Natural dyes as sensitizers to increase the efficiency in sensitized solar cells

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Abstract. A dye-sensitized solar cell (DSSC) is a sandwich type solar cell consisting of a photoelectrode, a counter electrode and a liquid electrolyte. The photo electrode comprises of a titanium dioxide semiconducting thin film grown over a glass substrate which in-turn has a transparent thin conducting layer of tin oxide film doped with fluorine (FTO) coated over it. The aim of this work is to develop photoelectrodes with different dyes to increase the efficiency of this type of solar cells. Dyes obtained from fresh sources of maqui, black myrtle, spinach and a dye mixture of spinach and spinach-maqui-myrtle were used. The technique used for the extraction of the dyes was maceration for one day, in methanol. Colourants and photoelectrodes were studied using, UV-vis spectrophotometer for their spectral properties. Their photovoltaic properties such as efficiency, fill factor, open circuit voltage and short circuit current were studied using a solar simulator and source meter unit.

1. Introduction
Since the development of Gratzel’s Dye Sensitized Solar Cell (DSSC) in 1991[1], this has had considerable attention because it is environmentally friendly and has low production costs. A DSSC is composed of a nanocrystalline semiconductor porous electrode with absorbed dye, a counter electrode, and an electrolyte containing ions of iodide and tri-iodide. In DSSC, sensitizing dyes plays a key role in absorption of light and the transformation of solar energy into electrical energy. Many metal complexes and organic dyes have been synthesized and have been used as sensitizers. Although DSSC have provided high relative efficiency, use of precious metals like ruthenium (Ru) complexes is its disadvantages: noble metals are considered as limited resources, so its production is costly. Moreover, the organic dyes are not only cheaper but have been reported to show efficiency of 9.8 %. However often natural dyes have presented problems because of its complicated synthesis and low yield. However, natural dyes found in flowers, leaves and fruits can be extracted by simple procedure. Due to its cost efficiency, non-toxicity and retrogradations, natural dyes have been a popular research topic. Until now various natural dyes have been used as sensitizers in DSSC, such as carotene, chlorophyll, etc.

2. Experiment
2.1. Sensitizers preparing natural dyes
For all dyes methanol was used as the extraction solvent. The extracted dyes were obtained by the following steps: fresh fruit and vegetables were washed with distilled water. They were...
then cut into small pieces, immersed in methanol at room temperature and left to macerate for a day. This was then filtered using a vacuum pump and the filtrate was used as a sensitizer.

2.2. Preparation of dye sensitized solar cells

FTO conductive glass sheets were first ultrasonically cleaned using a mixture containing 10 ml of ethanol, 10 ml of propanol and 10 ml of distilled water for 30 minutes.

Titanium dioxide (TiO$_2$) paste was prepared using Degussa P-25, whose average TiO$_2$ particle size was 26 nm. P-25 (0.14 g) was set in a shaker, and HNO$_3$ (0.6 ml) was added into the shaker. Later, polyethylene glycol (PEG) was added into it. The obtained TiO$_2$ paste was coated using Doctor Blade method onto the FTO clean glass substrate. The obtained substrate was set in an electric oven for annealing at 450°C for 30 min in order to eliminate water vapour and the polymer binder. This formed the pre-prepared TiO$_2$ photoelectrode which is to be sensitized. Sensitization was done by immersing this electrode in a methanol solution containing the extracted dye for 1 day in dark.

Platinum (Pt) counter electrodes were fabricated by spreading a drop of 5 mM chloroplatinic acid hexahydrate (H$_2$PtCl$_6$·6H$_2$O) in isopropyl alcohol onto the FTO surface followed by heating it at 450°C for 30 min. Pt electrode was used because it is most resistant to corrosive attacks by the redox couple ($I^-/I^{3-}$) and facilitates a reversible redox reaction to occur. Since only very small quantity of Pt is been used in making the counter electrode, this still reduces its cost at the same time maintaining its transparency for photon entry. The dye sensitized TiO$_2$ photoelectrode and the Pt counter electrode was assembled to form a sandwich solar cell. Solution composing; 0.6 M butylmethylimidazolium iodide (BMII), 0.05 M I$_2$, 0.1 M LiI, and 0.5 M tert-butylpyridine in 1:1 acetonitrile/valeronitrile was used as the redox electrolyte.

2.3. Measurements

UV-Vis spectrophotometer was used to determine the absorbance of the natural dyes extracted and the sensitized photoelectrodes. The photovoltaic parameters were obtained from the current-voltage (I-V) curves that were measured using a solar simulator and a Keithley source meter.

3. Result and discussion

We tried to use 3 types of natural dyes as sensitizers for DSSCs. Table 1 absorbance data shows absorption of dyes extracted using methanol from the maqui fruit, black myrtle and spinach.

| Natural dye         | $\lambda_{max}$(nm) | $V_{oc}$(V) | $I_{sc}$(A) | FF  | $\eta$% |
|---------------------|---------------------|-------------|-------------|-----|--------|
| maqui               | 546                 | 0.06        | 0.00002     | 4.73| 0.006  |
| black myrtle        | 542                 | 0.40        | 0.00002     | 4.89| 0.040  |
| spinach             | 437                 | 0.10        | 0.00001     | 3.03| 0.005  |
| spinach-black myrtle| 437                 | 0.39        | 0.00001     | 0.59| 0.009  |

Table 1. Photoelectrochemical parameters

The main components of spinach is chlorophyll, the for maqui it was anthocyanins.

3.1. Photovoltaic properties

Photovoltaic properties of these assembled DSSCs using these natural colorones as sensitizer were studied by measuring their current-voltage curves under white light irradiation from a solar simulator. The performance of these DSSCs were assessed by their open circuit voltage $V_{oc}$, short circuit current $I_{sc}$, fill factor (FF) and conversion efficiency $\eta$; obtained parameters are listed in the table 1.
Figure 1. Absorbance spectrum of the natural dyes

Figure 1 shows the absorbance of the natural dyes extracted. We can see that spinach has two main peaks one to the 660 nm and other to 450 nm, these peaks corresponds to chlorophyll peaks a and b. Black myrtle, show a peak at 550 nm. Maqui showw a peak at 550 nm. Spinach-maqui and spinach-black myrtle have the same peaks as spinach.

Figure 2. Absorbance spectrum of the sensitized photoelectrodes

Figure 2 shows the absorbance of the sensitized photoelectrode. Spinach shows absorption
peaks at 400, 500 and at 650 nm. The maqui has good absorption between 500 and 650 nm. Black myrtle has a similar to that of maqui with good absorption between 500 and 650 nm. Maqui, spinach-maqui and black myrtle have the same absorption in 500-650 nm. 50-50 maqui-spinach and 50-50 black myrtle-spinach have the same absorption in 670 nm and 400-450 nm. Spinach-black myrtle has a good absorption in 400-700 nm.

4. Conclusion
DSSCs were assembled using the dyes extracted from maqui, black myrtle, spinach and even a mixture of some of them. For maqui three absorption peaks at 476, 546 and 661 nm were found. For black myrtle one absorption peak at 542 nm was found. For spinach six absorption peaks at 414, 437, 466, 535, 612 and 662 nm were found. For spinach-maqui mixture 6-absorption peaks 414, 436, 466, 535, 602 and 662 nm were found and for spinach-black myrtle mixture 6-absorption peaks 413, 438, 467, 535, 607 and 663 nm were found. The efficiencies of the DSSC were also studied. Extract used from black myrtle showed the highest efficiency among others.

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References
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