used a betalain pigment as a sensitizer. The highest reported $\eta$ in that report was 0.67% using betanin,$^5$ and the highest $\eta$ published for any natural dye was 1.49%.$^6$ The work presented here includes a betanin-DSSC without any modifications made to the TiO$_2$ electrode with a $\eta$ of over 2.0% and the highest $\eta$ value reported for any natural dye of 2.7% by incorporating a blocking layer into the solar cells design.

   There are a variety of other natural pigments that have been used as sensitizers, and future research should be directed toward optimizing DSSC performance using these dyes in terms of efficiency and longevity.

2) **The importance of purifying betanin and dye loading**

   Overall, the conclusion that purifying betanin from indicaxanthin in beet extract improves dye loading on the TiO$_2$ films was agreed upon with the previous report.$^1$
However, the affirmation that indicaxanthin preferentially adsorbs to TiO$_2$ was questioned. The work presented in this thesis provides clear evidence that the presence of indicaxanthin negatively affects dye loading of betanin, but it could not be confirmed that indicaxanthin itself adsorbs very well to TiO$_2$. An absorbance spectrum of indicaxanthin on a thin TiO$_2$ could not be measured, nor could it be visually observed. Regardless, reverse-phase medium pressure liquid chromatography (MPLC) is a useful and effective method for fast purification of appreciable amounts of betanin. This method is useful for sensitizing several TiO$_2$ electrodes but is not recommended for acquiring ultra-high purity aliquots of betanin. A column packing of C-18 silica bonded gel with a hydrophobic exterior and hydrophilic interior pores was found to be favorable for betanin/indicaxanthin separation as opposed to an entirely hydrophobic C-18 silica bonded gel. The improved separation technique divulged in this thesis work is considered to be a major contributing factor in obtaining higher efficiencies, given the comparison to similarly constructed DSSCs in Ref. 5.

3) Performance of betanin-DSSCs

A major factor contributing to the significantly higher $\eta$ values from the original betanin-DSSC report, is the greater purity of betanin obtained as a result of using the improved reverse-phase MPLC separation method. Although open-circuit voltage ($V_{oc}$) values of up to 0.44 V were comparable to those in Ref. 5, the real increase in $\eta$ resulted from increases in current production, with a maxim short-circuit current ($I_{sc}$) of 13.9 mA/cm$^2$. The $\eta$’s of DSSCs improved in the order of having no modifications made to the TiO$_2$ electrode, to post-treatment with aqueous TiCl$_4$, and incorporating a blocking
layer. There is not however a clear trend in data for the factors that determine $\eta$; meaning that high or low $V_{oc}/I_{sc}$ values were not necessarily consistent with one another. The data does not rule out the possibility of obtaining maximum $V_{oc}$ and $I_{sc}$ values and such results can be expected in the near future.

4) Fluorescence and resonance Raman spectroscopy of betanin, applications for future experiments

Betanin is a fluorescent molecule, which makes it difficult to acquire a Raman spectrum. The fluorescence of betanin can be quenched with aqueous TiO$_2$. This information can be used to design experiments that measure the efficiency of electron injection from betanin to TiO$_2$. After quenching fluorescence, it is possible to measure the Raman spectrum of betanin and the first reported spectrum appears in this work. The method of quenching fluorescence with TiO$_2$ to measure the Raman spectrum can be used to probe the excited state structure of betanin, and hence betanin-TiO$_2$ bonding and electron transfer.

5) Future work, improving DSSC performance and longevity

There should be two primary areas of concern with betanin dye sensitized solar cell research moving forward, and these are increasing the $V_{oc}$ and extending their longevity. Both can be approached through already established methods.

Although the $I_{sc}$ for these solar cells are comparable with other types of dyes, the $V_{oc}$ remains much lower in comparison, as is the case for most natural dye sensitizers. The highest $V_{oc}$ obtained for a betanin DSSC is 0.44 V, many synthetic organic and
metal-organic dyes exhibit $V_{oc}$'s of 0.6-0.8 V.\textsuperscript{7,8,9} The maximum $V_{oc}$ possible in a DSSC is the difference in the energy of the conduction band and the redox potential of the redox couple. Therefore, increasing $V_{oc}$ is a matter of either raising the conduction band energy or using a different redox couple in the electrolyte. Given the effectiveness of the $I/I_3^-$ redox couple, the focus should be on raising the conduction band of the electrode.

One common method of increasing $V_{oc}$ is to add pyrimidine or pyridine to the TiO$_2$ paste used to make electrodes.\textsuperscript{10} Tert-butylpyridine (TBP) for instance, has been effective at increasing both the $V_{oc}$ and the overall $\eta$ of DSSCs, but these improvements are also accompanied by lower $I_{SC}$ values. Intercalation of TiO$_2$ particles with lithium is another interesting prospect.\textsuperscript{11} This method has been reported to significantly enhance the $V_{oc}$ with only very slight losses in $I_{SC}$. Another effective method is to apply a coating of Al$_2$O$_3$ to the TiO$_2$ electrode, which also acts to prevent charge recombination with the electrolyte interface.\textsuperscript{12} Other methods include using a co-adsorbant with a negative dipole moment, which correlates a higher TiO$_2$ conduction band, through the exact mechanism is debated.\textsuperscript{13,14} Co-adsorbants also have the positive effect of preventing dye aggregation where charge recombination is likely to occur.\textsuperscript{14,15}

Apart from hermetically sealing DSSCs, the most effective way to resist losses in efficiency is to use an electrolyte with little to no volatility. Gel electrolytes have successfully been used,\textsuperscript{16,17} as have solid state electrolytes\textsuperscript{18} and negligibly volatile ionic liquids.\textsuperscript{19,20} However, electrolytes consisting of solids, gels, or ionic liquids also offer slower rates of electron transfer and lower efficiencies.
References


