Dragon Fruit Dye as a Sensitizer for Dye Sensitized Solar Cells

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Abstract
Natural dye sensitized solar cells are a preferred alternative to ruthenium-based dye sensitized solar cells due to the fact that they are environmentally-friendly and less expensive. We report work on dye sensitized solar cells fabricated using a natural dye extracted from the dragon fruit. Dragon fruit is a type of fruit that is derived from a species of cactus. It is rich in potent antioxidants including anthocyanin, catechins and epicatechins, and has strong absorption in the visible region. The extracted dragon fruit was characterized via UV-vis and fluorescence measurements. The wavelength at maximum absorption was 535 nm while the emission wavelength was around 610 nm. The photo electrochemical performance of the dragon fruit dye sensitized solar cell displayed an open-circuit voltage ($V_{oc}$) of 0.39 V, a short-circuit current ($I_{sc}$) of 0.88 mA cm$^{-2}$, a fill factor (FF) of 0.27 and an overall conversion efficiency ($\eta$) of 0.09% at 100 mWcm$^{-2}$ light intensity. To demonstrate the sensitizing capacity of the dragon fruit dye, the current-voltage characteristics of the dragon fruit dye sensitized solar cell were compared to that of solar cells fabricated with blank TiO$_2$ without a sensitizing dye.

Introduction
The dye-sensitized solar cell works by absorbing photons from sunlight to induce a transfer of electrons, creating energy in the form of electricity. The dye-sensitized solar cell (DSSC) has a number of advantages over other forms of solar cells, the chief among them being their relatively low cost of production and easily available materials for the fabrication of the solar cell.

A dye sensitized solar cell is comprised of two electrodes- the anode and the cathode- made from a transparent conductive glass. The conductive layer is usually a fluorine doped tin oxide (FTO) or indium doped tin oxide (ITO). One glass slide, the photoanode, is coated with a dye sensitized titanium dioxide film while the other glass electrode, the counter electrode, is coated with either carbon or platinic acid. An electrolyte, iodine/tri-iodide, is sandwiched between the two electrodes to aid in the regeneration of charge. When light hits the cell, the dye molecules absorb photons and electrons are excited. The dye subsequently injects the excited electron into the nanocrystalline titanium dioxide film. The oxidized dye accepts electron from the electrolyte and the ground state of the dye is restored. The injected electron is transported through the nonporous semiconductor to the conductive side, and afterwards, through an external circuit to the cathode. At the cathode, the electron is transferred to the electrolyte and the system is regenerated.

Figure 1: Fruit (left) and juice of dragon fruit (right) used in the fabrication of dye sensitized solar cell.

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The dye sensitizer, therefore, plays a very important role in the performance of the solar cell device.\textsuperscript{4-6} A number of different dyes have been employed in the fabrication of dye sensitized solar cells. These include: natural dyes,\textsuperscript{7-9} ruthenium based dyes,\textsuperscript{10-13} porphyrins,\textsuperscript{14-18} and infrared dyes.\textsuperscript{19-22} The use of natural dyes as sensitizers for dye sensitized solar cells has gained a lot of attention in recent years due to the abundance of natural dyes which could be extracted from leaves, fruits, flower petals, barks and roots of various plants and trees.\textsuperscript{23-25} These dyes contain very important pigments such as anthocyanin, flavonoid and carotenoids which can be applied as light harvesting pigments for dye sensitized solar cells.\textsuperscript{26-27} Materials for the fabrication of DSSCs are low cost compared to artificial dyes, which are obtained by means of expensive chemical synthesis. Natural dyes also do not pose any environmental threats. The goal of the study was to evaluate the light absorbing properties of the dragon fruit dye and its application as a sensitizer for the dye-sensitized solar cell.

**Experimental section**

Absorption and Emission spectra were measured with UV-3600 and RF-5301PC, respectively. Both instruments were purchased from Shimadzu, MD, USA. Titanium dioxide paste was printed on FTO glass using WS-650 Series Spin Processor from Laurell Technologies Corporation, PA, USA. Carbon paint used in making cathode slides were purchased from TED PELLA, INC, USA. The cell performance was measured using a 150 W fully reflective solar simulator with a standard illumination of air-mass 1.5 global (AM 1.5 G) having an irradiance of 100 mW/cm\textsuperscript{2} (Sciencetech Inc.), London, Ontario, Canada and Reference 600 Potentiostat/Galvanostat/ZRA from GAMRY Instruments (Warminster, PA).

The dragon fruit dye was extracted from the fruit using a commercial fruit juice extractor, purified by centrifugation, and stored in the refrigerator until ready to use. The dye was diluted with water prior to spectroscopic measurements.

The dragon fruit dye sensitized solar cell was fabricated according to a protocol used in the fabrication of dye sensitized solar cell with minor modifications.\textsuperscript{28-30} The working electrode was prepared by depositing a thin film of TiO\textsubscript{2} on the conductive side of a fluorine doped tin oxide (FTO) glass using a spin coater and annealing the film at 380°C for 2 hours. The counter electrode (cathode) was prepared by painting this conductive side of the FTO glass slide with colloidal graphite. The dragon fruit dye sensitized FTO glass and the carbon electrodes were assembled to form a solar cell by filling the gap between the anode and cathode with redox (I\textsuperscript{-}/I\textsuperscript{3-}) electrolyte.

**Results and Discussion**

**Absorption studies**

The absorption spectra was acquired to study the absorption characteristics of the dragon fruit dye. The absorption spectra, as displayed in Figure 2, shows the dye absorbing strongly at 535 nm. The broad spectra response from, 425 nm to 625 nm, allows for the capture of enough photons, which ultimately results in a higher solar-to-electric energy efficiency. The absorption is also consistent with the absorption band of anthocyanin, a potent light harvesting pigment found in dragon fruit dye and other types of natural dyes.

**Field Emission Scanning Electron Microscopy and Energy dispersive X-ray Spectroscopy Studies**

The morphology and porosity of the fabricated dragon fruit dye sensitized titanium dioxide film was evaluated using a Field Emission Scanning Electron Microscope (FESEM). Figure 4a and 4c are FESEM images of photoanode with and without dragon fruit dye, respectively. The nanocrystalline and porous nature of the Titanium is clearly visible. The nanocrystalline titanium dioxide is very porous which increases the surface area and number of dye molecules that get adsorbed to it. The elemental composition of dragon fruit dye sensitized titanium dioxide film was also studied using Energy Dispersive X-ray Spectroscopy (EDS). An EDS spectra of a bare TiO\textsubscript{2} (Figure 4d) showed the presence of mainly Ti and O. The EDS signal for carbon is almost negligible in the spectra of the bare TiO\textsubscript{2} but the signal intensity of carbon in the spectral of the dragon fruit dye sensitized TiO\textsubscript{2} (Figure 4b) is very high.
which is indicative of the presence of organic matter in the dyes compared to the bare TiO$_2$.

**Figure 4:** FESEM images (a&b) and EDS spectra of dragon fruit dye sensitized titanium dioxide film (c) and bare titanium dioxide film.

**Current Voltage Characteristics**

The photoelectrochemical performance of the dragon fruit dye sensitized solar cell showed an open-circuit voltage ($V_{OC}$) of 0.39 V, a short-circuit current ($I_{SC}$) of 0.88 mA cm$^{-2}$, a fill factor (FF) of 0.27 and an overall conversion efficiency ($\eta$) of 0.09% at 100 mWcm$^{-2}$ light intensity. The current-voltage characteristics of a blank TiO$_2$ film was fabricated to assess the effect of the dye on the efficiency of the dye sensitized solar cell. The efficiency of the dye sensitized solar cell was much higher than that of solar cell fabricated with a dye-free titanium dioxide nanocrystalline film.

**Figure 5:** Current and voltage characteristics of dragon fruit dye sensitized solar cell in comparison with blank TiO$_2$ without the dye.

**Impedance studies**

Electrochemical impedance measurements were carried out to assess the charge transfer and recombination dynamics of the fabricated dragon fruit dye sensitized solar cells. The results of the EIS studies are displayed in Figure 6 (Nyquist Plot) and Figure 7 (Bode Plot). The measurement were carried out under one sun illumination and $V_{OC}$ bias. The Nyquist plot as exhibited in Figure 6, shows two semicircles with a small semicircle for the dye and a larger one for the blank TiO$_2$. The impedance data is a measure of resistance to the flow of electricity. The Bode plot showed that Dragon fruit dye sensitized solar cell shifted to a higher frequency than that of the blank TiO$_2$ dye sensitized solar cell. The two graphs below are representations of that resistance to the flow of current.

**Table 1:** Current and voltage characteristics for the dragonfly dye sensitized solar cells in comparison with blank TiO$_2$ without the dye.

<table>
<thead>
<tr>
<th>DSSC</th>
<th>$V_{max}$</th>
<th>$I_{max}$</th>
<th>$V_{OC}$</th>
<th>$I_{SC}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dragon Fruit Dye</td>
<td>0.19</td>
<td>0.49</td>
<td>0.39</td>
<td>0.88</td>
<td>0.27</td>
<td>0.09</td>
</tr>
<tr>
<td>Blank TiO$_2$</td>
<td>0.15</td>
<td>0.29</td>
<td>0.47</td>
<td>0.88</td>
<td>0.13</td>
<td>0.04</td>
</tr>
</tbody>
</table>

**Conclusion**

Dye sensitized solar cells convert sunlight into electricity with the aid of a dye sensitizer. The dye sensitizer therefore plays a very important role in the performance of the solar cell device. In this work, we have used a natural dye, dragon fruit dye, as a sensitizer for the fabrication of dye sensitized solar cell to test its solar-to-electric power efficiency and the viability of the device for use as solar cell. The dragon dye sensitized solar cell was tested along with DSSC fabricated without dye for comparison purposes. The photoelectrochemical performance of the dragon fruit dye sensitized solar cell showed open-circuit voltages ($V_{OC}$) which varied from 0.39 V, a short-circuit current ($I_{SC}$) of 0.88 mA cm$^{-2}$, a fill factors (FF) of 0.27 and an overall conversion efficiency ($\eta$) of 0.09% at 100 mWcm$^{-2}$ light intensity.
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