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Synthesis of solar cells sensitized using natural photosynthetic pigments & study for the cell performance under different synthesis parameters

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Abstract. In this study we used photosynthetic pigments extracted from spinach and purple cabbage for their potential application in dye sensitized solar cells (DSSC). Pigments were extracted by dissolving small amounts of each one of these plant products in methanol and distilled water. The extraction was also done at two different temperatures (70°C and 80°C respectively). This was to assess for the solvent that promotes better extraction of the pigments. A parallel study was also carried out using a mixture of both these dyes in 1:1 ratio. Good absorption, about 60 % to 80 % was obtained for spinach pigments diluted in methanol in the visible range between 400-480nm, and between 9 % to 15 % for purple cabbage pigments in the wavelength range between 480-630 nm when extracted using distilled water at 80°C. In contrast, the diluted mixture in methanol shows good absorption of 20 % and 32 % for wavelengths in the range 400-480nm. Solar cells sensitized using these natural dyes were studied for their photovoltaic properties by measuring current-voltage behavior. Efficiencies ranging from 0.011% to 0.0719% were observed. Mixture of spinach & purple cabbage pigments extracted using methanol was found to have the highest efficiency of 0.0719%.

1. Introduction

The solar cells produced today are generally divided into several types such as monocrystalline silicon (Si) solar cells, polycrystalline Si solar cells, amorphous Si solar cells and dye-sensitized solar cells (DSSC). The so-called "solar cells" generally refer to cells made of crystalline silicon and its popularity is due to its higher photoelectric conversion efficiency compared to DSSC. However, the production cost of solar cells based on glassy silicon are higher than the DSSC. Simply because of its advantage of lower manufacturing costs, the DSSC are highly interesting [1]. With its simple and easy process of manufacture, DSSC are easy to mount and the cost is only about one-third of what it costs to manufacture solar cells based on silicon.
In the future, the cost can be further reduced for DSSC having the same efficiency as Si based solar cells. The predicted total cost will be only one tenth. Efficiency of DSSC is mainly determined by the sensitizer (photosynthetic pigment in this case) used. The marketed dyes are mainly synthetic chemicals, such as N719 and N3 dyes, both of which have a satisfactory conversion efficiency. However, these dyes contains some heavy metals, which are expensive and produce environmental contamination. Moreover, the synthesis process is very complex and expensive. With the purpose of replacing these dyes, many types of natural dyes have been

actively studied and tested. However, natural dyes usually gave poor photovoltaic response [2] due to its weak binding energy with TiO_2 thin films and low charge transfer due to optical absorption in the entire region of the visible spectrum, but these dyes are very cheap and can be easily prepared in comparison to the synthetic dyes.
The energy conversion efficiency is less than 1%, which is typical for most natural extracts. Several studies published in recent years have made remarkable progress in the use of organic dyes for DSSCs. Natural dyes have high value at low cost. In this work, extracts from spinach leaves and red cabbage were used as light sensitizers for preparing DSSC. Effectiveness of dyes extracted from these two plants under different conditions, namely, variation in temperature and solvent medium used for extraction, is been discussed.

2. Experimental Details

Synthesis of solar cells sensitized using natural dyes were divided into four stages: Extraction of the photosynthetic pigments, deposition of TiO_2 thin films, preparation of electrolyte and finally the DSSC assembly.

2.1. Extraction of photosynthetic pigments

Mainly two different extraction methods were adopted:

- Spinach and purple cabbage leaves were diluted in methanol and the extraction was done at room temperature.
- Spinach and purple cabbage leaves were diluted in deionized water and the extraction was done at two different temperatures; [70°C and 80°C].

In both cases, 10 g of each plant product was taken and was then dissolved in 40 mL of the respective solvents [i.e., methanol or deionized water].

Table 1. Methodology used for extracting the photosynthetic pigments.

Sample	Spinach [g]	Purple Cabbage [g]	solvent, Volume [mL]	Temperature [°C]
1	10	—	Methanol, 40	Room
2	—	10	Methanol, 40	Room
3	10	10	Methanol, 80	Room
4	10	—	Deionized water, 40	70
5	—	10	Deionized water, 40	70
6	10	—	Deionized water, 40	80
7	—	10	Deionized water, 40	80
8	10	10	Deionized water, 80	70

Once the extraction was done the samples were filtered out and were stored in dark.

2.2. Preparation of TiO_2 thin films

Titanium Dioxide Powder (EMSURE®, purity 99,5%, 1.5 gm), 100 mL of acetylacetone, 1.8 mL of distilled water and 50 mL of TRITON X-100, were taken and mixed in a mortar to form a paste. This paste was deposited over a glass substrate coated with FTO (fluorine doped tinoxide), on the FTO side. The films were deposited over an area of 2.5 cm x 2.5 cm, using "*Doctorblade*" method [3]. After allowing it to dry for 1 hour, they were sintered at 450°C for 30 minutes.

2.3. Preparation of electrolyte

The electrolyte or the redox couple was prepared using 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.

2.4. DSSC assembly

To initiate the DSSC assembly, TiO_2 layer deposited on FTO should be sensitized first, using the natural dye extracts. For this, the TiO_2 films were immersed into 20 mL of the dye solution in dark, over night. Then the following day, they were rinsed with ethanol and left to dry. This formed the photoanode. A thin layer of platinium coated over another FTO coated glass substrate, formed the counter electrode. It was synthesized by centrifugation process by using chloroplatinic acid solution (H_2PtCl_6 $.6H_2O$) (0.005 M in isopropanol). Then this Pt-FTO electrode was sintered at 400°C for 20 min.

These two electrodes were assembled face to face. Subsequently, the electrolyte that was already prepared was injected into this sandwich layer. A thin layer of surlyn (25 μ m) was used to seal this liquid electrolyte and also to hold the electrodes intact, avoiding short circuiting, fig. 1.

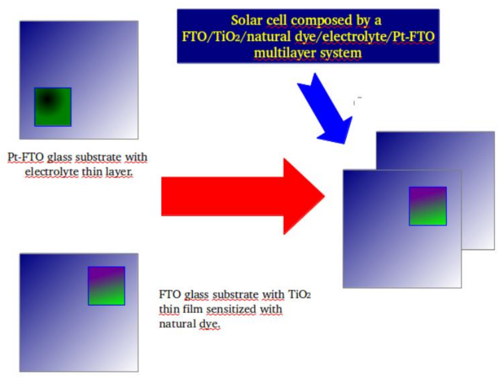

Figure 1. Scheme depicting a basic DSSC assembly.

Figure 1. depicts a basic DSSC aasembly. The configuration shown in fig. 2, basically corresponds to the cell structure. To measure cell efficiency their I-V characteristics were studied using a solar simulator unit coupled with an Keithley source meter.

cells were irradiated using 1sun, AM 1.5, light source from the solar simulator. Thus a multilayer system (Figure 2): FTO/TiO_2/natural-dye/electrolyte/Pt-FTO, was obtained as dye sensitized solar cell.

3. Results and Discussions

3.1. Optical properties of natural dyes

Absorbance spectra of the dye coated photoanode samples were measured in visible range between 400 to 700nm, fig. 3 and 4. For spinach, significant absorption was obtained for the case of sample 1 where the solvent used was methanol, fig. 3a. Four principal absorption peaks 413.2 nm, 466.2 nm, 437.2 nm and 662.4nm were identified using Lorentzian curve fitting. Absoption peaks located at 413.2 nm and 662.4 nm correspond to charateristic absorption peaks of chlorophyll-a, and absorption peaks located at 466.2 nm 437.2 nm correspond to characteristic absorption peaks of carotenoid. On the other hand, extractions done using aqueous medium (sample 4 and 6), showed no significant absorption peaks.

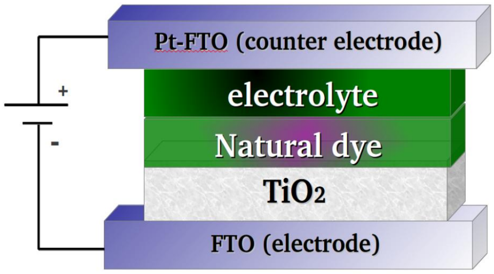

Figure 2. Dye sensitized solar cell composed by a FTO/TiO_2/natural-dye/electrolyte/Pt-FTO multilayer system.

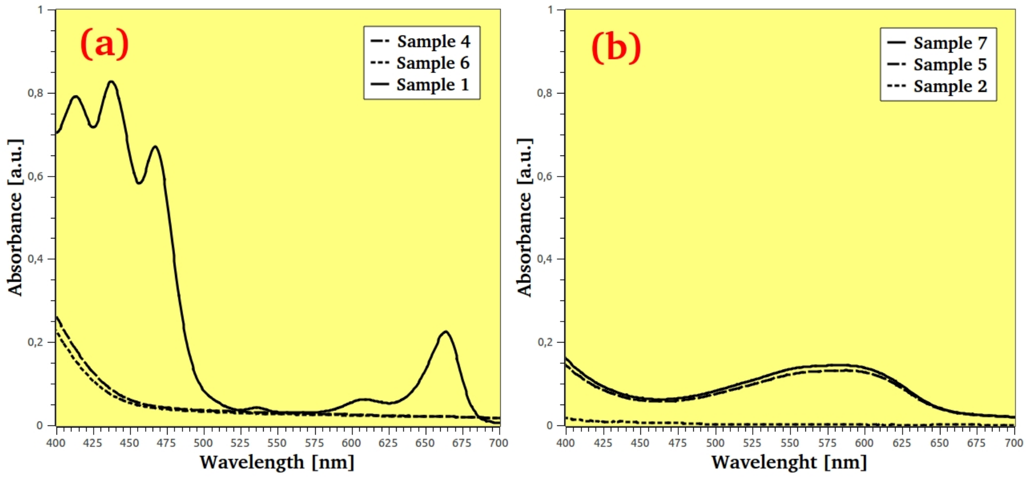

Figure 3. Absorption spectra obtained for natural dyes extracted from spinach (a) and purple cabbage (b).

For pigments extracted from purple cabbage, absorption peaks for samples 5 and 7 (fig. 3b) showed a broad peak in the range between 475nm to 640nm. Whereas for sample 2 no significant absorption peak was observed eventhough the solvent used for extraction was methanol. As the absorption spectrum was pronounced for sample 7, we took this for the study, in this case. The absorption peak seemed like a superposition of two or more peaks, thus an Lorentzian fitting was used to deconvolute the mixed peaks, one at 540.8 nm and another at 608.1nm.

According to literature [6], these peaks corresponds to characteristic absorption peaks of phycoerythrin and ficoeritrocianina pigments (blue colour) and phycocyanin (red colour) pigments respectively. That explains the superposition or mixture of two pigments and the origin of purple colour for purple cabbage.

For the mixture samples, absorption spectra for sample 3 is similiar to sample 1 and 8 similar to sample 7, except that the absorption peaks are less intense, but conclusions are identical to the cases of the samples 1 and 7, so in case of mixture diluted in methanol a better extraction of chlorophyll-a and carotenoids were obtained and a better extraction of phycoerythrin and phycocyanin were obtained in case of mixture diluted in deionized water, that can be seen in Figures 3 and 4.

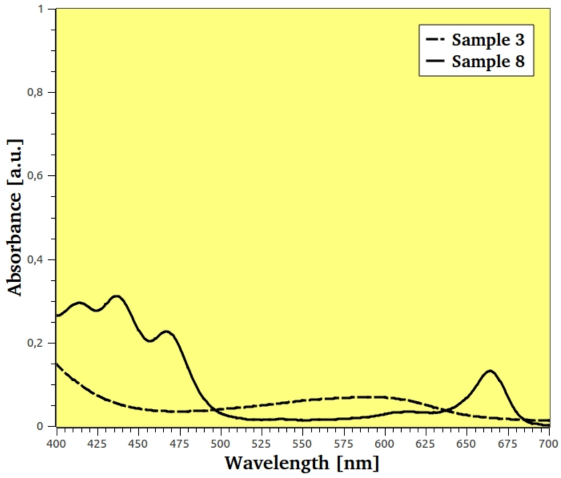

Figure 4. Absorption spectra obtained for natural dye composed of spinach and purple cabbage mixture.

3.2. Optical properties of sensitized TiO_2 layers

All the sensitized TiO_2 samples showed increased absorption in the spectrum range between 400nm to 620nm compared to the un-sensitized TiO_2 samples, fig. 5.

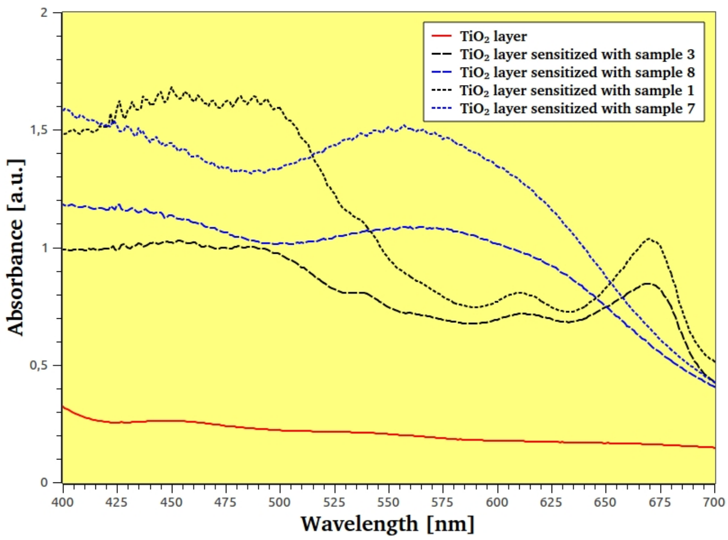

Figure 5. Absorption espectra of TiO_2 layer sensitized with different natural dyes.

However TiO_2 layers sensitized with samples 1 and 3 correspond to pigments diluted in methanol, which presents better absorption in visible range compared to TiO_2 layer sensitized with samples 7 and 8 that corresponds to pigments diluted in deionized water. In the later case, the absorption begins to decay to after 620nm.

TiO_2 layers sensitized with samples 1 and 3 showed characteristic absorption peaks in the wavelengths range 620 nm - 700 nm, whereas higher wavelength peaks over 620nm were not observed for sample 7 and 8.

3.3. I-V characteristics and solar cell efficiency

Solar cell efficiency (η) is the percentage of absorbed sunlight converted to electrical energy when a solar cell is connected to an electrical circuit. This term is calculated using the following relation, under standard conditions (STC);

$$\eta = \frac{P_{max}}{I \times A_c} \tag{1}$$

Where, P_{max}, is the maximum power; I, Light irradiance on the cell (in W/m^2); Ac, Surface area of the solar cell that is been irradiated by the light

STC specifies a temperature of 25°C and irradiance of 1000 W/m^2 with a spectral air mass 1.5 (AM 1.5).

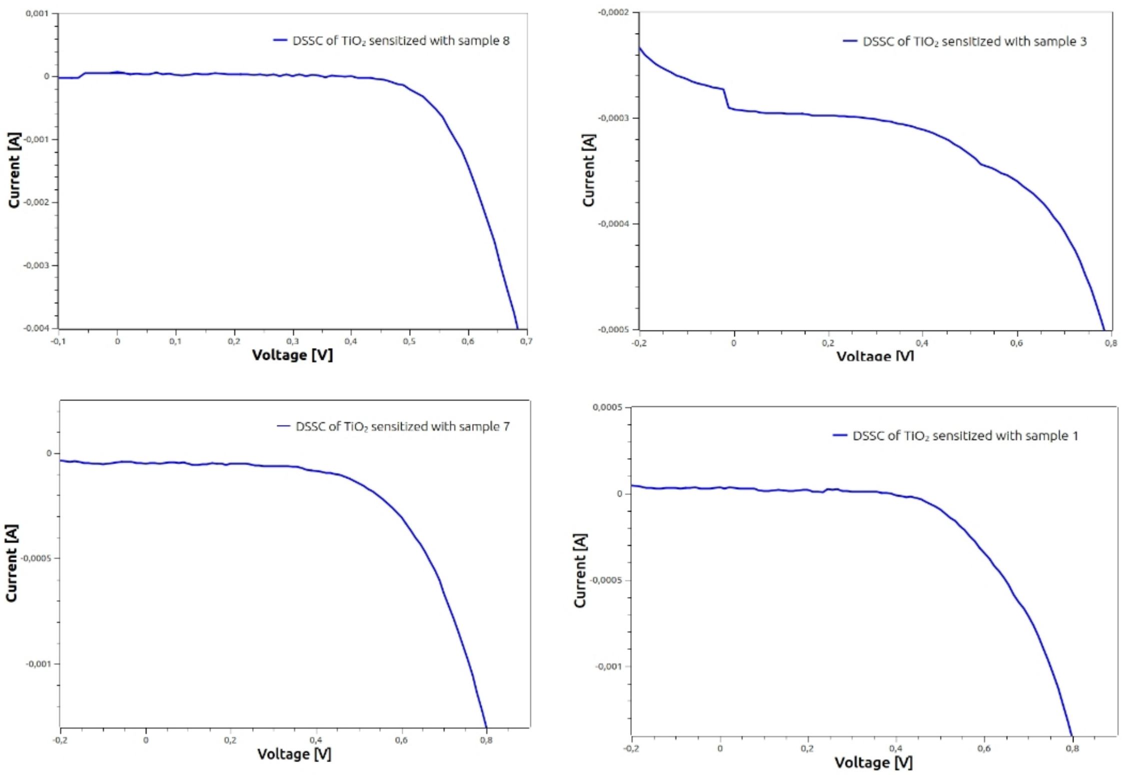

Figure 6. I-V curves of dye sensitized solar cells.

Table 2. I-V characteristics of solar cells measured by PET.

TiO_2 sensitized layer	V_{max} [V]	I_{max} [mA]	P_{max} [mW]	Efficiency [%]
Sample 3	0.27	0.270	0.072	0.072
Sample 8	0.11	0.619	0.069	0.017
Sample 1	0.26	0.048	0.012	0.012
Sample 7	0.23	0.048	0.011	0.011

The current-voltage characteristics and efficiency of each cell shown in fig. 6, were measured using a solar cell simulator PET (Photo Emission Tech, Inc., USA, Model CT80AAA) incorporated with a 1000 W/cm^2 Xenon arc lamp. The sweep voltage was from -0.3 to 0.8V over an effective area of ($1cm^2$) of the cell. Measurements show efficiencies ranging from 0.011 to 0.072% where lowest efficiency obtained 0.011 %, was for the cell corresponding to the sample composed of TiO_2 layer sensitized with sample 7 and highest efficiency 0.072 %, for the cell composed of TiO_2 layer sensitized with sample 3. Table 2 shows some main electrical parameters obtained for each cell in terms of current-voltage behavior.

4. Conclusion

Pigments were extracted from spinach and purple Cabbage using methanol and deionized water. When using methanol, the extraction was done at room temperature, whereas when using deionized water the extraction was done at 70°C and 80°C. Extracts done using methanol as the solvents showed better absorption of visible photon. The extracted dyes were used to sensitize the TiO_2 layer, which was used as the photoanode to assemble the DSSC. These TiO_2 layers were prepared using doctor blade method over an FTO coated glass substrate. The counter electrodes were prepared by platinizing the FTO coated glass substrate. After injecting an electrolyte inbetween the sandwiched electrodes, it formed a DSSC. The cells were further studied for their efficiencies under standard conditions. A composite extract of spinach and purple cabbage in methanol showed the maximum efficiency of 0.72 %.

5. Acknowledgement
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6. References

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