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Chlorophyll and Betalain as Light-Harvesting Pigments for Nanostructured TiO_2 Based Dye-Sensitized Solar Cells

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Abstract: Chlorophyll and betalain pigments extracted from scent leaves and flower of *Bougainvillea Spectabilis* were used as sensitizers for nanostructured TiO_2 based dye-sensitized solar cells (DSSCs), and their perfomances were investigated systematically. The light harvesting pigments have shown absorption in broad range of the visible region of the solar spectrum and appreciable adsorption onto the semiconductor surface. The photovoltaic (PV) parameters such as short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF), and overall solar conversion efficiency (η) were determined under 100 $mAcm^{-2}$. The DSSC fabricated with betalains pigment from *Bougainvillea Spectabilis* was found to be superior to that obtained from chlorophyll pigment of scent leave (*Ocimum Gratissimum*). The DSSC gave a short circuit current density of 0.093 $mAcm^{-2}$, open circuit voltage of 0.433 V, fill factor of 0.550, and an overall solar conversion efficiency of 0.040%. The cell sensitized with betalains pigment exhibits: (i) ~ 1.90 times improvement in conversion efficiency, (ii) ~ 2.11 times enhancement in photocurrent density, and (iii) ~ 1.38 times improvement in fill factor compared to the results obtained with the chlorophyll sensitized solar cell. The sensitization performance related to interaction between the dye and TiO_2 surface is discussed.

Keywords: DSSCs, TiO_2, Natural Pigments, Betalain, Chlorophll, Electron Transfer, Sensitization

1. Introduction

Solar cell is a promising renewable energy technology that converts sunlight to electricity at visible region of electromagnetic spectrum, with good prospect of solving the future energy crises that humanity will face [1, 2]. Renewable energy sources such as solar energy are seen as a reliable alternative because "Energy from sunlight that reaches the Earth in one hour (4.3×10^{20} J) alone is more than all of the energy consumed by humans in an entire year (4.1×10^{20} J) [3]. Efforts in harvesting a fraction of the solar energy reaching the Earth may solve many problems connected with both the energy and global ecosystem [4].

In chronological order, solar cell technologies have have been developed three generations [5]. The first generation photovoltaic solar cells are based on a single crystalline semiconductor wafer. The second generation solar cells utilized thin layer of polycrystalline semiconductor, they are cheaper to produce, flexible and lightweight; however, the efficiency is still lower than first generation cells.

In 1991, Professor Grätzel reported a new low cost chemical solar cell by the successful combination of nanostructured electrodes and efficient charge injection dyes, known as Grätzel cell or dye-sensitized solar cell which falls under the third generation photovoltaic cell [6]. Other examples in this category include; quantum dot-sensitized solar cells (QDSSCs), colloidal quantum dot solar cells (CQD), organic solar cells, perovskite solar cells (PSCs) etc.

DSSC came into existence in an attempt to mimic photosynthesis, the natural processes plants convert sunlight into energy in this case by sensitizing a nanocrystalline titanium dioxide (TiO_2) film using novel ruthenium (Ru) bipyridl complex. In dye sensitized solar cell, charge separation is accomplished by kinetics competition like in photosynthesis leading to photovoltaic action. While the organic dye in the photoelectrochemical or dye sensitized solar cell replaces light absorbing pigments, the wide bandgap nanostructured semiconductor layer replaces oxidized dihydro-nicotinamide adenine-dinucleotide phosphate (NADPH), and while carbon dioxide acts as the electron acceptor, the electrolyte replaces the water while oxygen as the electron donor and oxidation product, respectively [7, 8].

However, the efficiency of conversion for DSSC remains modest and the stability has also posed concerns. In realizing better device performance and stability in DSSC, various light harvesting materials are employed to enhance photovoltaic performance and their properties are investigated.

It was once reported that the presence of sensitizer in the vicinity of TiO_2 can absorb more photons [9].

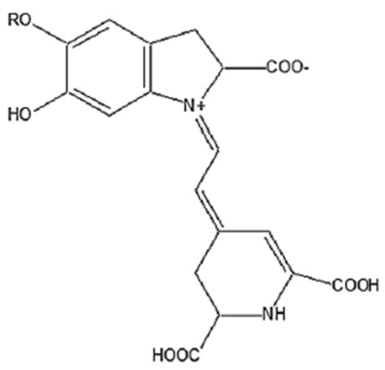
The dye is an important part of the DSSCs, playing an important role in absorbing light, generating photo-stimulated carriers and injecting these carriers into the conduction band of TiO_2 network. Thus, the capability of the dye to absorption light and how many carriers it stimulates directly affect carrier injection determine DSSCs performance [10]. Therefore, enhancing dye light absorption should be an effective way to increase the conversion efficiency.

The use of natural dyes have been considered as potential alternatives to the expensive synthetic dyes in enhancing the light response of semiconductor in active layers of solar cells, and have been demonstrated on several solar-cell materials [11-22].

Several dye pigments from plant sources have been studied among the most exploited include: chlorophylls, anthocyanins and betalains [23].

Conversely to the anthocyanins, that present functional groups (-OH), betalains have the requisite functional groups (-COOH) to bind better to the TiO_2 surface [24-26], than the functional group (-OH) present in the anthocyanins. The general structure of betalain is shown in Figure 1a. [23].

It contains carboxylic functional group which allows good bond formation between the TiO_2 and the extract.



R=H or $C_6H_{12}O_6$

Figure 1a. *General structure of Betalain [23].*

In this work, we present the influence of sensitizer on TiO_2 layer on the photovoltaic parameters of solar cell by performing a comparative study between betalain and chlorophyll extract. The effect of sensitizer on the PV performance of the formed solar cells were investigated systematically. Comparative analysis on the performance of the solar cells showed that the DSSC sensitized by the betalain pigment of *Bougainvillea Spectabilis* outperformed the DSSC with chlorophyll pigment from scent leave. The related PV performance enhancement mechanisms and the dye interaction with TiO_2 surface are analysed and discussed.

Structure of a DSSC

A typical DSSC is composed of transparent conducting (working) and counter conducting electrodes separated by an electrolyte. The transparent conducting electrode consists of a mesoporous wide band gap semiconductor layer that is attached to the conducting glass. A monolayer of charge transfer dye is then attached on the surface of the mesoporous wide band gap semiconductor. This photoanode section is in contact with a redox electrolyte or hole conductor. The structure is completed by coupling with a counter electrode (cathode) as shown in Figure 1b. [3]

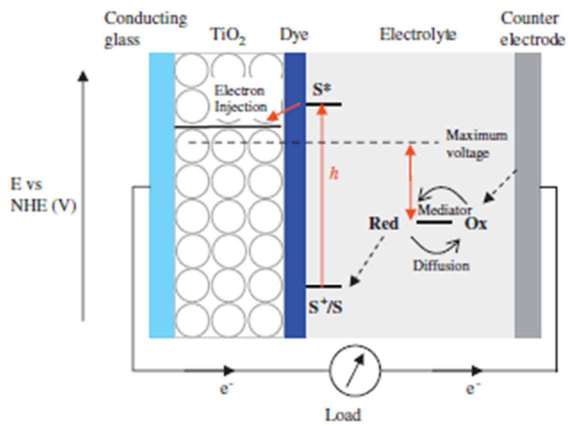


Figure 1b. *Structure and operating principle of a typical DSSC [3].*

2. Materials and Method

2.1. Materials

Acetonitrile, Platisol, acetaldehyde, and Triton-X 100 were purchased from BDH chemicals. Ethanol (99.8%), were purchased from Sigma-Aldrich and used as received. FTO was purchased from solaronix. The surface resistance of the FTO was 15 ohms/m^2, P25 TiO_2 powder was obtained from Alfa Aesar.

2.2. Preparation of the Natural Dye

The natural dyes were extracted with deionized water employing the following procedure: fresh flower of *Bougamvillea spectabilis* (B S) and Scent leaves (S L) were washed and air dried. 5 g each of *Bougamvillea* and scent leaves were grinded to small particles using a blender with 100 ml deionized water each as extracting solvent. The solution was filtered to separate the solid resisdue from the pure liquid and the filtrate was used as the light harvesting pigment without further purification.

2.3. Preparation of TiO_2 Paste

The TiO_2 films was prepared using a modified sol–gel method, in which 2 g of P25 TiO_2 powder was dissolved in 10 ml of deionized water mixed with 0.2 mol of Triton-X 100 and 0.4 g of acetaldehyde, then vibrated ultrasonically for 24 hours [11].

2.4. Preparation of Photo Anode

FTO conductive glass sheets, were first cleaned in a detergent solution using an ultrasonic bath for 10 minutes, rinsed with water and ethanol, and then dried. The nanocrystalline TiO_2 layers used in DSSCs devices often contain small holes that allow direct contact between the electrolyte and conducting electrode and result in the charge leakage. In order to prevent the carriage leakage, a blocking layer has been used between the conducting electrode and the nanocystalline TiO_2 layer.

The photoanode was prepared by first depositing a blocking layer on the FTO glass (solaronix), followed by the nanocrystalline TiO_2. The blocking layer was deposited from a 2.5 wt% TiO_2 precursor and was applied to the FTO glass substrate by spin coating and subsequently sintered at 400°C for 30 mins. Motivated by this analysis, we utilized screen printing method to achieve the design of FTO/TiO_2 with thickness of 9 μ m. It was then sintered in air for 30 mins at 500°C. The dyes were anchored onto the surface of the TiO_2 film electrode by immersing it into the dye extract for 12 hours.

2.5. Preparation of Counter Electrode

The counter electrode was prepared by screen printing a platinum catalyst gel coating onto the FTO glass. It was then dried at 100°C and annealed at 400°C for 30 minute.

2.6. DSSCs Assembly

The dye-sensitized TiO_2 electrode and the screen printed-Pt counter electrode were assembled to form a solar cell by sandwiching a redox (tri-iodide/iodide) electrolyte solution. Therefore, the open side of the cell assembly was sealed properly with epoxy resin.

2.7. Characterization and Measurement

The current density-voltage (*J-V*) characteristics of the cells were recorded under an irradiance of 100 mW/cm^2 (AM1.5) simulated illumination (keithley 2400 source meter from a Newport A solar simulator). The surface morphology of the TiO_2 was observed by scanning electron microscopy (Phenom Pro X model, Eindhoven de Netherlands). The presence of chlorophyll and betalain was confirmed by using the UV-visible absorption spectroscopic technique (Ava-spec-2048 spectrophotometer) in the region of 350–700 nm.

3. Results and Discussion

3.1. Scanning Electron Microscopy (SEM)

Figure 4 shows the scanning electron micrograph of the TiO_2 film. The TiO_2 film shows a mesoporous spherical nanoparticles with thickness of 9 μ m and mean particle size of 15 nm.

3.2. Absorption Spectra of Natural Dyes and TiO_2

Figure 2a shows the absorption spectra of the water extracs of SL and BS. From this figure, it is indicative that these natural extracts absorb in the visible region of light spectrum and hence meet the requirement for their use as light harvesting pigments in DSSCs. The *Ocimum Gratissimum* has a peak of 390 nm which is consistent with the characteristic absorption band of chlorophyll [11]. *Bougainvillea Spectabilis* has absorption peak of 370 nm which indicate presence of betalain pigment. The differences and variations in the absorption characteristics of the dyes can be attributed to the different colors of the extracts due to respective pigments present in them and their varied abilities towards adsorption onto the semiconductor surface. No obvious absorption peak was observed with TiO_2 electrode (Figure 2b). The absorption for betalain was stronger than that for chlorophyll pigment. Therefore, a better DSSC performance could be expected from the DSSC sensitized using betalain pigment.

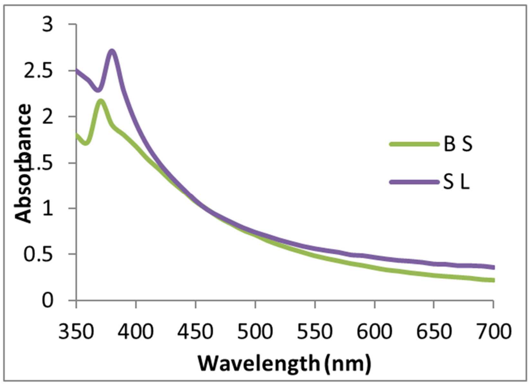


Figure 2a. *Shows the UV–vis spectra of B S, and S L extracts.*

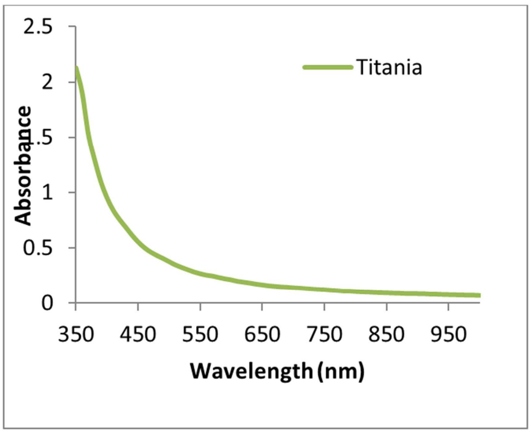


Figure 2b. *UV-vis spectra of TiO_2 without dye.*

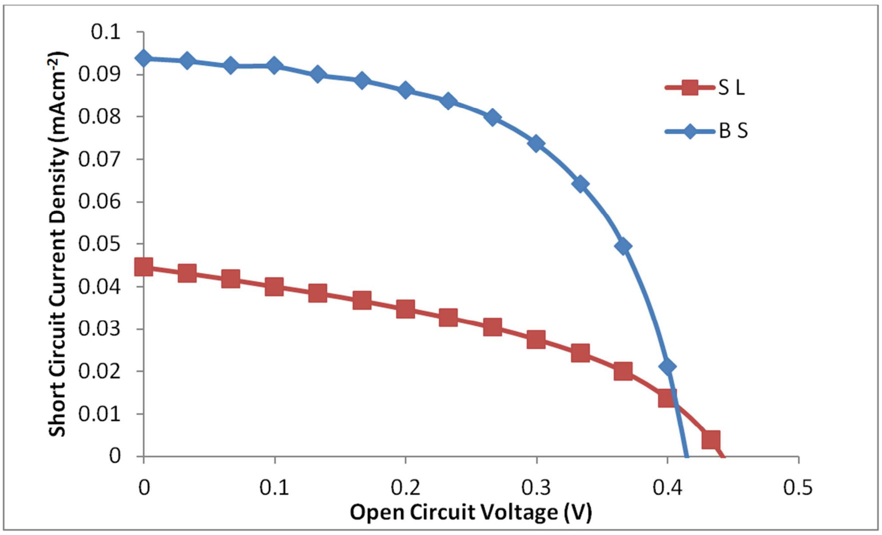


Figure 3. *Photocurrent density–voltage (J –V) curve of DSSCs with different natural pigment.*

Table 1. *Photovoltaic performance of DSSCs with Scent leave and Bougainvillea spectabilis pigments under 100 mWcm^{-2}.*

Sample	J_{sc} (mAcm^{-2})	V_{oc} (V)	*FF* (%)	η (%)
S L	0.044	0.466	40.00	0.021
B S	0.093	0.433	50.50	0.040

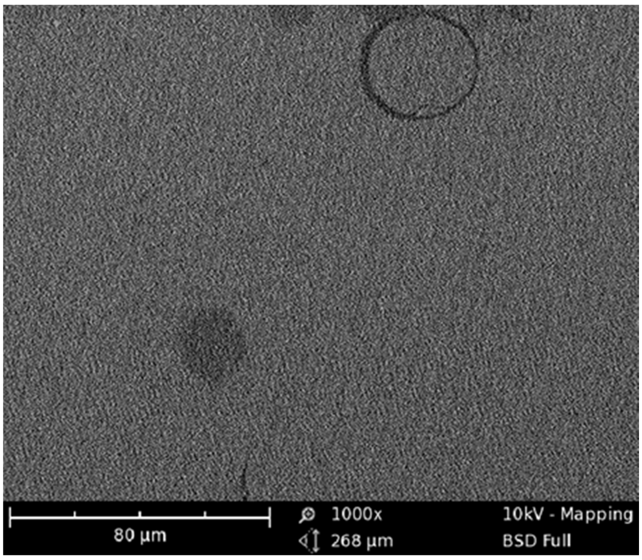


Figure 4. *The Scanning electron micrograph surface morphology of TiO_2 sample.*

3.3. Photoelectrochemical Properties of DSSCs Sensitized with Natural Dyes

The current density voltage characteristics of the DSSCs sensitized with the extracted pigments (Figure 3) is recorded as shown in table 1.

Based on the *J-V* curve, the *fill factor* (*FF*) which measures the ideality of the device, and describes how close to a square the shape of the *J-V* curve is: and the *solar cell efficiency* (η) which is the ratio of the electric power, supplied by the cell at the maximum power point, to the power of the incident radiation, were determined using equations (1) and (2) [13] respectively.

$$FF = \frac{J_{max} \times V_{max}}{J_{SC} \times V_{OC}} \quad (1)$$

$$\eta = \frac{FF \times J_{SC} \times V_{OC}}{P_{IRRADIANCE}}.100\% \quad (2)$$

Where
V_{max} = maximum voltage (V);
J_{max} = maximum current density (mA/cm^2);
J_{sc} = short circuit current density (mA/cm^2);
V_{oc} = open circuit voltage (V) and
$P_{IRRADIANCE}$ = light intensity (mW/cm^2)

The perfomance of the DSSCs sensitized with the chlorophyll extract showed a conversion efficiency of 0.021%. The betalain pigment showed active photoelectric activities on photoanode with conversion efficiency of 0.040%. The results obtained indicated that the betalain pigment performed ~ 1.90 times in efficiency, ~ 2.11 times in current density, and ~ 1.38 times in fill factor compared to the results obtained with the chlorophyll sensitized solar cell. The improvement in performance may be attributed to the presence of carboxylic functional groups (-COOH) in betalains pigment to anchor better to the TiO_2 nanoparticles than the chlorophyll pigment which lacks available bonds between the TiO_2 and the dye molecule through which electrons can transport from the excited dye molecule to the conduction band of the TiO_2 film. The interaction between TiO_2 film and carboxylic functions should bring a stronger electronic coupling and rapid forward and reverse electron transfer reactions which generates higher photocurrent [23]. Results suggest that betalain pigment has more ability to absorb light energy and transfer the excited electrons to the semiconductor TiO_2. The poor perfomance noticed with the chlorophyll sensitized solar cell may be explained as follows; sometimes a complication such as dye aggregation on semiconductor film produces absorptivity that results in either the non-electron injection or steric hindrance preventing the dye molecules from effectively arraying on the semiconductor film [27]. This leads to the weaker binding and greater resistance, resulting in the low output of the chlorophyll sensitized solar cell. When our study is compared to Yirga et., al [28], which recorded the following parametres for *Bougainvillea spectabilis* (J_{sc} =0.088 $mAcm^{-2}$, V_{oc} =0.2 V, η =0.0066%, and FF=37.4%), our results were superior to their findings which is attributed to the extracting solvent (water in our research and ethanol in their work). This might be due to the fact that our extracted pigment is more soluble in water as a result; the aggregation of dye molecules decreases as expected leading to Better dispersion of dye molecules on the oxide surface.

Also, most of the natural dye which have a good and a broader absorption in the visible spectrum are expected to show a good rectification of the *J-V* curve that is responsible for good current density and power conversion efficiency [29]. In this study, water extract of *Bougainvillea spectabilis* shows a better rectification which results relatively good photoelectrochemical performance for water extract than the ethanol extract.

4. Conclusions

Dyes obtained from nature, were used as sensitizers in DSSCs. The extracted dyes contain chlorophyll and betalain pigments. The betalains pigment was used as dye sensitizer to obtain an enhanced cell performance with an increase in efficiency and photocurrent upto about 1.90 and 2.11 times compared to the chlorophyll pigment. Hence, though the short circuit current densities and open circuit voltages obtained with these natural dyes are somewhat low, they are quite promising as viable alternative to expensive and rare organic sensitizers and could be used for the production of low-cost and environment friendly DSSCs.

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