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Hibiscus Flower Extract as a Natural Dye Sensitiser for a Dye-sensitised Solar Cell

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ABSTRACT: *The conversion of solar light into electricity was successfully accomplished by using hibiscus as a dye sensitiser. A solar energy conversion efficiency of η = 0.11% was obtained with a short circuit current of up to J_{sc} = 0.96 mA cm^{-2}, an open circuit voltage of V_{oc} = 0.268 V and a fill factor of 0.43. This paper presents an interesting preliminary study for alternative energy development using the rich biodiversity of Malaysia to promote sustainable energy sources. In this paper, the methodology and its limitations are reported and discussed with the roles of the different TiO_2 structures.*

Keywords: Dye-sensitised solar cells, *Hibiscus rosa-sinensis*, TiO_2, photovoltage, natural dye sensitiser

1. INTRODUCTION

Increasing energy demands and a growing awareness of environmental issues are the driving force in the search for cleaner, sustainable and renewable energy. As the most abundant clean source of energy, solar energy has a large potential to become the next energy source to rival fossil fuel. Solar cells, which are also called photovoltaic cells (PV), can be used to harvest solar energy. However, this process only becomes feasible if it has a low cost, long lifespan and reasonable efficiency.[1]

Generally, three basic generations of solar cells are considered. The first generation of photovoltaic cells, which are also known as silicon wafer-based solar cells, have a low efficiency (~6%–10%), and are labour intensive and expensive to manufacture.[2] The second generation of solar cells such as amorphous Silicon (a-Si)-based photovoltaic cells have been dominant in recent commercial production. Silicon is obtained from the silica (SiO_2) in sand, which is abundant. However, pure silicon production is a very high-energy process. Therefore, this research addresses thin-film solar cells.[3] Thin-film solar cells, such as thin-film dye-sensitised solar cells (DSSCs), are easy to fabricate under

ambient conditions. DSSCs are made of purely organic components or of a mixture of organic and inorganic components, and they do not require severe purity measures to reduce production costs.[4]

Natural dyes that are responsible for several colours are found in anthocyanins, with different plants having different sensitising performances.[5] Numerous efforts have been made by several research groups around the world to utilise natural dyes from various plant components as sensitisers for solar cells.[6–10] According to Wong et al., the red flower of *Hibiscus rosa-sinensis* contains high concentrations of anthocyanins that are potential natural dyes for solar cells.[10] However, research regarding the performance of hibiscus dye-sensitised solar cells is still lacking.

In this study, DSSCs were prepared using hibiscus dye extracted from *Hibiscus rosa-sinensis* flowers. Two types of TiO_2 aeroxides, P25 and R-5566, were used to prepare thin uniform layer films, and their efficiencies were discussed. This discussion would be useful for the production of dyes for DSSCs. Additionally, the absorption spectra of the hibiscus are also reported.

2. EXPERIMENTAL

A TiO_2 suspension was prepared according to Chopra et al.,[1] with only minor modifications. Initially, 6 g of titanium dioxide powder was measured and placed in a mortar. Next, 9 ml of nitric acid was pipetted into the mortar before grinding the mixture with a pestle until the mixture was homogenous. Then, the suspension was stored in a small plastic capped bottle and allowed to equilibrate for 15 min. Next, the resultant suspension was spread over a glass plate to prepare a thin uniform film. Finally, the film was dried and heated in an oven at 150°C for 30 min before cooling to room temperature.

The natural dye sensitiser used in this research was prepared by extracting anthocyanins from hibiscus petals. The extraction was performed as described by Chang et al.,[11] with only minor adjustments. First, 10 g of *Hibiscus rosa-sinensis* flower petals were cut into small pieces and crushed using a mortar and pestle. Next, the crushed petals were mixed with 200 ml of a 95% ethanol solution and maintained at room temperature. Then, the extract was stored in a dark container (away from direct sunlight) overnight. The next, day, a slurry paste of the natural dye was prepared by concentrating the dye on a hot plate at 40°C.

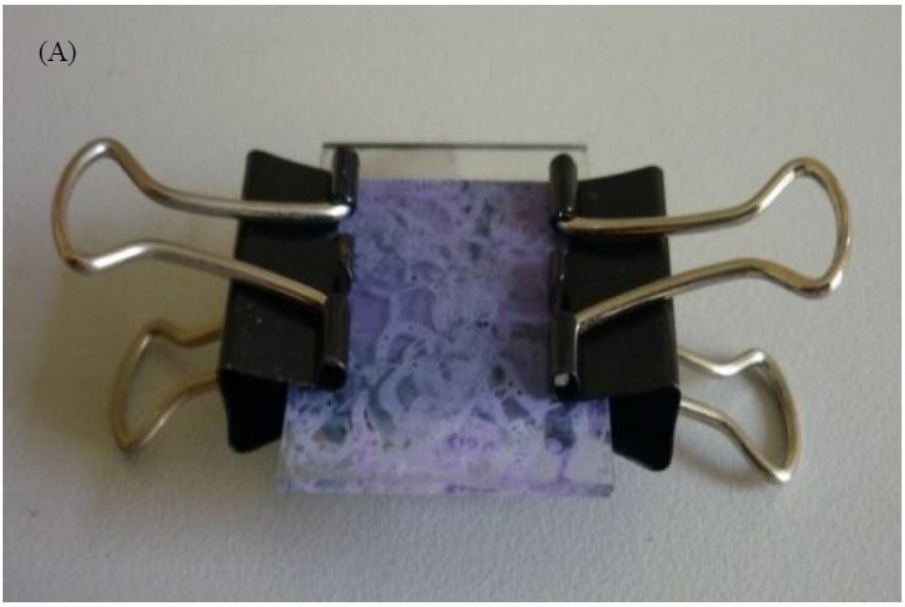
The DSSC was assembled by preparing two slides, a dye-stained slide (electrode) and a graphite-coated slide (counter electrode). To prepare the dye-

stained slide, the TiO_2 coated slides were immersed in the dye for an hour. During this stage, the colour of the TiO_2 layer changed from white to slightly purple. Subsequently, the stained film was rinsed in water and ethanol. Next, the dye-stained slide was gently blotted dry with tissue paper.[12]

To prepare the graphite-coated slide, the conductive side of the glass plate was coated with carbon by gently sweeping the surface with a graphite stick (2B pencil). Next, the carbon-coated glass plate was coated with black by holding the carbon-coated side of the glass plate above a candle flame. Then, the carbon coated glass plate was heated on a hot plate at 150°C for 15 min before allowing it to cool at room temperature.[13]

Next, the cell device was assembled by placing the graphite-coated slide face down on top of the stained titanium dioxide coated side. The two opposing slides were placed on top of each other with a slight offset to ensure that all of the stained titanium dioxide was covered by the counter electrode and that a space was available for connecting the crocodile clips. Next two binder clips were used on opposite edges to gently hold the slides together.[14] Then, two drops of the iodide/iodine electrolyte solution were placed at the edges of the plates. The complete cell is shown in Figure 1. Subsequently, the two binder clips were alternately opened and closed to promote the uniform dispersion of the iodide/iodine electrolyte between the slides. Then, the alligator clips that were attached to the overhanging edges were connected to the multi-meter. The negative and positive terminals were attached to the stained titanium dioxide (electrode) and graphite stained (counter electrode) slides, respectively.[14]

The electrical output and cell performance were measured using a 500 Ω potentiometer as the variable load. Point by point current and voltage data were gathered at each incremental resistance value and were plotted on graph paper.[15] The sample morphologies were measured using a scanning electron microscope (SEM) (EVO 50, Zeiss Inc.). The absorption spectra of the dye were measured on a Jasco 650 UV-Vis spectrophotometer using a 1 × 1 cm plastic cuvette.



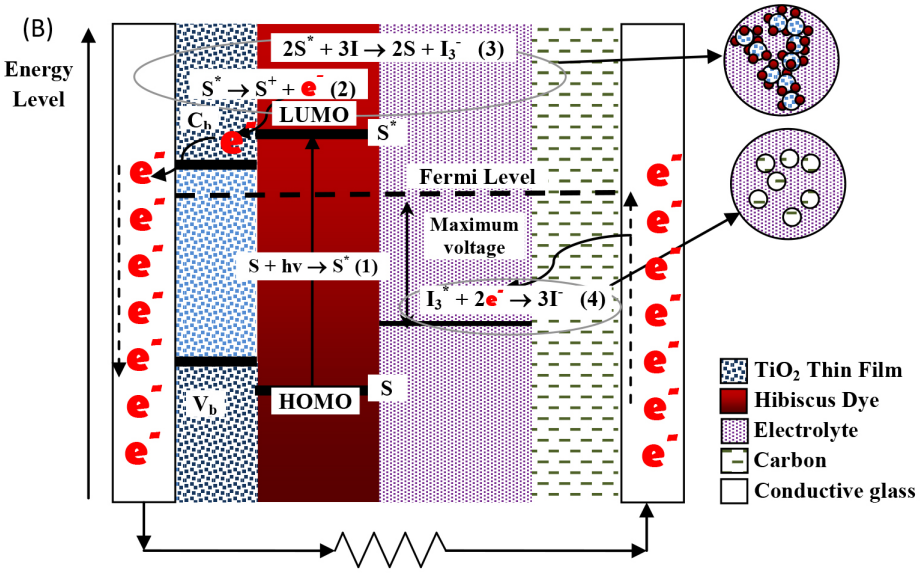


Figure 1: (A) Assembled solar cell; (B) Schematic diagram of DSSC with Cb = Conduction band, Vb = Valance band, LUMO = Lowest Occupied Molecular Orbital; HOMO = Highest Occupied Molecular Orbital; hv = Photon, S = Dye and S^* = Excited dye.

3. RESULTS AND DISCUSSION

3.1 Optical Properties of the Dye Solution

Figure 2 shows the UV–Vis absorption spectra of the hibiscus dye extract between 400 to 780 nm. The absorption peak of the hibiscus dye occurred at approximately 516 nm. The absorption spectrum was slightly different from those reported by Fernando and Senadeera[16] for *Hibiscus rosa-sinensis* dye that was extracted using acidified ethanol, which resulted in an absorption peak at 540 nm. The difference in the absorption characteristics resulted from the different types of functional groups on the anthocyanins and the colours of the extracts.

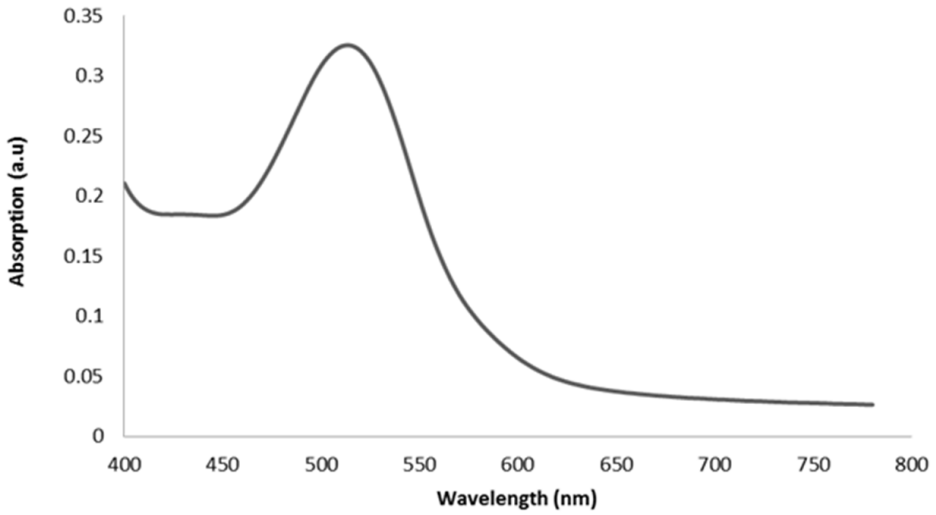


Figure 2: Absorption spectra of *Hibiscus rosa-sinensis* extract.

In addition, the presence of some impurities or particles potentially caused the differences observed in our results. Ideal dye sensitisers are determined according to the amount of light that they absorb from the visible light region of the spectrum. Thus, all light should be absorbed below a threshold wavelength of approximately 920 nm. Wider absorbed spectrum ranges correspond with the conversion of more energy to electricity.[17] As observed from the absorption spectra of the hibiscus extract, the range of the spectrum was from 400 to 800 nm.

3.2 SEM Analysis

The SEM images of the TiO_2 film may not be consistent because the morphology was destroyed when the TiO_2 film was scratched. Alternative methods, such as coating the TiO_2 film, are recommended for future studies. In addition, the uniformity of the film is very important for obtaining better analysis results.

Figure 3(a) shows the SEM image of TiO_2 R-5566, which consists of a wide particle size distribution and several agglomerates. The particles size varied from 20 to 100 μm. In addition, the SEM image of the TiO_2 aeroxide P25 powder is shown in Figure 3(b). Here, the TiO_2 particles were uniformly dispersed with a narrow particle size range. However, this result was not proven in any of the analyses conducted in this study. The crystallite particle sizes were approximately 20 nm. By visually observing and comparing the SEM images shown in Figures 3(a) and 3(b), it was deduced that the TiO_2 Aeroxide P25 powder had a more porous structure than the TiO_2 R-5566.

Figure 3(c) shows the SEM image of the Aeroxide P25 TiO_2 film after gentle scratching to disrupt the surface layer. From the SEM image, the film thickness was estimated to be approximately 30–60 μm. Furthermore, Weerasinghe et al.[18] reported that a large contact area and strong bonding between the individual TiO_2 particles are important for producing sufficient connectivity in the TiO_2 particle network. Sufficient connectivity is likely to result in good electrical conductivity in the particle network and the efficient conversion of photons to electrons.

The SEM images of the TiO_2 films may not be consistent due to the morphology that was destroyed when the TiO_2 film was scratched. Alternative methods, such as coating the TiO_2 film, are recommended for future studies. In addition, the film uniformity is very important for obtaining better analysis results.

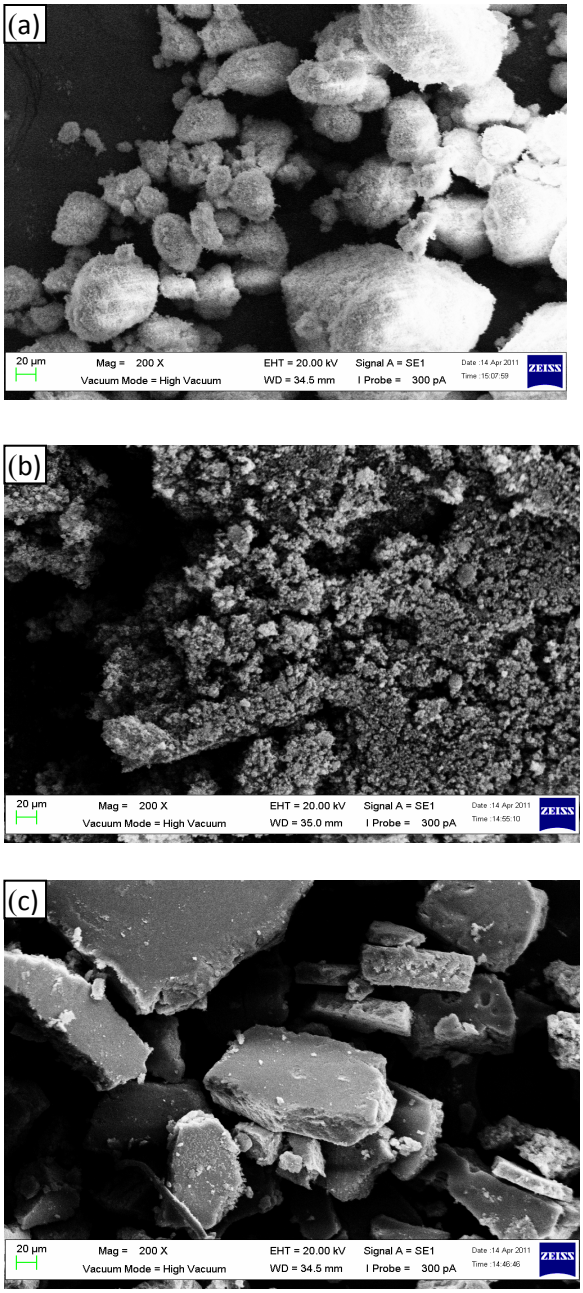


Figure 3: SEM images of (a) TiO_2 R-5566 TiO_2, (b) Aeroxide P25 and (c) cross-section of the TiO_2 layer.

3.3 Solar Cell Analysis

To obtain a more realistic cell efficiency, outdoor measurements (on a cloud-free day at 1:00 PM in Kota Kinabalu, Sabah, Malaysia) were performed. The Aeroxide P25 TiO_2 coated solar cell showed better results than the R-5566 TiO_2. For the DSSC using R-5566 TiO_2, a voltage of 0.040 V and an electric current of 0.04 mA were recorded when using direct sunlight. The voltage that was produced by using an overhead projector (OHP) was much lower (approximately 0.020 V). The R-5566 TiO_2 coated DSSC produced an unstable I-V output (the I-V curve is not shown in this paper).

Figure 4 shows the I-V curve of the outdoor measurements using the Aeroxide P25 TiO_2. The recorded open circuit voltage was 0.268 V and the recorded short circuit current was 0.96 mA cm^{-2}. These characteristics exhibited a fill factor of 0.43 and a deduced efficiency of 0.11% (See Table 1). The higher performance of the Aeroxide P25 TiO_2 resulted from the smaller particle size of the Aeroxide P25 TiO_2. The nanoparticles of the Aeroxide P25 TiO_2 are potentially packed more efficiently onto the substrate surface because the voids among the particles decrease with decreasing particle size. The small size of the TiO_2 nanoparticles results in a large surface area that allows for maximum adsorption of the dye sensitiser on the semiconductor. In addition, this structure could offer the desired directionality for electron transport in the TiO_2 electrode, which could result in a faster photo-response and higher electron collection efficiencies.[19]

Furthermore, the Aeroxide P25 TiO_2, which is more porous than the R-5566 TiO_2, results in a higher electrolyte penetration. A greater number of pores in the TiO_2 film enhance the regeneration of the oxidised dye and the charge transport. Xu et al. reported an increase in the redox mediator transport rate in the higher porosity TiO_2 film, where it was found that the cell efficiency was greatly enhanced in the porous structure.[20]

The measured efficiencies of the conversion of sunlight to electricity were low in this study relative to the published efficiencies that were obtained using similar materials and methods.[16] Although the values obtained were small, they demonstrate the applicability of hibiscus dye for photovoltaic energy conversion. One potential reason for the small efficiencies is the TiO_2 film thickness with the presence of discrepancies in the layer.[21–23] The uniformity of the TiO_2 film thickness affects the conversion efficiency of the solar cell module. Furthermore, if the film thickness is not uniform, charge recombination can occur and the energy conversion efficiency of the DSSC will be reduced.[24]

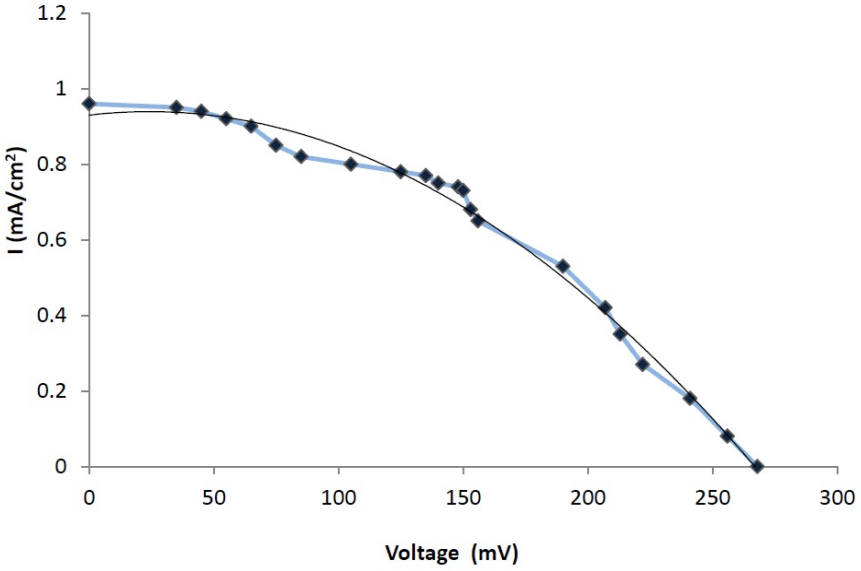


Figure 4: Current-Voltage curve under illumination for DSSC coated with P25 TiO_2.

The TiO_2 film thickness in this study was approximately 30–60 μm, which was too thick for efficient electron transportation and resulted in poor cell performance. Hamadanian et al. found that the efficiency of the TiO_2 films increased with thickness up to 15 μm due to increased dye adsorption. Further increase in the thickness of the TiO_2 thin films stabilised and nearly decreased the efficiency. This result occurred because the thicker film increased the electron transport path. Moreover, the recombination of the electrons with the electrolyte ions is possible during electron transport over a long pathway. Thus, the DSSC performance largely depends on the TiO_2 film thickness. Changing the film thickness changes the dye adsorption, current density and efficiency.[21–23]

The electrolyte used in this cell was composed of an I^-/I_3^- redox couple in an organic solvent. This electrolyte suffers from leakage and vaporisation, which results in poor long-term stability. The corrosiveness of the electrolyte damages the metals that are used. To increase the efficiency, these problems should be avoided and a high conductivity should be maintained by ensuring good interfacial contacts between the porous TiO_2 layer and the counter electrode.

The combined defects of the fabricated hibiscus extract DSSC potentially contributed to the low efficiency that was observed in this study. However, this study was the first to use hibiscus extract from a local Borneon species as a dye sensitiser. This study analysed the use of local Borneon products in dye-

sensitised solar cells. In addition, hibiscus dye, which is the cheapest anthocyanin source, can be used to create low cost and environmental friendly DSSCs.

4. CONCLUSION

In this study, DSSCs were prepared using dye that was extracted from the flowers of *Hibiscus rosa-sinensis*. The dye exhibited a UV-Vis absorption peak at 540 nm. Two types of semiconductor electrodes, TiO_2 aeroxide P25 TiO_2 and R-5566 TiO_2, were used in the fabrication of the DSSCs. The DSSC with Aeroxide P25 TiO_2 (smaller particle size) had a better I-V output than the DSSC with the R-5566 TiO_2 thin film (larger particle size). The DSSCs with Aeroxide P25 TiO_2 obtained a voltage of 0.268 V, an electric current of 0.96 mA cm^{-2}, a fill factor of 0.43 and an efficiency of 0.11%. However, the efficiency of the DSSC with the R-5566 TiO_2 thin film was not obtained from the I-V curve due to the instability of its I-V output. In direct sunlight, the voltage was 0.040 V and the electric current was 0.04 mA cm^{-2}.

5. ACKNOWLEDGEMENT

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