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Article

Efficacy of rotten and fresh fruit extracts as the photosensitive dye for dye-sensitized solar cells

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SUMMARY

Global demand for energy is increasing exponentially, developing the need for renewable energy sources such as solar cells. Dye-sensitized solar cells (DSSC) use dye as the photoactive material, which capture the incoming photon of light and use the energy to excite electrons. These excited electrons then travel to a titanium dioxide (TiO2) layer, while the electrolyte in the cell closes the circuit by accepting the electrons and recycling them to the dye. Research in DSSCs has centered around improving the efficacy of photosensitive dyes. A fruit's color is defined by a unique set of molecules, known as a pigment profile, which changes as a fruit progresses from ripe to rotten. This project investigates the use of fresh and rotten fruit extracts as the photoactive dye in a DSSC. Dyes were extracted from cherries, plums, nectarines, peaches, kiwis, avocados, blueberries, and blackberries, both fresh and rotten. TiO2 coated electrodes were soaked overnight in the dyes and assembled into a DSSC using a graphite-coated counter electrode and an iodide-triiodide (3I-/I3-) electrolyte solution. The dye efficacy was determined by measuring the electric potential (voltage) with a multimeter. In fresh fruits, blackberries and blueberries produced the greatest potential. In most colors, the fresh dyes produced a greater potential than the rotten dyes. However, in kiwi, the rotten dye produced a greater potential than the fresh dye. In fruit crops, wastage levels are high due to quick rotting and market standards — the use of fruit-based dyes in DSSCs can convert this wastage to useful energy.

INTRODUCTION

The current demand for energy is greater than ever—the U.S. Energy Information Administration predicts that by 2040, world energy consumption will increase by 56% (1). Fossil fuels create 80% of the world's energy but cause serious environmental damage due to hazardous chemicals and greenhouse gases (1). Renewable energy such as solar energy is one of the world's fastest-growing energy sources (1).

Solar energy is converted into electricity through the use of photovoltaic cells. Metallic elements exhibit a property known as the photoelectric effect as they can absorb photons of light and release spare electrons. These free electrons are captured to produce an electric current. Photovoltaic cells are composed of two layers of semiconductor materials such as silicon. Pure crystallized silicon is a poor conductor; however, when impurities are added through doping, its conductivity increases. The bottom silicon layer of the cell is usually doped with boron, which bonds with the silicon and creates a positive charge, while the top layer is doped with phosphorus, which creates a negative charge. The surface between the positive and negative semiconductors is called the P-N junction (2). Electron movement at this surface produces an electric field that allows electrons to flow only from the positive layer to the negative layer through thin wires running along the surface. When a photon of light strikes the photovoltaic cell, electrons are released from the silicon atoms. Electric conductors are attached to the positive and negative surface of the semiconductor to complete the circuit. This allows the released electrons to be captured and form an electric current. Solar cells can be placed in small groups to create a module, and multiple modules can form an array, resulting in a solar panel (3).

The downstream actions of photosynthesis also convert solar energy to electrical energy. A sensitizer molecule on one side of the cell membrane absorbs a quantum of light, which is then transferred to a carotenoid, a pigment molecule found in plants. Carotenoids can pass through the cell membrane, and then transfer the electron to an acceptor (4), chlorophyll a. The idea that pigment molecules could also participate in electron transfer and create a circuit resulted in the development of the dye-sensitized solar cell (DSSC) in 1988 (5). DSSCs contain two conductive glass plates (electrodes) sandwiching four layers: a titanium dioxide (TiO_2) layer, a dye (which is absorbed onto the TiO_2), an electrolyte, and a graphite layer. The dye is the photoactive material in the DSSC; it captures the incoming photon of light and uses the energy to excite electrons. These excited electrons then travel to the TiO_2 layer and are conducted away. The electrolyte in the cell closes the circuit by accepting the electrons and recycling them back to the dye (6) (**Figure 1**).

Traditional photovoltaic cells are expensive to produce and require near perfection in order to function properly. DSSCs consist of primarily low-cost materials, allow for a much higher margin of imperfections, and are easier to manufacture using conventional techniques. While their energy conversion efficiency is lower than that of traditional cells, the extremely low cost allows for respectable price/performance ratio (7).

Since the invention of DSSCs in 1988, research on this technology has been extensive. The photosensitive dye plays a pivotal role in a DSSC; therefore ample research has been completed on optimizing and designing dyes to increase efficiency of DSSCs. Dyes with ruthenium-based complexes were of high interest due to their stability and high efficiency (11.9%). Limitations of ruthenium-based dyes include scarcity and high cost, which limits their use at a commercial scale (8). Synthetic organic dyes have also been examined for DSSC use. Engineered organic dyes have reported efficiencies near 13%, but the synthesis process is complex. The compounds also have high environmental and health risks as they lack biodegradability and are potentially carcinogenic (8). Research is now focusing on the use of natural dyes such as anthocyanins from plums and carotenoids from carrots, among others (9).

A fruit's characteristic color is defined by pigment molecules. Every color is defined by a unique set of molecules, known as a pigment profile. Carotenoids cause the orange-yellow hues seen in mangos, peaches, and nectarines. Xanthophylls, another type of carotenoid, cause the yellow-green hues seen in avocados and kiwis (10). Both red and blue-violet pigments are caused by anthocyanins. However, the specific shade of these colors are dictated by the specific anthocyanin present in the fruit, as well as the pH (11). As a fruit progresses from raw to ripe to rotten, the pigment profile changes. When a tomato ripens, the pigment profile shifts from being chlorophyll-rich to containing primarily anthocyanins (12). Previous research has tracked the progression of ripening through analysis and quantification of the pigment profile (13).

In this project, DSSCs were created with water-based dyes extracted from both fresh and rotten fruits. Eight fruits, divided into four color groups, were used: red (cherry, plum), yellow (peach, nectarine), green (kiwi, avocado) and blue (blueberry, blackberry). The electric potential (voltage) of each cell was measured in low, medium, and high light settings, created using artificial and natural light. Linear equations were used to determine which cells provide the greatest potential.

RESULTS

DSSC Creation

To create the DSSCs, dyes need to be extracted from both fresh and rotten fruits and absorbed into a piece of fluorine-doped tin oxide (FTO) glass was covered with TiO_2 paste. The counter electrode was created by coating the conductive side of a half piece of FTO glass using a graphite pencil. The electrolyte solution, iodide/triiodide, was inserted in between the two electrodes using a Pasteur pipette (**Figure 2**).

Color Comparison

To determine which color dye(s) are most effective as the dye in a DSSC, the electric potential (voltage) was measured under bright sunlight (48000 lux). Measurements were taken for each fruit dye, both rotten and fresh.

Color had a significant effect on the voltage produced by a fruit dye ($p<0.0001$), as did the condition of the fruit ($p=0.00128$). In fresh fruits, the blue dyes created the greatest electric potential (350-420 mV, $p<0.0001$ for all differences). Plums produced the least potential (around 100 mV), but this difference was not always significant. All other fruits produced potentials around 200 mV (**Figure 3**). In rotten fruits, kiwi, blueberry and blackberry produced significantly greater potentials (around 300 mV) compared to the other fruits ($p<0.0001$ for all differences). The red dyes produced significantly lesser potentials (130-150 mV) than the other fruits ($p<0.05$ for all differences), while the other three fruits–nectarine, peach, and avocado–produced potentials around 200 mV (**Figure 4**).

Fresh versus Rotten Fruit Dyes

To determine which fruit dyes are more effective when rotten, the voltage was measured over low, medium, and high intensity light. Linear equations, generated by Microsoft Excel, were used to determine which dye was more effective across various light intensities.

In most colors, the fresh dyes produced a greater

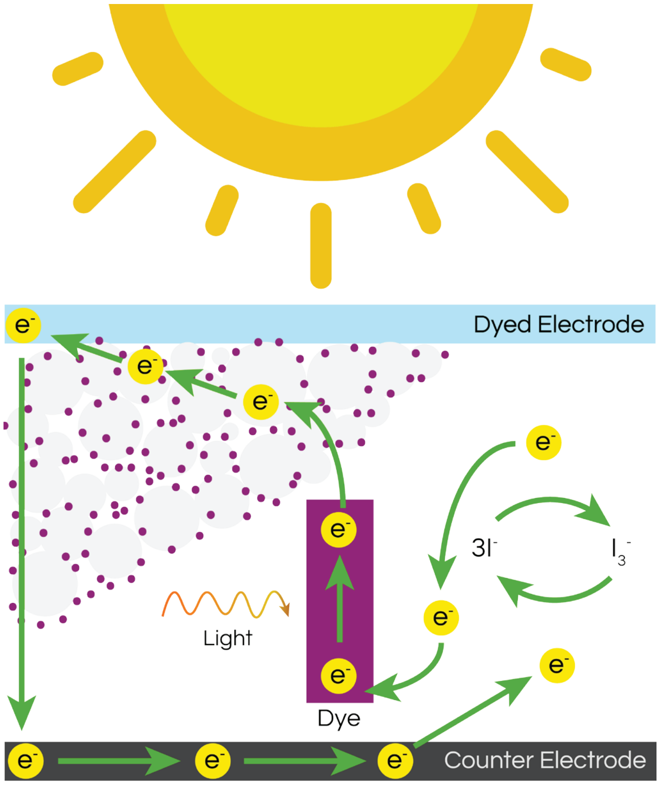

Figure 1: How a dye-sensitized solar cell (DSSC) works. When light strikes the dye, electrons are released to the TiO2 and transferred to the transparent electrode followed by the counter electrode, creating electricity Some electrons are reabsorbed by the electrolyte and returned to the dye to repeat this cycle.

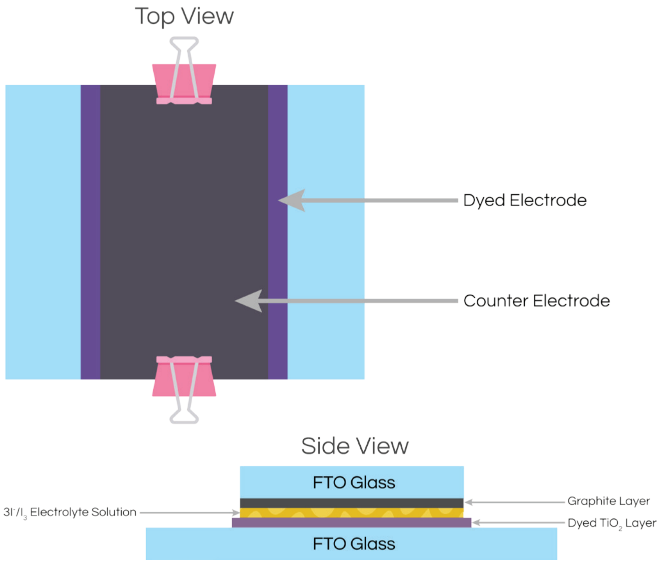

Figure 2: Schematic of DSSC assembly, displaying both a top and side view. The dyed TiO_2 layer and the bottom FTO glass layer make up the dyed electrode, while the graphite layer and the top FTO glass layer make up the counter electrode. The 3I-/I3 electrolyte solution is not visible in the top view.

potential than the rotten dyes. However, in kiwi, the rotten dye produced a significantly greater potential than the fresh dye (0.0079 vs. 0.0049, $p<0.0001$). A similar result was seen in plum, where the rotten dye had a slightly greater potential than the fresh dye (0.0036 vs 0.0028); however, this difference was not significant. All other fruits also showed insignificant differences between rotten and fresh fruit dyes (**Table 1**). Table 1 summarizes the slopes of all the graphs in linear form, as well as their respective R2 values.

DISCUSSION

On average, DSSCs created with fresh fruit dyes had an average potential of 240 mV, while rotten fruit dyes resulted in an average potential of 227 mV. Silicon-based photovoltaic cells produce between 400 and 600 mV of potential per cell (14). Therefore, fruit-based DSSCs produce around half the potential of silicon-based cells. It should be noted that fresh blueberry dyes produce over 400 mV of potential, within the range of silicon-base photovoltaics, and blackberry dyes produce around 350 mV, slightly below the range of silicon cells. This suggests that malvidin pigments contained in these fruits should be explored further as a photoactive dye in DSSCs.

Through the color comparison experiments, it was determined that blue dyes are the most effective in producing electric potential, followed by green, yellow and red dyes. Anthocyanins are the group of pigment molecules that produce red-blue hues, with the specific anthocyanin molecule and pH dictating the shade (15). Our results suggests that malvidin, the particular anthocyanin resulting in a blueberry or blackberry's blue color, is a strong candidate pigment for a DSSC (16). Cyanidin, another anthocyanin found in berries, has been identified to have a strong visible absorption, long excitation lifetime, and efficient electron transfer (17). These are the properties found in the ruthenium-based dyes previously used to created DSSC (18). Since cyanidin contains these properties, it is probable that malvidin may as well.

A multitude of compounds, including malvidin, comprise the pigments seen in fruits. Future directions for this project could involve investigating which specific compounds or combinations of compounds optimize DSSC potential. The fruit dyes can be fractionated using chromatography; the fractions can then be tested as separate dyes. Additionally, mass spectrometry can be used to identify specific pigment molecules in fruit dyes. These molecules can then be tested separately as a dye on DSSCs.

Comparing the fresh and rotten dyes from each fruit, it was determined that kiwi was much more effective as a rotten dye than a fresh dye. A similar result was seen in plum. This suggests pigment molecules produced in the metabolic processes during rotting are better dye sources for kiwis and plums. Nectarine and blackberry were close to equally effective in both forms. Since blackberries were one of the highest performing dyes and are close to equally effective when rotten, rotten blackberries may be a viable and environmentally friendly choice.

The Niagara Peninsula, a region located in Southern Ontario close to the United States-Canada border, is Canada's largest and most important tender fruit growing area. Crops that are considered as tender fruits include peaches and nectarines, pears, sweet and sour cherries, plums and apricots, as they have a soft skin and do not stay for long after harvest. The reduced shelf life of these crops increases the amount of food waste produced (19). Large tender fruit growing regions are also found in the East and West coasts of the United States, specifically in Georgia and California (20). Globally, approximately one-third of the fruit harvested each year for human consumption is wasted – this includes the fruits of the Niagara Peninsula. Western nations like Canada and the United States, as well as certain European nations, waste almost as much food as sub-Saharan Africa produces (21). This project demonstrated that certain tender fruits, such as plums and nectarines, produced equivalent or greater potentials as a rotten dye compared to a fresh dye. As seen in this research, dyes can be extracted from these rotten, waste fruits and used for solar energy.

While the results showed promise for both rotten and fruit dyes in DSSCs, some future improvements can be made to improve the efficiency of the cells. To allow for easier extraction, the dyes were extracted in 100mL of water. This extra step results in dilution of the dyes, potentially causing lesser and slower adhesion to the TiO_2 plates. To correct for this, the dyes should be directly extracted from the fruits without water, reducing any dilution factors and increasing pigment concentrations. Additionally, pigment quantities may differ between fruits, resulting in varied potentials. For example, blackberries may produce less malvidin naturally

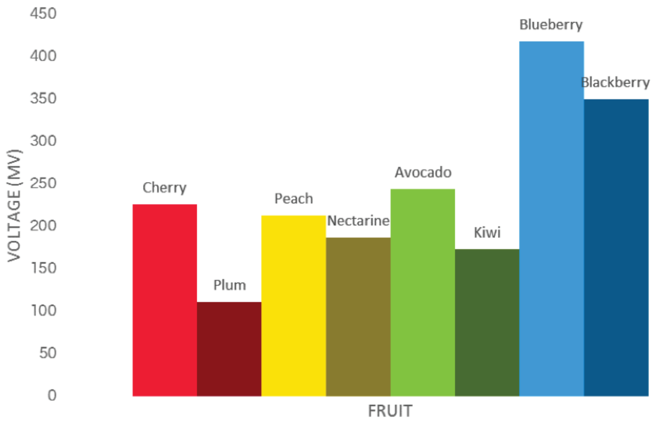

Figure 3: Electric potentials of fresh fruit dyes in sunlight. The blue dyes created the greatest electric potential (350-420 mV). Plums produced the least electric potential (around 100 mV), while all other fruits produced around 200 mV.

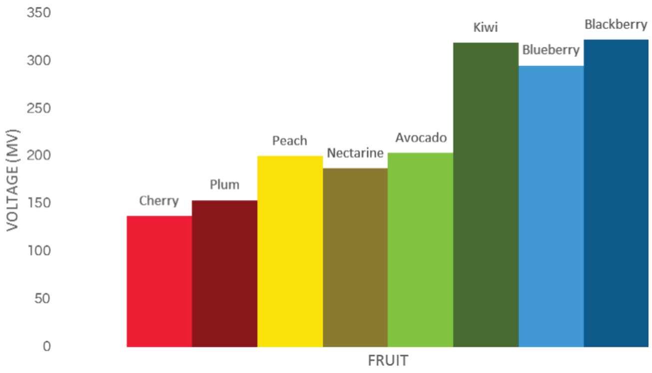

Figure 4: Electric potentials of rotten fruit dyes in sunlight. Kiwi and blue dyes produced the greatest electric potential (~300 mV). The red dyes produced the least electric potential (150 mV), while all other fruits produced around 200 mV.

	Cherry	Plum	Peach	Nectarine	Avocado	Kiwi*	Blueberry	Blackberry
Fresh	0.0047	**0.0028**	0.0053	0.0047	0.0058	**0.0049**	0.0093	0.0082
R	0.9909	0.7320	0.7057	0.6317	0.7973	0.7596	0.9039	0.8528
Rotten	0.0033	**0.0036**	0.0046	0.0043	0.0046	**0.0079**	0.0073	0.0076
R	0.8138	0.8642	0.9096	0.8963	0.9159	0.7163	0.6679	0.8222

Table 1: Potential coefficients (mV/lux) for fresh and rotten dyes from eight different fruits. Bold numbers indicate that the rotten dye had a greater coefficient compared to the fresh dye. An asterisk beside the fruit name indicates that the difference between the slopes was significant ($p<0.05$)

compared to blueberries, resulting in lower produced potentials. Further research should quantify pigment molecule concentrations and examine the effect of pigment quantity on produced potential. Another potential source of error was that sunlight was used as a light source to test the potential of the DSSCs. The illuminance was only approximation and was not consistently at 48000 or 24000 lux, due to the natural variability of sunlight. Therefore, the measured potentials from the DSSCs could be higher or lower compared to the actual values.

MATERIALS AND METHODS

Dye Extraction

To create the dye, 200 ± 10g of fruit was sliced and blended with 100mL of distilled water until a smooth consistency was achieved. To remove any large debris, the juice was filtered using a wire mesh and a cheese cloth. The filtered juice was transferred into 50mL tubes and frozen until use.

Electrode Coating

A DSSC contains two electrodes—a dyed electrode and a counter electrode. To create the TiO_2 layer, a piece of FTO glass was placed on a flat surface with the conductive side up and taped down (about 1 cm on each side). The TiO_2 paste was added using a Pasteur pipette and spread evenly across the surface to form a layer approximately 1 mm thick. The plates were left to sinter on a 100°C hot plate for 30 minutes. After the paste had sintered, the electrode was soaked in a petri dish containing the fruit dye overnight. The counter electrode was created by coating the conductive side of a half piece of FTO glass using a graphite pencil.

Assembly

To assemble the DSSC, the two electrodes were placed on top of each other so that the conductive sides were touching. The counter electrode was placed so that it was completely in the TiO2 lane. Binder clips were placed on each side to hold the two electrodes together. The electrolyte solution, iodide/triiodide, was inserted in between the two electrodes using a Pasteur pipette. Capillary action carried the solution throughout the cell.

Color Comparison

To determine which color dye(s) are most effective as the dye in a DSSC, the electric potential (voltage) was measured using a multimeter with alligator leads. The positive lead was clamped to the dyed electrode, while the negative lead was connected to the counter electrode. The cells were placed in bright sunlight (approximately 48000 lux), and the voltage readings were collected. Measurements were taken for each fruit dye, both rotten and fresh.

Fresh vs. Rotten Fruit Dyes

To determine which fruit dyes are more effective when rotten, the voltage was measured over varying light intensities. A low, medium, and high intensity light were used. High intensity light was the same bright sunlight used above, at 48000 lux. Medium intensity light was moderate sunlight, which measured at approximately 24000 lux. Low light was a desk lamp, which measured at 12000 lux.

Linear Analysis

A linear equation is an algebraic equation that consists of one independent variable, and are represented with the equation y=mx+b, where m is the slope, or rate of change and b is the y-intercept. Linear equations, generated by Microsoft Excel, were used to determine which dye was more effective across various light intensities Voltage readings were inputted into Microsoft Excel as the dependent variable (y); the light intensities were the independent variable (x). Since at zero light, no potential is produced, b=0. A scatter plot of both light intensity and voltage was produced, a linear trendline was added and an equation was created. The slope will dictate which dyes are the most effective; the higher the slope, the more effective the dye.

Statistical Analyses

All statistical analyses were run using R v. 3.5.0. Color comparison data was analyzed using a one-way analysis of variance (ANOVA); separate analyses were run for the fresh and rotten data. Analyses of covariance (ANCOVA) were run on each fruit separately to compare the effects of fresh and rotten dyes, with light luminosity as the covariate.

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