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Optimization of dye-sensitized solar cells (DSSCs) through co-adsorption and tri-adsorption of organic dyes

Saurin Kantesaria

North Carolina School of Science and Mathematics; 1219 Broad St, Durham NC

Key words: dye-sensitized solar cells (DSSCs), organic dyes, co-adsorption/tri-adsorption, conversion efficiency, band gap, HOMO/LUMO, IV curve, open circuit voltage, short circuit current

Author Summary: Today's world is lacking in greener methods of producing energy. Although traditional solar cells are used often, they are expensive, require complicated processes to manufacture, and are relatively inefficient. Dye-Sensitized Solar Cells (DSSCs), which mimic photosynthesis, provide a viable alternative in that they are inexpensive and can be made from simple procedures and easily attainable materials. The only drawback is their low efficiency when converting sunlight to electrical energy. The focus of my project was to optimize the dye through testing differing combinations of cheap, organic dyes within a DSSC to increase its efficiency and therefore its commercial viability.

Abstract

Although synthetic dyes are typically used in dye-sensitized solar cells (DSSCs), organic dyes provide a less expensive, and simple method of manufacturing such cells. The objective of this project was to produce a relatively low-cost DSSC with optimal conversion efficiency and a wide absorption spectrum through co-adsorption and tri-adsorption of inexpensive organic dyes. Four organic dyes (Pomegranate Juice, Anthocyanin, Rhodamine B, and Thymol Blue) were used as sensitizers on a titanium dioxide semiconductor film. Through measuring the absorption spectrum of varying ratios of these dyes, five cells were assembled through co-adsorption and one through a unique method of tri-adsorption. The photoelectrochemical properties (voltage, current, absorption spectra, fill factor, and conversion efficiency) of each were thereafter measured using appropriate equipment. These values reflected that open circuit voltages varied from 0.232 V to 0.464 V and conversion efficiencies ranged from 0.17% to 2.74%. The tri-adsorption of Pomegranate Juice, Anthocyanin, and Thymol Blue in a ratio of (65:43:2) produced the highest efficiency of 2.74%. This not only demonstrated that methods of co-sensitization and tri-sensitization could yield increases in conversion efficiency in organic DSSCs, but also that such cells could eventually become more commercially viable if optimized further using inexpensive approaches.

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* Email: saurin@live.unc.edu

Introduction

The field of solar cells is an ever-expanding area of interest today due to these cells' environmentally friendly method of producing energy through converting photons from sunlight to electrical energy. Despite this such cells are not very widely used in comparison to nuclear or fossil fuels as a source of power because they are inefficient in this process of converting sunlight to energy. Not only are traditional solar cells inefficient, (with conversion efficiencies typically around 15-20%), but they are also expensive, difficult to produce, and oftentimes utilize long and complicated methods to manufacture.

A new and emerging type of solar cell called a Dye Sensitized Solar Cell (DSSC) offers many benefits in comparison. They are simple to fabricate, inexpensive, and can be made from easily attainable materials such as blueberry extract to produce more commercially viable cells. Additionally, they can work indoors and function under indirect and diffuse light, even when clouds may obstruct the sun. The only drawback is that they have a low conversion efficiency in comparison, (with efficiencies ranging from 5-11% for synthetic DSSCs and 0.2-1.7% for organic DSSCs on average), however the fact that they are still in their prototype stage allows for a number of adjustments to be made to optimize these cells.

The DSSC itself consists of: a conductive glass substrate, a thin film semiconductor (typically TiO_2 paste), an organic or a synthetic dye that stains the semiconductor film, a counter-electrode catalyst, and an electrolyte as shown in the image below.

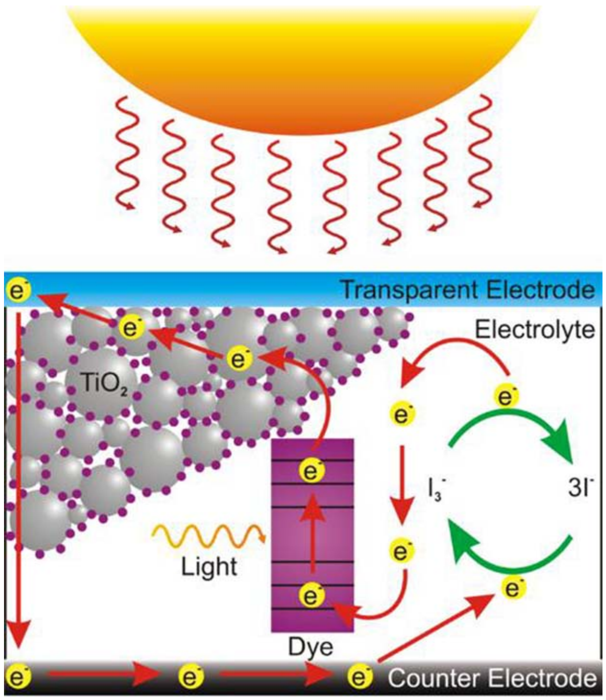

Figure 1. Diagram of DSSC Structure [10].

As a semiconductor, the film has a medium-sized gap between the conduction bands (lowest unoccupied molecular orbitals) and valence bands (highest occupied molecular orbitals) in each of its molecules referred to as a band-gap. Energy is produced when an excited electron moves from its highest occupied molecular orbital, to its lowest unoccupied molecular orbital and back. Therefore, the smaller the band-gap is, the higher the conductance (a conductor has an overlap in its conduction and valence bands allowing for the free movement of electrons between the two). The organic or synthetic dye itself is photosensitive and allows for a wide range of wavelengths of different photons to be absorbed and therefore allows for more electrons to become excited. These photons excite the dye molecules and cause them to lose an electron, which travels through the titanium dioxide and the anode to the cathode. As the electron travels from the anode, the conductive glass substrate, through a wire, it produces a current and powers devices that may be placed within the circuit. Because the dye has lost an electron, it will decompose if it does not receive one to fill the positive hole it has left. In its place, an electron from the electrolyte solution is donated to the dye and an electrolyte molecule becomes oxidized. In situations such as this, the electrolyte typically consists of the iodide and triiodide redox couple. The previous electrons cycling through the wire return to the cathode, the counter-electrode catalyst, and this same molecule of electrolyte is reduced to its original state when it receives these electrons. Through this cycle, a DSSC can produce power [6].

Although there are pieces of scientific literature that have shown success in optimizing several aspects of DSSCs utilizing synthetic dyes (mostly ruthenium-based metal-complex dyes), there are fewer that have done so with organic dyes [3]. This is because synthetic dyes alone have higher conversion efficiencies than organic dyes (around 5-8% in comparison to the 0.2-1.7% of organic dyes). Through a method called co-adsorption of such dyes, a mixture of two dyes in a certain ratio has been proven to increase both absorption spectrum and conversion efficiency in both organic and synthetic DSSCs [1]. Additionally, one piece of literature has been published that successfully utilized tri-adsorption, but only through the use of synthetic dyes [8]. The issue with the use of such dyes is that they are not only extremely expensive ($300-$500 for a small 50-250 mg bottle on average), but also that they require complicated, time-consuming processes to manufacture. In contrast, organic dyes are inexpensive, and more bountiful for use in DSSCs. Theoretically, if such methods can improve synthetic DSSCs, they can also improve organic DSSCs to the extent that, eventually, synthetic dyes will not be needed for their creation.

The goal of this project was to develop an effective, low-cost dye-sensitized solar cell in terms of cell voltage, current, conversion efficiency, fill factor, and absorption spectrum through use of co-adsorption and tri-adsorption of four, inexpensive, organic dyes (Rhodamine B, Thymol Blue, Pomegranate Juice, and Anthocyanin) with the hope of further improving this prototype technology to increase its potential commercial viability. It was predicted that the tri-sensitization of the three organic dyes of the highest conversion efficiencies would yield the maximum conversion efficiency overall due to its high absorption spectrum and therefore its ability to capture and convert more wavelengths of light into energy.

Materials and Methods

Initially, the solutions of each dye and the cells themselves had to be fabricated. 100% Pomegranate juice was purchased from a local grocery store whereas 0.5 mM ethanolic solutions of Thymol Blue and Rhodamine B were made from their corresponding salts. Additionally, Anthocyanin dye was made through crushing three blueberries in a solution of acetic acid, distilled water, and methanol in a 4:21:25 ratio by volume and filtering the resulting suspension. In order to prepare the solar cells themselves, FTO (Fluorine Tin Oxide) doped conductive glass slides were used as the substrate. To make the Titanium Dioxide paste, 6 g of Titanium dioxide powder was placed into a mortar and pestle to be uniformly mixed into a colloidal suspension by adding 1 mL increments of vinegar (serving as dilute acetic acid). Successively, a drop of Triton-100X was added as a surfactant to reduce the surface tension of the suspension. This paste was then spread across the conductive ends of each slide to produce a uniform layer and the finished slides were subsequently placed into a kiln to be annealed at approximately 450^{o}C for 15 to 20 minutes and to be cooled overnight.

In order to compare each dye solution, a UV-Vis Spectrophotometer was utilized to measure the absorption spectra of each individual dye as well as their corresponding co-sensitized and

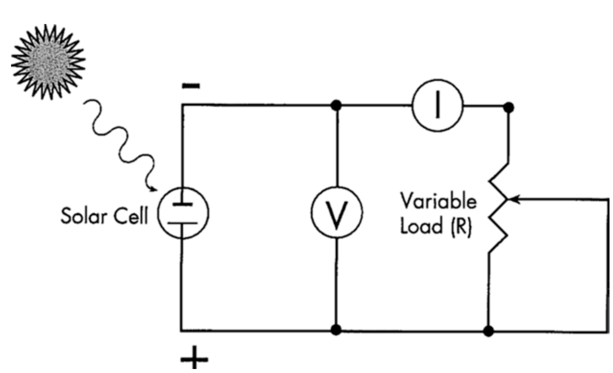

Figure 2. DSSC Short Circuit [9].

tri-sensitized solutions. The absorbance values of each were compared by recording the λ_{max} (maximum absorbance) as well as taking the integral of each absorbance curve. The latter method proved to be particularly useful when determining the most optimal ratio of dyes for the co-sensitizations and tri-sensitizations. For the individual dyes, Pomegranate juice was concluded to be the most efficient dye with a conversion efficiency of 1.5%, and a maximum absorbance of 2.942 at 410.6 nm. The best ratio for each co-sensitization was determined by creating 5 mL solutions of different integer ratios (thus, the four possible combinations were 1:4, 2:3, 3:2, and 4:1). The co-sensitized dye with the highest recorded absorbance yielded the lowest conversion efficiency (Pomegranate Juice and Anthocyanin in a 3:2 ratio, conversion efficiency of 0.17%). The highest conversion efficiency produced among the co-sensitized dyes was 1.30%, that of Anthocyanin and Thymol Blue in a 3:2 ratio. The most optimal ratio of the tri-sensitized dyes (Pomegranate Juice, Anthocyanin, and Thymol Blue) was then determined through a similar method as the co-sensitized dyes, except it was found through varied trial and error rather than a restricted number of ratios. After constructing each dye, the cells were assembled with carbon-coated counter-electrodes and potassium iodide electrolyte to be tested in both an open and a short circuits outside under direct sunlight. Direct sunlight was used as opposed to a lamp, due to the lack of one that would produce large enough current and voltage values to produce a proper IV curve and one that would prevent the drying of electrolyte as data was collected (any change in the electrolyte will also affect the voltage and current values therefore affecting the IV curve). Under direct sunlight, these problems weren't experienced; therefore enough points for a sufficient IV curve were gathered without having to replace the electrolyte. Also, supporting the consistency of this data, these types of solar cells work well under diffuse and indirect lighting and all IV curve data collection was performed at the same time of day in the same area, so the error in calculating the amount of light received was minimized. The following is a diagram of the short circuit constructed for obtaining voltage and current values.

Maximum voltage and current (V_{max} and I_{max}) were determined through use of an IV curve produced by plotting points of voltage vs current in LoggerPro recorded by two multimeters in a short circuit with the DSSC and determining the maximum power (voltage multiplied by current) achieved out of each of these values. The following equations were utilized for calculating fill factor and conversion efficiency respectively:

$$FF = \frac{Im * Vm}{Isc * Voc}$$

$$n = \frac{Isc * Voc * FF}{light\ intensity}$$

In this case, the light intensity, or incident light was assumed to be 100 mW/cm^2 since these values were recorded under the sun. Due to the ability of DSSCs to perform well even under diffuse or indirect light, any error caused by the variable angle of the sun was minimized. In addition to this, the values were recorded at approximately the same time in the same area each day to ensure precision of data. Several tables have been produced below of the recorded photoelectrochemical values of each DSSC:

Results

Table 1. Singular Dye DSSC Absorption Spectrum and Conversion Efficiency Information.

Dyes	Max Wavelength	Max Absorption	Literature Conversion Efficiency (n%)
Anthocyanin	457.7 nm	2.642	0.64
Pomegranate	410.6 nm	2.942	1.50
Rhodamine B	472.2 nm	1.968	1.26
Thymol Blue	457.7 nm	2.605	N/A

Table 2. Co-sensitized Dye DSSC Absorption Spectrum and Conversion Efficiency Information.

Dyes	Max Wavelength	Max Absorption	V_{oc}, I_{sc}	V_{max}	I_{max}	FF%	*n%*
Anthocyanin/Pomegranate (2:3)	398.5 nm 503.9 nm	1.861	.232 V .173 mA	.083 V	.080 mA	20.0	0.17
Anthocyanin/Thymol Blue (3:2)	424.4 nm	1.871	.425 V .371 mA	.182 V	.283 mA	32.7	1.30
Rhodamine B/Thymol Blue (1:4)	457.7 nm	2.641	.312 V .112 mA	.117 V	.108 mA	36.1	0.32
Rhodamine B/Pomegranate (4:1)	407.0 nm	2.367	.444 V .138 mA	.282 V	.086 mA	39.6	0.61
Thymol Blue/Pomegranate (1:4)	457.7 nm	2.778	.415 V .181 mA	.288 V	.128 mA	49.1	0.93

Table 3. Tri-sensitized Dye DSSC Absorption Spectrum and Conversion Efficiency Information.

Dyes	Max Wavelength	Max Absorption	V_{oc}, I_{sc}	V_{max}	I_{max}	FF%	*n%*
Anthocyanin/Pomegranate/Thymol Blue (43:65:2)	397.6 nm	2.059	.464 V .904 mA	.164 V	.662 mA	25.9	2.74

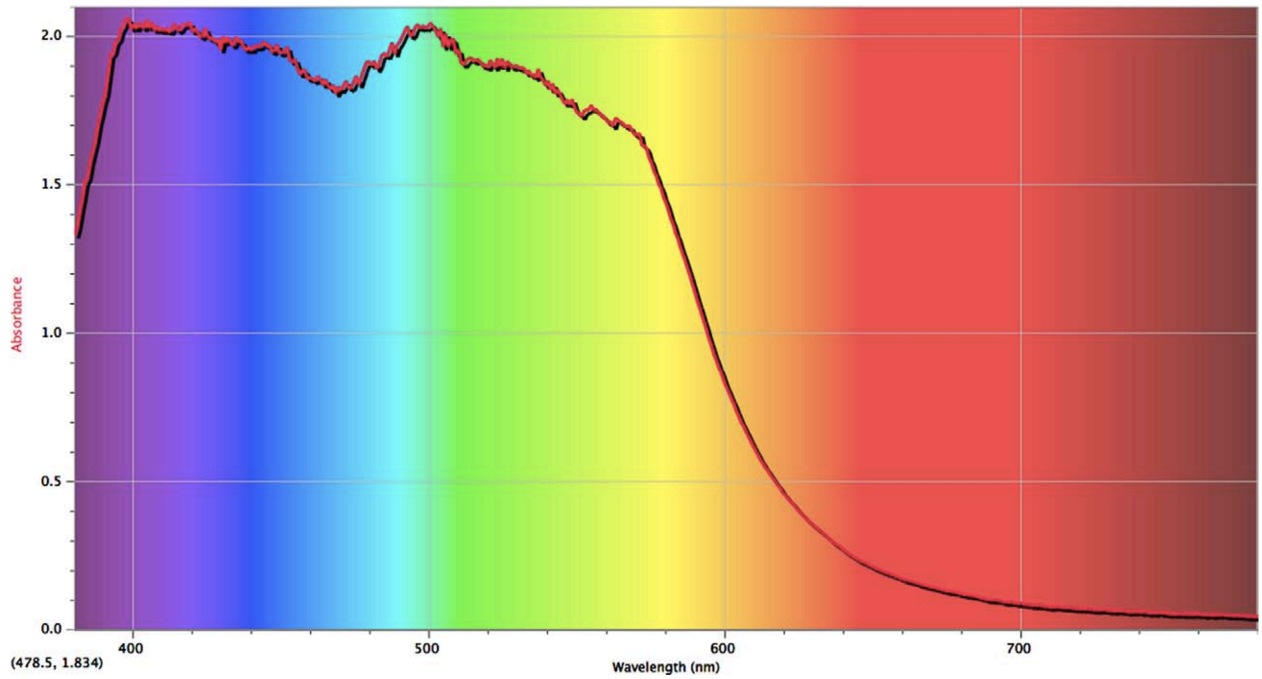

Figure 3. Tri-sensitized DSSC Absorption spectrum.

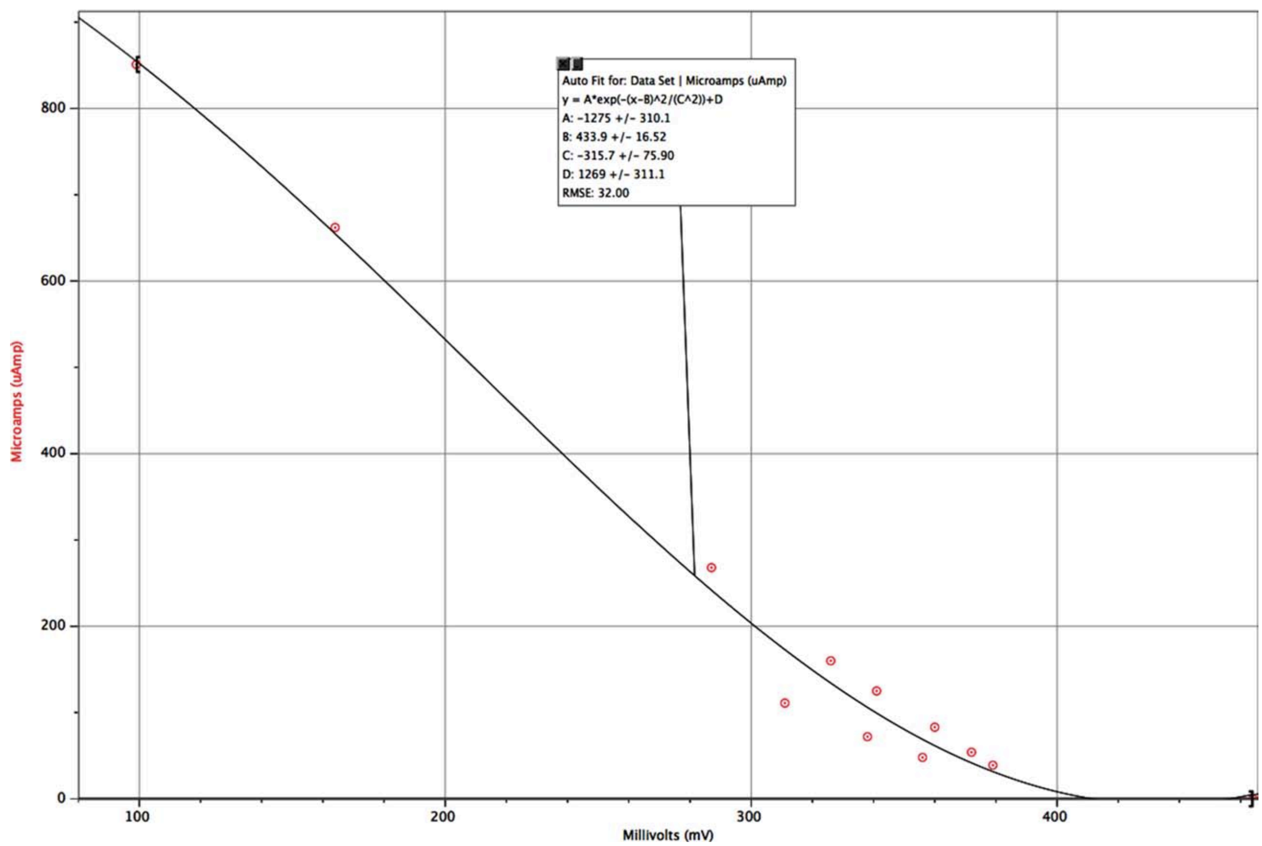

Figure 4. Tri-sensitized DSSC IV Curve.

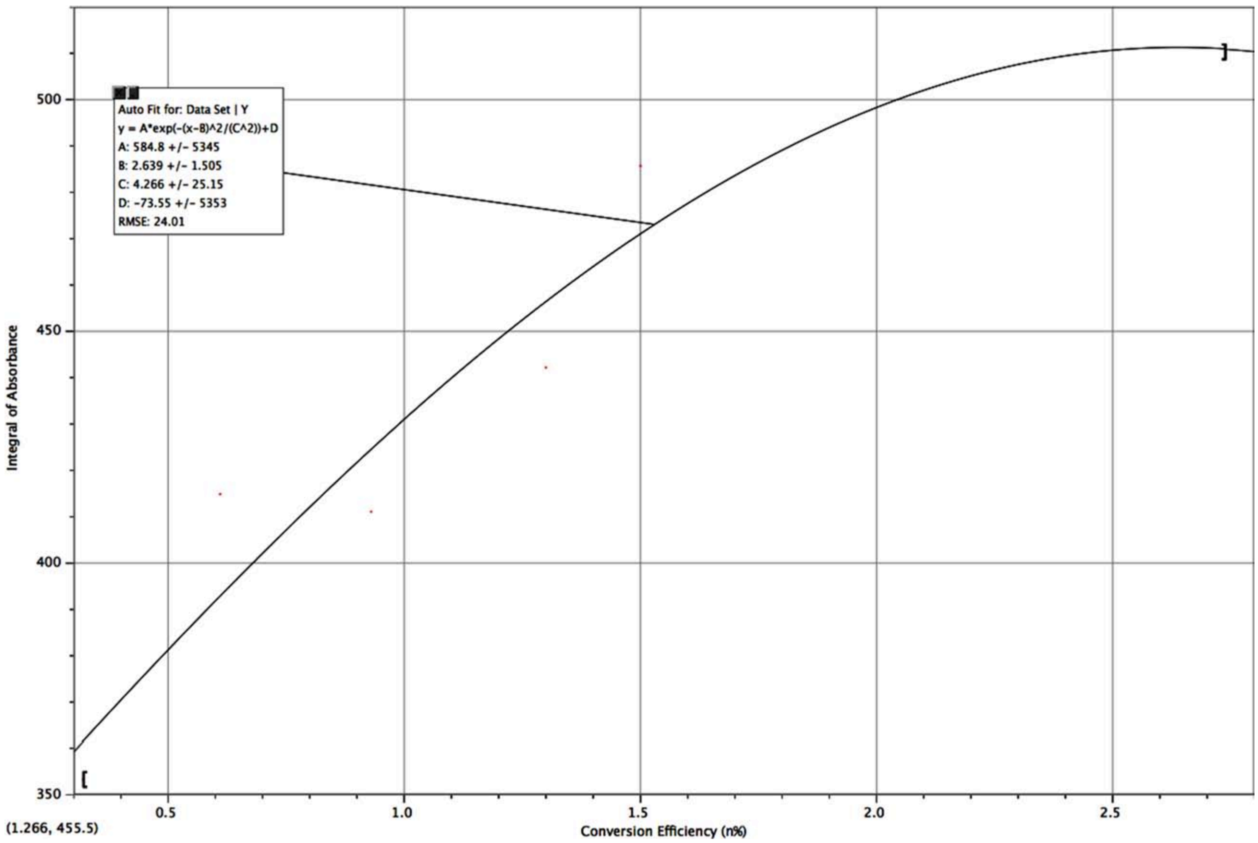

Figure 5. Positive Trend of Conversion Efficiency vs Absorption Spectrum.

Discussion

Overall, this research demonstrated that organic dye-sensitized solar cells could be improved to a significant extent using methods of co-adsorption and tri-adsorption and in fact, there is an overall positive trend between conversion efficiency and absorption spectrum. The initial prediction, in that the tri-sensitization would yield the highest conversion efficiency, was correct and this cell achieved an astounding conversion efficiency of 2.74% (1.24% higher than the highest individual dye, pomegranate juice). Although it may not seem noteworthy, it is a significant increase for organic DSSCs since their typical conversion efficiencies range from 0.2-1.7% on average. Interestingly enough, the co-sensitized dye that absorbed the most wavelengths, Anthocyanin and Pomegranate Juice, was the least efficient. This may have occurred due to degradation of the cell or the dye solution itself over time. In a larger context, the outcome of this research reflected that "greener" energies (more specifically, Dye-Sensitized Solar Cells) could be utilized if made commercially viable. Such an end cannot be achieved if only expensive, rare materials (i.e. expensive synthetic dyes, platinum catalysts, etc.) are used to optimize these cells. Only if inexpensive, simple procedures are used to improve all aspects of DSSCS (Titanium Dioxide, Catalyst, Dye, Electrolyte, and Substrate), then such technology can be made commercially viable.

In the future, further research would be conducted in optimizing organic dye-sensitized solar cells to an even greater extent. Before conducting further experimentation, reproducing these results, especially those of the tri-sensitization and the co-sensitization of Pomegranate Juice and Anthocyanin dyes would need to be performed. Poly-sensitization of dyes as well as optimization of catalyst, electrolyte, semiconductor, and substrate through inexpensive methods would be potential methods to investigate. Eventually, applications of the fully optimized DSSC would be able to be constructed if no further improvements could be made.

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