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Photoelectric Characterization of Dye Sensitized Solar Cells Using Natural Dye from Pawpaw Leaf and Flame Tree Flower as Sensitizers

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ABSTRACT

Natural dyes from flame tree flower, Pawpaw leaf and their mixtures were used as sensitizers to fabricate dye-sensitized solar cells (DSSC). The photoelectrochemical performance of the Flame tree flower dye extract showed an open-circuit voltage (V_{OC}) of 0.50 V, short-circuit current density (J_{SC}) of 0.668 mA/cm^2, a fill factor (FF) of 0.588 and a conversion efficiency of 0.20%. The conversion efficiency of the DSSCs prepared by pawpaw leaf extract was 0.20%, with V_{OC} of 0.50 V; short-circuit current density, J_{SC} of 0.649 mA/cm^2 and FF of 0.605. The conversion efficiency for the flame tree flower and pawpaw leaf dye mixture was 0.27%, with V_{OC} of 0.518 V, J_{SC} of 0.744 mA/cm^2 and FF of 0.69. Although the conversion efficiencies, Jsc and the Voc of the prepared dye cells were lower than the respective 1.185%, 7.49 mA/cm^2 and 0.64V reported for ruthenium, their fill factors (FF) were higher than that of ruthenium (0.497). It was also observed that both the short-circuit current density and the fill factors of the cells were enhanced using mixed dye.

Keywords: Dye-Sensitized Solar Cells; Flame Tree Flower; Pawpaw Leaf; Dye Cocktails; Natural Dyes

1. Introduction

Ddye-sensitized solar cells (DSSCs) are third generation solar cells developed by O'Regan and Gratzell in 1991 [1]. It converts inexpensive photon from solar energy to electrical energy based on sensitization of wide band gap semiconductor dyes and electrolytes [2]. In this process, several subsystems which work in tandem are interlaced with the adsorbed dye on a semiconductor surface that absorbs the visible and near—IR photons and pumps electrons into the conduction band of the semiconductor which is the electron-mediator for "hole" conduction and the counter electrode catalytic material [3]. The performance of the DSSC is highly dependent on the sensitizer dye and wide band gap material such as TiO_2, SnO_2, ZnO and Nb_2O_5 [4]. TiO_2 is highly preferable due to its ability to resist the continuous transfer of electron under illumination (in the ultraviolet range). Several studies have addressed the use of SnO_2 and ZnO [5,6]. In general, the performance of dye absorption on the surface of TiO_2 molecule determines the efficiency of the solar cell [2] and DSSCs efficiencies of up to 10.4% have been reported for devices employing nanocrystalline TiO_2 films [7]. One of the most efficient sensitizers is produced from the heavy transition metal coordination compound, ruthenium polypyridyl complex which is used widely due to its intense charge-transfer (CT) absorption in the visible light spectrum; good absorption, long excited lifetime and highly efficient metal-to-ligand charge transfer (MLCT) [8]. Ruthenium based complexes are however very expensive and hard to prepare, which restricts their large-scale applications in solar cells, stimulating the search for alternatives such as organic dyes [9]. Organic dyes with similar characteristics and even higher absorption coefficients used for DSSCs with efficiencies of up to 9% have been reported [10-12]. Organic dyes with higher absorption coefficients could translate into thinner nanostructured metal oxide films. This is advantageous for charge transport both in the metal oxide and in the permeating phase, allowing for the use of higher viscosity materials such as ionic liquids, solid electrolytes or hole conductors [13]. Organic dyes used in the DSSC do resemble dyes found in plants, fruits and other natural products and several of these have been used in the production of dye-sensitized solar cells [13-15]. Among

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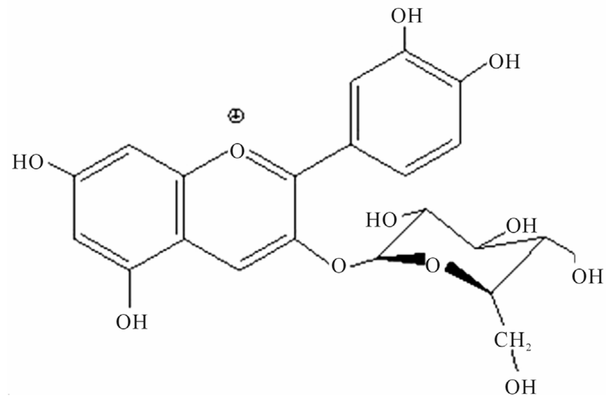
the advantages of natural dyes is their easy availability, environmentally friendly, ease of fabrication, low process temperature and low cost of sensitization material production.

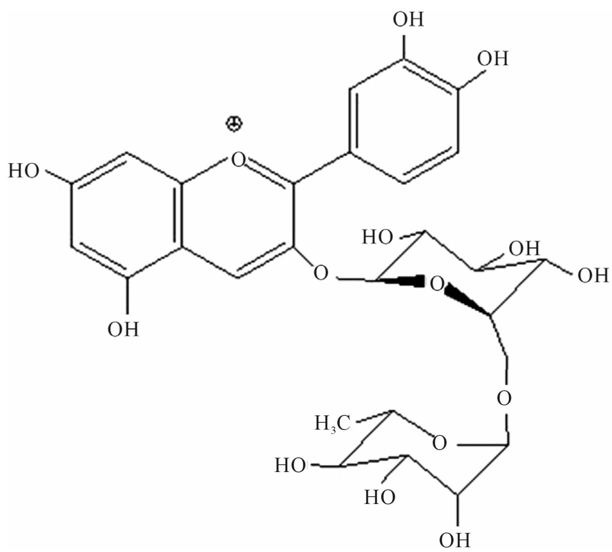
Naturally most fruits, flowers and leaves show various colours and contain several pigments which are easily extracted and then employed in DSSCs [16]. The leaves of most green plants are rich in chlorophyll and its application as natural dye has been investigated in many related studies [4,17,18]. Anthocyanins are natural compounds that give colour to fruits and plants and are also largely responsible for the purple-red color of autumn leaves and the red colour of flower buds [19]. In this paper, anthocyanin extracts of flame tree flower, chlorophyll extract from pawpaw leaf and their mixture were the natural dyes used as dye-sensitizers for the preparation of DSSCs.

The flame tree (*Delonix regia*), also known as royal Poinciana or flamboyant, is a member of the bean family (*Leguminosae*) widely regarded as one of the most beautiful tropical trees in the world [20]. The anthocyanins from the flame tree are composed of cyanidin 3-*O*-glucoside (**Figure 1(a)**) and cyanidin 3-*O*-rutinoside (**Figure 1(b)**) [21].

Pawpaw (*Carica papaya Linnaeus*), belongs to the family of *Caricaceae*. It is not a tree but an herbaceous succulent plants that posses self supporting stems of spongy and soft wood [22] Pawpaw is a large perennial herb with a rapid growth rate and thrives in tropical climate that is dry when cold and wet when warm [20] The leaves emerge directly from the upper part of the stem in a spiral on nearly horizontal petioles 30 - 105 cm long, hollow, succulent, green or more or less dark purple [23]



(a)



(b)

Figure 1. Chemical structure of (a) cyanidin 3-*O*-rutinoside and (b) Cyanidin 3-*O*-glucoside, main components of Flame tree flower anthocyanin.

2. Experimental Details

2.1. Extraction of the Natural Dyes

Fresh flame tree flower and pawpaw leaves each of 10 g were separately weighed on an electronic weighing balance and crushed with a porcelain mortar and pestle, each crushed sample was then mixed with 50 cm^3 of ethanol (99% absolute) at room temperature in a dark room. Solid dregs in the solution were filtered by filter paper to acquire a pure and natural dye solution. Then, flame tree flower and pawpaw leaf extracts were blended at volume ratio of 1:1 to serve as a natural dye mixture.

2.2. Preparation of DSSC

The TiO_2 film was prepared by blending 0.2 g of commercial TiO_2 powder (Degussa, P25), 0.4 cm^3 of nitric acid (0.1 M), 0.08 g of polyethylene glygol (MW 10,000) and one drop of a Triton x-100 (a nonionic surfactant). The mixture was well mixed using an ultrasonic bath for 1 h and the resulting paste was spread over an FTO conductive glass plate (SOLARONIX) having 15 Ω/cm^2**.** The TiO_2 nano-particles thus produced had a mean particle size of 20 nm. TiO_2 pastes were deposited on the FTO conductive glass by rigid squeegee and screen printing procedure (polyester mesh of 90) in order to obtain a TiO_2 film with a thickness of 18 μm. The active area of DSSC was 0.54 cm^2 (1.4 cm × 0.39 cm). The TiO_2 thin film was sintered at 450˚C for 1h to increase compactness of the thin film. The TiO_2 film was consolidated through heat treatment, increasing the internal voids of film organization and thus enhancing its absorption performance. Then the sintered TiO_2 thin film was immersed for 24 h in natural dyes prepared, allowing the natural dye molecules to be adsorbed on the surface of TiO_2 nanoparticles. Anhydrous alcohol was used to remove any natural dye that had not been adsorbed on the surface of TiO_2 nanoparticles. Finally, after cleaning, the DSSCs photoelectrode was complete and ready for testing.

Glass insulation spacers in long strips were used in assembling and these were stuck on the four edges of the base plate of conductive glass at the bottom. These formed a space between photoelectrode and counter electrode enabling the injection of electrolyte.

2.3. Current Voltage Characterization

In the performance test of the prepared DSSC, xenon (Xe) light of 150 W was selected to simulate sunlight (AM 1.5), and an I-V curve analyzer (Model 4200 SC) was employed to measure the photoelectric conversion efficiency of the prepared DSSC. The measured results were plotted in an I-V curve, from which the data of open-circuit voltage V_{oc} (V), short-circuit current density J_{sc} (mA/cm^2), fill factor (FF) and conversion efficiency η% were further acquired.

3. Results and Discussion

Figure 2 shows the SEM image of TiO_2 nanoparticles fabricated using screen printing procedure. The TiO_2 nanoparticles had a mean particle size of 20 nm (TiO_2 nanoparticle that is well sintered enhanced the adsorptivity of natural dye molecules).

Absorption spectra provide necessary information on the absorption transition between the dye ground state and excited states and the solar energy range absorbed by the dye. **Figures 3** and **4** show the absorption spectra of Flame tree flower and Pawpaw leaf dye extracts respectively as against N719 dye. The absorption range of N719 dye was from 400 - 600 nm with an absorption peak at 475 nm. The flame tree flower dye extract had an absorption in the frequency range 350 - 500 nm with an absorption peak at 415 nm. The chlorophyll dye extract from the pawpaw leaf had an absorption peak at 430 nm characteristic of chlorophyll pigment and an absorption range from 350 - 550 nm. Chlorophyll absorbs most strongly in the blue and red regions of the absorption spectra.

Figure 5 shows the absorption spectrum of the mixed dyes from the flame tree flower and pawpaw leaves with the absorbability range of 350 - 500 nm while the absorption peak was at 430 nm. This indicated that the absorption peaks of the mixed dye and that of pawpaw leaves dye were the same which could be as a result of them having the same colour or composition as different dyes show different absorption wavelengths due to differences in their compositions [24,25]. The weak absorption of the natural dye pigments in the red is a disadvantage, which affects the efficiency of the DSSC. The op-

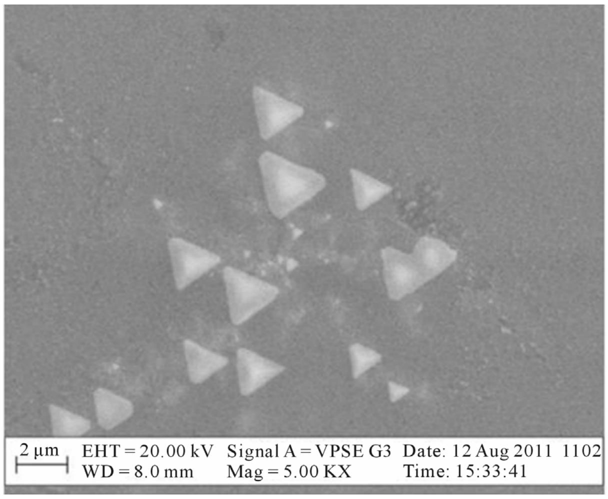


Figure 2. SEM image of fabricated TiO_2.

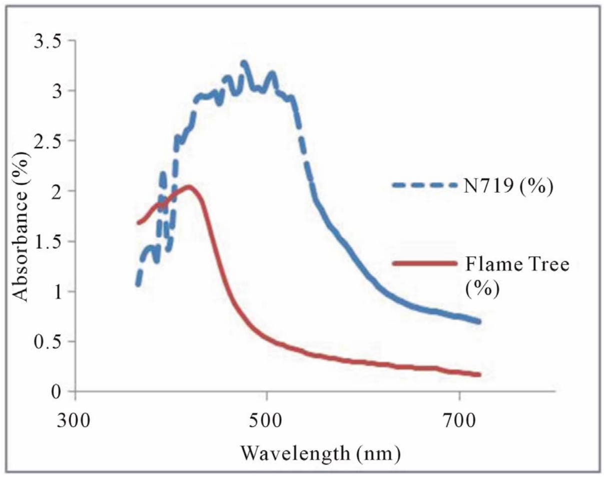


Figure 3. Absorption spectra of N719 dye and flame tree flower.

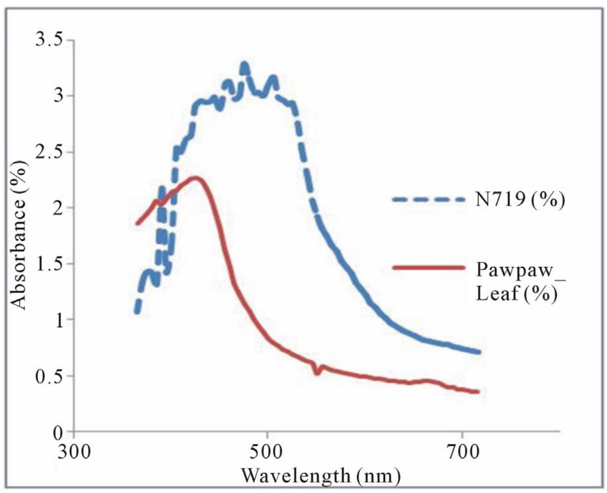


Figure 4. Absorption spectra of N719 dye and Pawpaw leave.

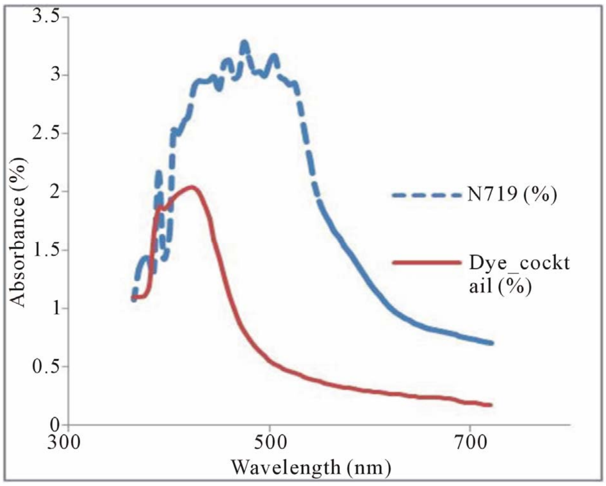


Figure 5. Absorption spectra of N719 dye and cocktail dye.

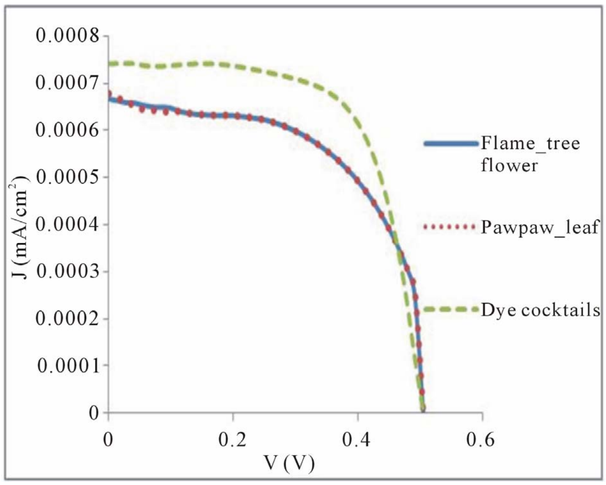


Figure 6. J-V characteristics of DSSCs with flame tree flower, pawpaw leaf and combination extracts dye.

timization of the sensitizing dye, electrolyte solution and metal oxide surface chemistry will improve the solar cell performance.

Current-Voltage (J-V) curves of solar cell gives important information on the operational parameters such as the short circuit current I_{sc}, open circuit voltage V_{oc}, the current I_{mp} and voltage V_{mp} at the maximum power point of a solar cell. **Figure 6** shows the J-V characteristics of the prepared DSSC taking flame tree flower extract, pawpaw leaf extract and cocktail as the natural dye while ruthenium (N719) was characterized as a standard. **Table 1** shows the data acquired from measuring the photoelectric conversion efficiency of the DSSCs.

The conversion efficiency of the DSSCs prepared from the dye extracted from flame tree flower is 0.20%, with open-circuit voltage (V_{oc}) of 0.503934 V, short-circuit current density (J_{sc}) of 0.668 mA/cm^2 and fill factor (FF) of 0.588. The conversion efficiency of the DSSCs prepared from dye extracted from pawpaw leaf was 0.20%, with V_{oc} of 0.503938 V and J_{sc} of 0.649 mA/cm^2 and FF of 0.60526. The conversion efficiency of 0.27% was recorded for the dye cocktails with V_{oc} of 0.517958 V and J_{sc} of 0.74418 mA/cm^2 and FF of 0.69. The power conversion efficiency (η) of the solar cells was calculated from the following equation:

$$\eta = \frac{FF \times J_{sc} \times V_{oc}}{P_{in}} \times 100\%$$

P_{in} is the power density of incident light [26].

From the result in **Table 1**, the DSSC of the combined dye mixture had improved photoelectric conversion efficiency. This is attributed to a synergistic sensitization by the dye mixture leading to higher efficiency [17]. The V_{oc} of natural dye was lower than that of ruthenium dye which could have been because of molecular structure of natural dye which mostly has OH and O ligands that lack -COOH ligands possessed by ruthenium dye which combine with the hydroxyl of the TiO_2 particles producing ester that boost coupling effect of electrons on TiO_2 conduction band leading to a rapid electron-transport rate [27] These values were, however, comparable with those obtained for the DSSCs of frozen blackberries by Zhu *et al*. (2008) where 0.33 V was obtained as the open-circuit voltage while 0.59 V and 0.4 V were reported as the respective open circuit voltages for the DSSCs of dye extracts of blueberries and Jaboticaba's skin [28].

Table 1. Characteristics of dye-sensitized solar cells.

Dye	I_{SC} (mAcm^{-2})	V_{OC} (mV)	FF	η%
Ruthenium	7.4920	0.639993	0.4972	1.185
Flame tree flower	0.6680	0.503934	0.5880	0.200
Dye cocktail	0.74418	0.517958	0.6900	0.270
Pawpaw leaf	0.6490	0.503938	0.6053	0.200

4. Conclusion

Dye sensitized solar cells were prepared from anthocyanin extracts of flame tree flower, chlorophyll extracts of pawpaw leaves, and a mixture of the two extracts. The photoelectric conversion efficiency with flame tree flower extract and pawpaw leaf extract as the natural dye both reach 0.20%, while the conversion efficiency of dye-sensitized solar cell from the mixed could reach as high as 0.27%. The mixed dye has higher conversion efficiency than dyes prepared by either flame tree flower or pawpaw leaf extracts. Therefore, the mixed dye in this study provides a more efficient incident photon-to-electron conversion. The effect of mixed ratio of the dyes on the efficiency is being investigated further.

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