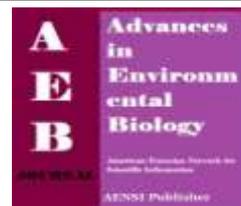




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Comparative Study of Natural Anthocyanins Compound as Photovoltaic Sensitizer

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ABSTRACT

Fabrication and characterization of different natural dyes extracts of dye sensitized solar cell (DSSC) are reviewed in this paper. Inorganic metal complex, N3 dye is also studied as a comparison. The paper focussed on the performance of sensitization which is related to the interaction between dye and TiO₂ surface. The electrical performances of the cell such as short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF), and overall conversion efficiency (η) was also investigated via current-voltage characteristic measurement as well as light absorption of dye loaded on TiO₂ film. The resultant study showed that higher ratio of active compound and higher interaction of dye-TiO₂ will results in higher conversion efficiencies.

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INTRODUCTION

Dye sensitized solar cell (DSSC) is a type technology for converting light energy into electrical energy based on the sensitization of wide bandgap semiconductors. A DSSC is composed of a dye modified wide band semiconductor electrode such as TiO₂, ZnO, Nb₂O₅ and a counter electrode and the redox electrolyte [7,11]. Similar to typical thin films photovoltaics [2,13], the performance of the cell mainly depends on the active layer; dye used as sensitizer. The absorption spectrum of the dye and the anchorage of the dye to the surface TiO₂ are important parameters in determining the efficiency of the cell. Basically, the transition metal coordination compounds (ruthenium polypyridyl complexes) are used as the effective sensitizers, due to their intense charge-transfer absorption in the whole visible range and highly efficient metal-to-ligand charge transfer.

However, ruthenium polypyridyl complexes contain a heavy metal, which is undesirable from the point of view of synthesization as it is complicated and costly [3,5]. Alternatively, natural dyes can be used for the same purpose with an acceptable efficiency. A great attention has been paid to dye sensitized solar cells (DSSC) as cheap, effective and environmentally benign candidates for a new generation solar power devices since the pioneering work of Regan and Gratzel [3,10]. The sensitization of wide bandgap semiconductor using natural pigments is usually ascribed to anthocyanins. The anthocyanins belong to the group of natural dyes responsible for several colors in red-blue range, found in fruits, flower and leaves of plants. Compared with a silicon solar cell [6], the cost of DSSC fabrication is 20% cheaper for practical application. However improved efficiency and long term stability is needed [7,5].

Experimental procedures:

A. Materials Preparation:

For the purpose of preparing the natural dye, pieces of fresh dragon fruit flesh, Roselle, turmeric and lemon leaves with weight approximately 50g is mixed into 50 ml distilled water at room temperature of 28±5°C. The mixture is further blended using an electric blender for 10 minutes until a homogenous color is seen by the naked eye. For N3 dyes, the resulting films are then immersed in a 0.5 mM ethanol solution of N3 dyes for 20 minutes and then rinsed with ethanol to remove the additional dye. The iodide electrolyte solution, which is a mixture of 0.5M potassium iodide and 0.05M iodine in water, is placed at the edge of the glass plates. The counter electrode

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consisted of a thermally platinized conductive glass, 5mM H_2PtCl_6 in dry isopropanol, heated at 380°C on the same type of conductive glass substrate for 10 minutes.

B. Device Fabrication:

ITO glass shows resistivity reading of 19 Ω /cm using the multimeter measurement. The two piece of conductive glass were merged separately into two identical beakers containing 10ml of 95wt% ethanol solution. Both of the beakers undergoes ultrasonic bath for 25minutes at medium mode. The resistivity of ITO coated glass decreased to 17 Ω /cm after the cleaning process. A porous film TiO_2 paste was prepared using technique reported by [14]. Commercial TiO_2 nanoparticles of 0.2g (Sigma-Aldrich;634662) are blended using an agate mortar with 0.4ml nitric acid solution (0.1M), 0.08g of polyethylene glycol and one drop of nonionic surfactant Triton-100 until it forms thick paste without any clots. A scotch tape at four sides was used as the masking material on the conductive layer to restrict the thickness and area of the paste, spreading a thin layer using a glass. The coated plate was then sintered at 450°C for 2 hours. After annealing process and the temperature of the film paste drop to 50°C-70°C, the coated glass is immersed into natural dye solution and left for 24 hours. Excess non adsorbed dye, were washed using anhydrous ethanol.

DSSCs were assembled by the following experimental procedure. First, the TiO_2 film coated glass was immerse into the anthocyanin TiO_2 film. The Pt thin film was coated on ITO coated glass of the other electrode. One or two drops of the iodine/iodide electrolyte solution are then placed at the edge of the plates and the two binder clips are alternately opened and closed while in place. The liquid is drawn into the space between the electrodes by capillary action and can be seen to “wet” the stained TiO_2 film.

C. Characterization and Measurement:

The absorption spectra of all dyes before and after drying were measured using a UV-Vis spectrophotometer. The absorption spectral analysis was carried out in the wavelength range from 350 to 900 nm. The *I-V* characteristic curves were measured at 900 W/m² irradiations. The shape of the *I-V* curve for the solar cell determines the fill factor of the solar cell which is the ratio of the maximum output power from the solar cell to the theoretical maximum power.

Table 1: Maximum absorbance wavelength (λ_{max}) of used Turmeric dyes and N3 dyes in solution and TiO_2 on films [9,12].

Dye	λ_{max} solution (nm)	λ_{max} TiO_2 film (nm)
Turmeric	460	415
Lemon Leaves	475 and 675	390
N3 (Ru535)	315,394 and 533	510

RESULTS AND DISCUSSION

The absorption spectrum of extracted dragon fruit (purple), rosella (red), lemon leaves (green) and turmeric (yellow) was obtained using the spectrophotometer. The absorption peak of rosella extracted is about 520nm while those of dragon fruit dye have peak absorption at 535nm as shown in Figure 1. The dragon fruit show good absorption level between 450nm to 600nm. The difference in the absorption characteristics is due to different type of color of the extracts. The data in Table 1 shows that the shifted wavelength of turmeric, lemon leaves and N3 dyes. For turmeric, wavelength shifted from 460 nm to 415 nm upon absorption of turmeric dye solution on the TiO_2 film. The lemon leaves display the absorption peaks about 675nm. The N3 dye shows the λ_{max} reach about 510nm corresponds to the stronger bonding between carboxyl groups of the N3 dye [9]. A blue shift is also noticed in case of lemon leaves (from 475 nm to 390 nm) but this may be attributed to the linkage between the ester groups in chlorophyll and TiO_2 surface.

From the full assembled DSSC, it is interesting to evaluate the solar energy conversion efficiency. Figure 2 show the result of high efficiency simulation of the *I-V* curve for dragon fruit extract source. Obviously, the efficiency of cell sensitized by the rosella extract was significantly higher than that sensitized by the dragon fruit extract. This is due to a higher intensity and broader range of the light absorption of the extract on TiO_2 and the higher interaction between TiO_2 and anthocyanins in the rosella extract leads to a better charge transfer [9]. Turmeric extract sensitized anchoring group of both active components in their extract (-O-, =CO, and -OH'). Lemon leaves extract represents the chlorophyll which is showed lower photoelectron chemical performance due to its lower affinity.

N3 dye is Ruthenium metal complex dye which effectively delivers electrons injected to the TiO_2 mesoporous film. The corresponding efficiency, η of the cells is shown in Table 2. From the table, we can see that the highest efficiency was obtained for cells sensitized with N3 cell and the values were close to each other, for rosella and dragon fruit, 0.37 and 0.22 respectively, for turmeric and N3 is 0.03 and 0.52 respectively [4,8,12].

The efficiency of the cell sensitized by the Ru-complex dye is significantly higher than that sensitized by the natural extracts [4,8,12]. Nevertheless, based from the results, it is proven that extracted of dragon fruit and rosella are applicable for DSSC preparation. Therefore, these three types of extract could be an alternative

anthocyanins source for DSSC preparation especially in the tropical country such as South East Asia.

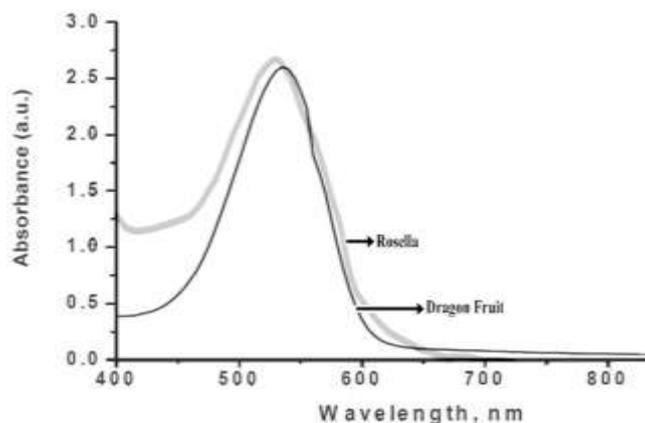


Fig. 1: The dye absorption spectrum of rosella and dragon fruit dye in range of 400nm to 900nm [1,9].

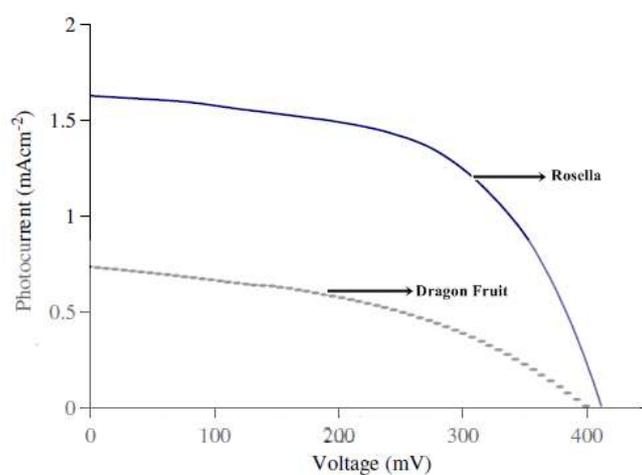


Fig. 2: Current-voltage curve for a dragon fruit and rosella extract sensitized solar cell [1,4,9].

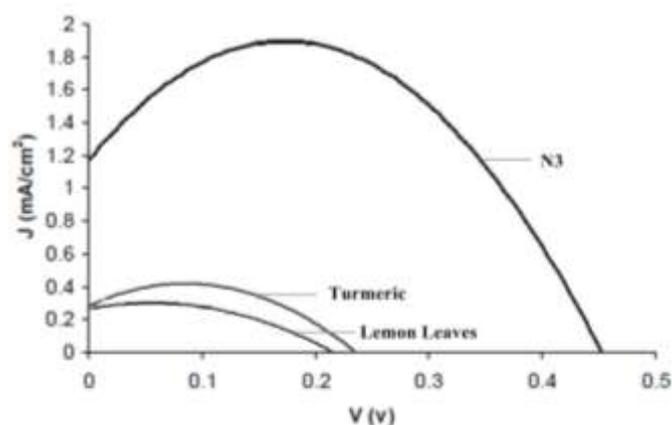


Fig. 3: Current-voltage curve for a turmeric extract, lemon leaves extract and N3 dye sensitized solar cell [4,8,12].

Table 2: Photoelectrochemical parameter of DSSC of illuminated sunlight present and simulation curve result [4,8,12].

Extract Source	I_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)
Dragon Fruit	0.630	400	0.44	0.22
Rosella	1.630	404	0.57	0.37
Turmeric	0.288	529	0.48	0.03
Lemon Leaves	0.286	539	0.74	0.05
N3	1.168	457	0.76	0.52

Recommendations:

The performances of DSSC is affected by many factors which is the nature of the dye pigment, the light spectrum and intensity, the thickness of the TiO₂ layer, the size of the active region, types of the electrolyte and also the extracting solvent that have been used. An efficient, rapid charge injection, transportation and also light absorption are necessary for amelioration of the solar cell. The efficiencies obtained using natural dyes are still low for large scale practical application but the results obtained may boost some additional studies to explore new natural sensitizers [11]. In fact, the dye can be affected by the active component which is carboxyl group, the pH, temperature and others parameters that lead to its degradation that affected overall performance of the DSSC. Hence, further studies in the predefined areas must be performed in order to improve the stability and also the performance of the dye sensitized solar cell.

Conclusion:

In this paper, dye-sensitized solar cells (DSSCs) were assembled using four natural extracts from various plant source to be used as sensitizers. The used dyes are extracted from dragon fruit, rosella, turmeric and lemon leaves. For comparison, N3 dye has also been studied. The reactions of natural dye with the TiO₂ surface have good indicator leading to a photoelectrochemical reaction when the cells exposed to light. The natural dye promotes the sensitization with different conversion efficiency according to spectral absorption range. The N3 dye was obtained a highest current density (1.168 mA/cm²). The N3 dye also has the highest efficiency, 0.52 %, followed by rosella, 0.37%. Dragon fruit, lemon leaves and turmeric dyes have efficiency about 0.22%, 0.05% and 0.03% respectively. Therefore, the natural dyes extract shows potential to be used as green energy generator for third generation of solar cell technology.

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