Natural Sensitizers for Dye Sensitized Solar Cell Applications

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Abstract— In the Present work, Dye Sensitized Solar Cells were assembled with the natural dyes extracted from three different flowers, namely, Nerium Oleander, Buogainvillea and Hibiscus. The ethanolic extract of the dyes were subjected to UV-Vis absorption and emission spectroscopic studies inorder to confirm the presence of anthocyanin and betalain. The DSSC's were assembled with the extracted dyes using standard fabrication procedures and tested under 85 mW / cm^2 solar simulation for their photoresponses. Of the three dyes tested onto the fabricated DSSC's, the dye extracted from red hibiscus exhibited best conversion efficiency with a maximum open circuit voltage (V_{OC}) of 0.515 V , short circuit current density (J_{SC}) of 0.765 mA/ cm^2 , fill factor (*FF*) of 0.479 and a overall conversion efficiency (η) of 0.19%. The other two dyes, obtained from Nerium Oleander and Buogainvillea also showed photoresponses under similar irradiation conditions.

Index Terms—Anthocyanins, Betalains, Dye-Sensitized Solar Cell, Natural Dyes, Absorption and Emission Spectra

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1 INTRODUCTION

The ever increasing Industrialization and Urbanization has led to the exhaustion of the available fossil fuels. This situation has led to find alternative resources of energy in order to meet the energy demands of the growing population. Therefore renewable or the non conventional sources of energy are preferred widely. Though there are various natural energy sources available to be utilized effectively, solar energy forms a major area of research. For the past few decades, importance was given to the conventional silicon based photovoltaic cells. In recent days, intensive research is being carried out in Dye sensitized solar cells (DSSCs), commonly referred to as Grätzel cells, generally belong to the category of third generation solar cells. Enormous research is performed in various aspects of Dye sensitized solar cells especially on the Photosensitizers, electrolytes, preparation of counter electrodes, and efficient fabrication procedures, ever since the report made by Brian Ó Regan and Michael Gratzel in 1991. DSSCs have gained utmost importance in recent days owing to their low cost, simple fabrication procedures, high overall conversion efficiency and also environmental friendly technology [1-3].

DSSC is basically a photoelectrochemical device used for the conversion of solar energy into electrical energy. It consists of a wide band gap semiconductor such as Titanium Dioxide (TiO_2) onto which the dye molecule or a photosensitizer which possess suitable attachment group is strongly attached, a counter electrode and an electrolyte is sandwiched between the two oppositely charged electrodes.

Soon after the absorption of light, an electron from the excited state of the dye molecule is injected into the TiO_2 Semiconductor layer. Injected electrons travel through the nano crystalline semiconductor into the external circuit to generate electric current. This electron is inturn generated by the electrolyte used, usually, I^-/I_3^- Redox couple. The device is said to generate electric current without undergoing any permanent chemical changes [3], [4].

The photosensitizer is an essential component of a complete DSSC that requires special consideration and attention to improvise on the overall conversion efficiency of the cell. The light absorption behavior of the dye molecule and the attachment to the semiconductor surface influences the overall conversion efficiency of the cell [5], [6].

Presently, ruthenium sensitizers were reported with their highest conversion efficiency exceeding 11% in AM 1.5 sunlight conditions, the high efficiency is attributed to the wide absorption range in the NIR region [7-9]. With much research on ruthenium based sensitizers, considerable research interest are constantly focused on metal free organic dyes which includes the wide application of triphenylamine dyes with a reported efficiency of 9.1% [10], unsymmetrical squaraine dyes with a reported efficiency of 6.74% [11]. Additionally, importance is given to the naturally available dyes found in flowers, fruits and vegetables from which the pigments are extracted in a cost effective manner and tested for their performance. Anthocyanins[12-19], Betalain [17], [18] and Chlorophyll [15], pigments which are generally found in the bright coloured fruits, vegetables and flowers are successfully used as photosensitizers in DSSCs.

Anthocyanins are basically responsible for colours from red to blue range found in the flowers, leaves, fruits, roots, stems of the plant [18-20]. They are the flavonoid pigments which are in abundance. The carbonyl and hydroxyl groups found in the anthocyanins can bind themselves to the TiO_2 film, which inturn facilitates the electron transfer from the dye molecule in to the conduction band of TiO_2 layer. Anthocyanins from variety of plant sources show various performances [14]. Betalains are those pigments which show

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bright colours in flowers found in plants of the order caryophyllales. Their light absorption behavior is in the visible region and they possess (-COOH) functional groups inorder to attach themselves to the TiO_2 layer [18].

Dyes from various natural sources, especially from the flowers have been extracted and reported in recent years with different conversion efficiencies. Shanmugam *et al.* used extracts from ivy gourd fruits and red frangipani flowers as sensitizers and reported the efficiency of red frangipani flowers with 0.301% [13]. Mounir alhamed *et al.* used the anthocyanin dyes and their combinations and reported that the combination of the extracted natural dyes exhibited better photovoltaic performance with an efficiency of 3.04% [19]. Ho Chang *et al.* tested the anthocyanin extract of purple cabbage to report a conversion efficiency of 1.47% [15]. Khwanchit Wongcharee *et al.* reported the efficiency of natural dyes extracted from blue pea and rosella exhibiting an efficiency of 0.33% and 0.57% [14] respectively.

In conjunction with the present research on the natural dyes, in the present work, natural dyes were extracted from three different flowers, namely, Nerium Oleander (Family: Apocynaceae, common name: Kaner, colour chosen: reddish pink), Bougainvillea bracts (Family: Caryophyllales, common name: Paper flower, colour chosen: dark pink), and Hibiscus (Family: Malvaceae, common name: Gurhal, colour chosen: red), and were used as photosensitizers in the assembled DSSCs. These flowers are found abundantly in various parts of India and are widely used as ornamental plants. The natural dyes thus extracted were characterized by UV-Visible spectra and emission spectra inorder to understand the capabilities of these compounds as a photosensitizer and the solar energy to electric energy conversion processes. The *J-V* characteristics of the fabricated DSSCs were also recorded inorder to calculate the required parameters such as short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (*FF*) and the conversion efficiency (η).

2 EXPERIMENTAL DETAILS

2.1 Extraction of Natural Dyes and Characterization

The chosen natural floral species such as Nerium Oleander, Bougainvillea, and Hibiscus were collected freshly from Sathyabama University Campus, Chennai, India, in August 2013. Then we extracted the required coloured dyes. The modified extraction procedure is as follows. The coloured petals were separated and they were washed with distilled water and then dried with a hair dryer for few minutes. The petals were then crushed properly in a mortar and pestle and then put in 95 wt % ethanol solvent (AR - 99.9%) and heated at 45 °C for a time period of 40 mins [16], [25]. The dye thus obtained was filtered and properly stored without direct exposure to sunlight and used as a photosensitizer in the assembled DSSCs without further purification. The colour possessed by the extracted dye from Nerium Oleander was reddish pink in nature, from Buogainvillea it was pink in colour and that with Hibiscus the dye was deep red in colour. The ethanolic extract of the dyes were characterized using absorption and emission spectroscopic studies inorder to understand the light absorption and emission characteristics.

Fig 1: Images of Nerium Oleander, Bougain Villea and Hibiscuc flowers chosen for present extraction of dyes

Fig 2: Solutions of the ethanolic extracts of the dyes

The UV-Visible spectra of the extracted dyes were recorded in a 10 mm length quartz cell by using JASCO V 630 spectrophotometer. This was performed inorder to understand the light absorption behavior of the extracted dyes. Additionally the dyes were also subjected to emission studies by using a Shimadzu RF-5301 PC spectrofluorophotometer inorder to understand the light emitting properties of the dyes.

2.2 DSSC Assembling and Photovoltaic Measurement

The components required for the assembling of DSSCs such as conductive glass slides (Fluorine doped Tin oxide; FTO) (2.5cm x 2.5cm), titanium dioxide powder (Degussa P25), graphite pencil, and the iodide electrolyte solution were procured from the Institute for Chemical Education, Wisconsin, USA, and directly used to fabricate the cell without any further treatment.

The DSSCs were assembled with the standard procedures available. 6 g of nanocrystalline TiO_2 powder (Degussa P25) was weighed and made into a smooth suspension in a mortar and pestle with dilute acetic acid (pH 3-4 in distilled water) which was added dropwise until a lump free smooth suspension was obtained. To the TiO_2 paste obtained, 2 drops of clear detergent solution was added and left undisturbed for 15 min. The square glass slide was cleaned with ethanol and the conducting side of the glass slide was identified with a multimeter and the counductance observed was 28 Ω. A smooth nanocrystalline TiO_2 layer was made on to the conducting side of the glass slide with a clean glass rod. The smooth film formed was air dried for a minute and sintered in an oven for 30 mins at 450 °C and cooled. The ethanolic extract of the dyes were taken in a petridish and the TiO_2 coated glass slide was immersed in it for 24 h without exposure to light. The carbon counter electrode was prepared by identifying the conductive side of the glass slide. The dye coated glass slide was washed gently with ethanol and dried. A drop of iodide electrolyte solution was sandwiched between the positively and negatively charged electrodes and clipped together to form a complete cell and the response of the assembled cell was recorded [21].

The conversion efficiencies were recorded under simulated solar light conditions under 85 mW/cm². The *J-V* charecteristics were recorded with potentiostat/galvanostat (Autolab-84610) set up.

3 RESULTS AND DISCUSSION

3.1 Absorption Spectra and Emission spectra of the Ethanolic Extracts of the Dyes

The absorption spectra of the ethanolic extract of the dyes were recorded for the three extracts prepared. Nerium Oleander is reported for its anthocyanin content [12], [20]. The dye from Nerium Oleander showed a sharp absorption peak in the UV region exhibiting a maximum wavelength of 383 nm and another peak in the visible region between 500-670 nm and exhibiting a maximum wavelength of 542 nm. Emission spectra for the flower was also recorded and the emission peak is observed at 380 nm. The absorption spectrum matches with the reported absorption wavelength region for the flower [24]. Buogainvillea bracts are known for their betalain content. The dye from Buogainvillea bracts showed a sharp absorption peak in the UV region exhibiting a Maximum wavelength of 386 nm and another peak in the visible region between 430-600 nm and a shoulder peak at 670 nm. Emission spectrum for the flower was also recorded and the emission peak is observed at 810 nm. The absorption spectrum matches with the reported wavelength range [23]. Hibiscus is identified to contain anthocyanins [22] .The Dye from Hibiscus exhibited a sharp peak at 380 nm and a broad peak in the visible region between 500-650 nm with an absorption maximum at 550 nm. Emission peak is observed at 810 nm. The absorption spectrum matches with the reported maximum absorption wavelength in the UV and Visible regions [19].

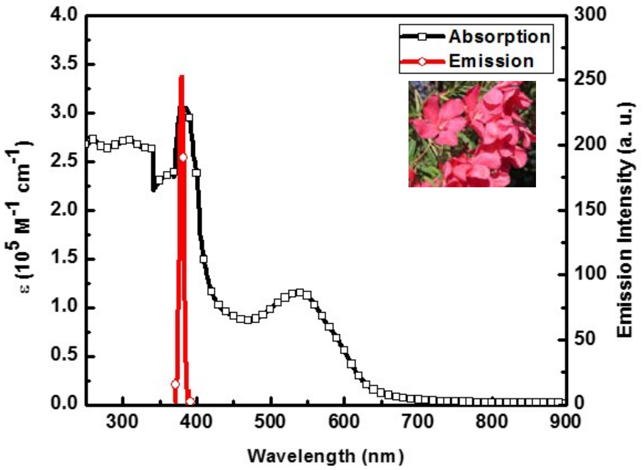


Fig 3, Photophysical properties of Nerium Oleander in ethanol. The inset shows the picture of the flower used for analysis.

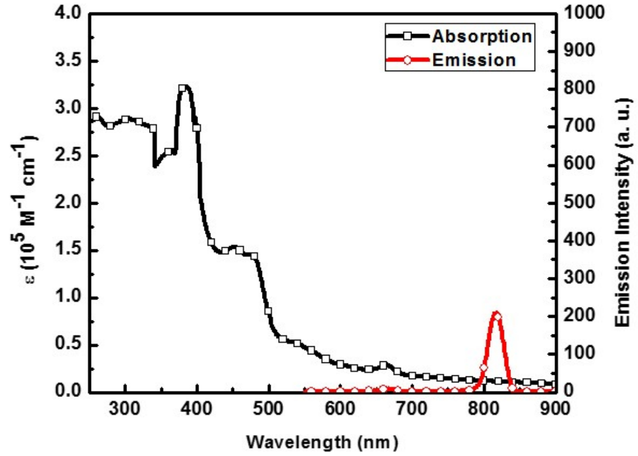


Fig 4, Photophysical properties of Buogainvillea in ethanol. The inset shows the picture of the flower used for analysis.

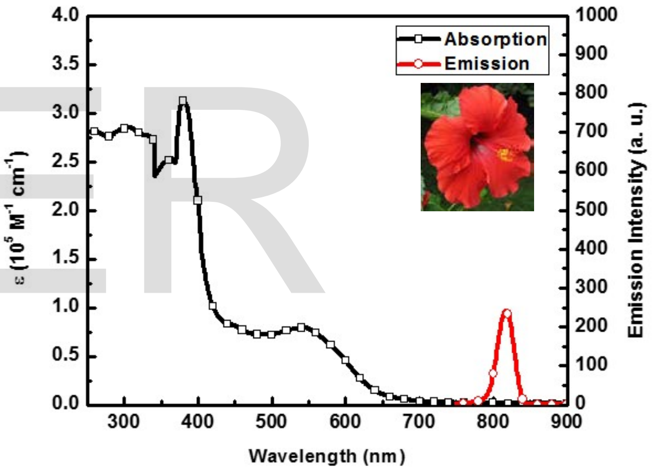


Fig 5, Photophysical Properties of Hibiscus in ethanol. The inset shows the picture of the flower used for analysis.

3.2 Performance of DSSCs with the natural photosensitizers

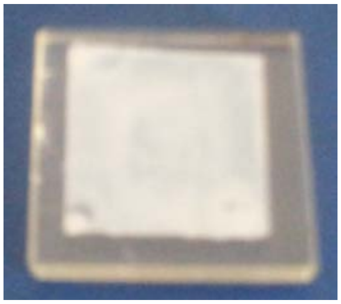


Fig 6: Image of the glass slide coated with TiO_2

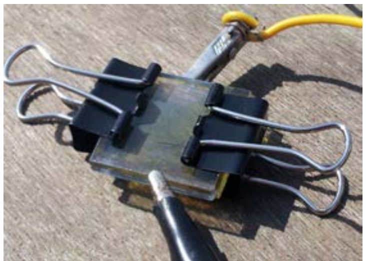
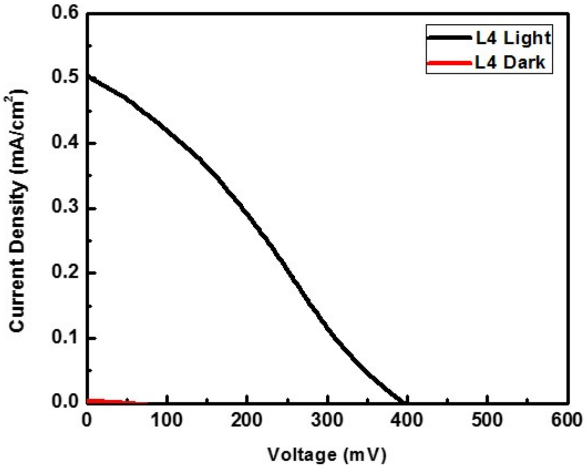


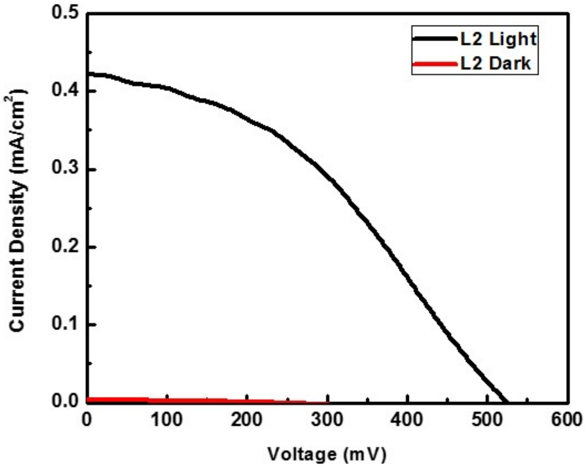
Fig 7: Image of the constructed cell with electrical contacts

The extracted natural dyes were used as photosensitizers in the assembled DSSCs. The DSSCs were assembled using the ethanolic extract of the natural dyes. All three samples were tested onto the assembled cells. At first, the cells were tested under direct solar radiation and then with a solar simulator. The light exposed areas of the DSSCs were 1 cm². The performance of the device was obtained with 85 mW/cm² solar illumination. The essential cell parameters such as, Short circuit current density (J_{SC}), Open circuit voltage (V_{OC}), Fill Factor (*FF*) and the overall conversion Efficiency, (η) for the ethanolic extracts of the dyes from Nerium Oleander, Buogainvillea and Hibiscus are summarized in the Table 1, and the corresponding photocurrent-voltage (*J-V*) curves are also shown for all the three samples in Fig 8, Fig 9 and Fig 10. The cell constructed with Hibiscus exhibited the maximum conversion efficiency of 0.19%. The cell based on Nerium Oleander gave an efficiency of 0.061% and the cell constructed with Buogainvillea dye exhibited a conversion efficiency of 0.053%.

Table 1 Photoresponse of the assembled DSSCs with different natural dye extracts

Dyes Tested	J_{SC} (mA/cm²)	V_{OC} (mV)	*FF* (%)	η (%)
Nerium Oleander (Red. Pink)	0.421	0.525	0.274	0.061
Buogainvillea (Dark Pink)	0.502	0.394	0.269	0.053
Hibiscus (Red)	0.765	0.515	0.479	0.19





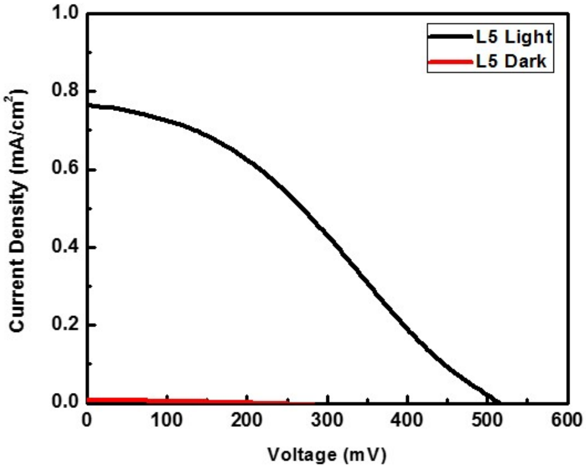
The J-V Curves were recorded under 85 mW/cm² Solar Simulation conditions with potentiostat/galvanostat (Autolab-84610) set up.

Fig 8: J-V Curve of the DSSC Constructed with Nerium Oleander
Fig 9: J-V Curve of the DSSC Constructed with Buogainvillea
Fig 10: J-V Curve of the DSSC Constructed with Hibiscus

The open circuit voltage and the short circuit current play a pivotol role in determining the overall conversion efficiency of the cell. The cell sensitized with the Hibiscus extract showed a maximum short circuit current compared to the other two dyes and a high efficiency exhibited by the cell constructed with Hibiscus is due to the alcoholic groups present in the anthocyanin molecule which favoured the attachment of the dye to the semiconductor layer.

4 CONCLUSION

The ethanolic extracts of the dyes obtained from Nerium Oleander, Buogainvillea and Hibiscus were used as photosensitizers in the DSSCs. The cell sensitized with Red Hibiscus showed a significantly higher short circuit current



with a maximum conversion efficiency of 0.19%, and the cell constructed with Nerium Oleander with a conversion efficiency of 0.061% and that with the extract of Buogainvilla with 0.053%.

Though the Solar energy to electrical energy conversion efficiency are very less for the dyes extracted, the results obtained are academically interesting. Advanced fabrication procedures followed may result in obtaining good efficiency measurement. By adopting proper coating procedures for Titanium dioxide layer, using platinum counter electrode, by varying the thickness of the TiO_2 layer formed, and more effective extraction procedures may also pave a way for producing better results with DSSCs sensitized with natural dyes. Additionally, the quantification of anthocyanin pigment present in the extracted dye can also be performed to extend the present research work.

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