Performance of *P. betle* extraction as sensitizer in dye-sensitized solar cells (DSSCs)

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Abstract Natural dyes extracted from *Piper betle* (*P. betle*) pigment, was utilized and researched as sensitizer in DSSCs application. The optical characteristics of the extracted dye and photovoltaic performance of the cells were studied. The extracts showed UV–vis absorptions in the range of 530–560 nm with broad maxima absorption at~430 nm. For *P. betle* the photovoltaic performance of the sample with 3.16μm-thick ZnO produced the best results with open-circuit voltage (*V*<sub>OC</sub>), short-circuit current density (*J*<sub>SC</sub>), fill factor (FF), and energy conversion efficiency (η) values of 0.33 V, 6.35 mA/cm<sup>2</sup>, 0.52, and 1.09%, respectively.

1. Introduction

Dye-sensitized solar cells (DSSCs) have received great attention due to the low cost and ease of its fabrication process as well as its high power conversion efficiency [1-2]. A typical DSSC consists of multiple components i.e. transpiring conductive glass which usually utilizes fluorine-doped tin oxide (FTO) or indium-doped tin oxide (ITO). The mesoporous metal oxide layer developed from TiO<sub>2</sub> acts as photoanode with the inclusion of sensitizers (dye molecules), electrolyte (iodide-triiodide electrolyte is mostly used) and counter electrode. Sensitizer is the central component in DSSC as it harvests sunlight and produces photo-excited electrons at the semiconductor interface. There are several requirements for the sensitizer to perform efficiently. These involve chemical adsorption to load on the semiconducting material, high molar extinction coefficients in the visible and near-infrared region for light harvesting. Others include, good photostability and solubility to create space between the electrolyte and photoanode for recombination prevention [3]. Various metal complexes and organic dyes have been utilized as sensitizers and the best, to date, is ruthenium-bipyridyl dyes (N719) which displays a high energy conversion efficiency of about 11% [4]. In conventional DSSC, ruthenium complexes are the best known, most effective and proven sensitizers. However, ruthenium dye is complicated to synthesize, expensive and not environmentally friendly because of its high toxicity [5-6].

Therefore, a search for novel and alternative dye-sensitizers, especially from natural sources, has become the focus for many researchers [7]. Flavonoids comprise a 15-carbon (C15)-based structure with two phenyl rings linked by three carbon bridges, creating a single ring [8]. The degree of oxidation of the phenyl ring (C-ring) distinguishes the various colours of the flavonoids. Not all flavonoids, though, have the capacity to consume visible light, while they have identical structures. Flavonoid molecules are discerned by loose electrons and the energy needed for LUMO electron excitation is thereby minimized such that pigment molecules can be energetically rejuvenated by visible light. The different colours of flavonoid pigment depend on the wavelength of the visible light, which is absorbed and expressed in the pigment molecules.
Many researchers have noticed that natural flavonoid pigments have been the most energy efficient to enhance DSSC efficiency. For instance, tangerine peel as a sensitizer in DSSC provided 0.28 % of energy conversion efficiency [8]. The *Piper betle* extract displays strong light absorption with peak absorption at 667 nm in line and higher short circuit current (Jsc) with SnO$_2$ [10]. *Piper betle* is also classified as a betel of a Piperaceae family wine. The leaf of betle is primarily eaten by Asian emigrants in Asia and elsewhere in the world. The leaf of *Piper betle* has been recommended in ancient medical schemes for the healing of the burns, bruises, insect bites and better digestion. In this work, extracts of *Piper Betle* was used for sensitizer as they are plentiful in tropical countries and have large content of flavonoids that lead to the improved production of DSSC.

2. Experimental

2.1. Preparation of Natural Dye Sensitizers

The natural dyes used in this analysis was extracted from the *P. betle*. The raw natural material was washed with purified water and dried in the oven at 40 °C before being ground into fine powder with a grinder. This sample powder was weighed at 20 g. Next, 200 ml of ethanol was applied to beaker (1:10) and stirred. The mixture was kept in a dark location for 24 hours at room temperature. The extraction was filtered using filter paper in order to remove the solid substances that were contained in the extraction and the filtrate was purified again using liquid-liquid extraction to produce pure natural dye. The natural dye extraction was concentrated using a rotary evaporator at 50 °C for 4 h. The extraction was stored in a dark bottle to shield it from direct light exposure.

2.2. Preparation of ZnO Photoanode

The ZnO paste was formulated by adding 1 g of ZnO nano-powder and 0.1 g of polyethylene glycol (G) and then stirring the mixture for half an hour until a homogeneous paste was produced. 5 mL of ethanol was added to the paste in order to achieve an acceptable viscosity for the preparation of the coating. FTO conductive glass (Sigma-Aldrich Chemie, USA) were rinsed with ethanol and then dried. FTO conductive glass was detected for its conducting site using a digital multimeter (All-Sun EM420B digital multimeter). The identified conductive site was stacked up and three sides of conductive glass were taped with a first adhesive tape thickness of 1.83 μm, a second thickness of 3.16 μm and a third thickness of 7.60 μm. The consistency of the ZnO paste has been adjusted by increasing the weight of the ZnO material in the paste. The doctor blade method was revised to apply the ZnO paste onto FTO glass layer. The adhesive tape was then carefully discarded and the ethanol was swapped over the taped region to eliminate the remaining sticky

![Figure 1. Chemical structure of flavonoid [9]](image-url)
adhesive tape. The glass was then sintered on a hotplate at 400 °C for 30 min until the paste was completely dried and allowed to settle.

2.3. Preparation of counter electrode
The carbon paste was prepared by combining the activated carbon powder with ethanol and then stirred for 1 hour. The carbon paste was applied at the conductive site of the FTO glass using the same doctor blade technique, referring to the scale of the ZnO paste coated on the glass. The electrode was heated at 250 °C for 30 minutes to minimize the organic contamination and to strengthen the material.

2.4. Assembly of DSSC
The ZnO coated glass was immersed in *P. betle* natural dye for 24 h for dye staining. The glass plates were cleaned with ethanol and dried in the air for a few minutes. Lastly, the dye-sensitized solar cells are constructed by sandwiching the redox electrolyte between the dye-adsorbed ZnO film electrodes and the coated counter electrode by binding it tightly.

2.5. Cell Characterization
UV-vis (HP 8453) was used to evaluate the absorption spectra of all samples. The photocurrent – voltage (I – V) curves of the DSSCs were quantified using a computer-controlled digital source meter (Keithley 2400) with an irradiation exposure of 100 mWcm\(^{-2}\).

3. Results and Discussion

3.1. UV-vis spectroscopy
In order to investigate the optical properties of the natural dye, UV-vis spectroscopy analysis was carried out. Figure 2 shows the absorption spectrum of natural dye for *P. betle*. The absorption spectrum of natural dyes in Figure 2 shows visible absorption at 530 – 560 nm. The higher absorbance of *P. betle* may indicate that the sensitizer can generate more photoelectrons.

![Absorption spectrum of *P. betle* dye](image_url)
3.2. Photovoltaic performance with different thicknesses of ZnO layers

Table 1 indicates that 3.16 μm thick ZnO gave the highest result of 6.35 mA/cm² followed by ZnO 7.60 μm and 1.83 μm in thickness which gave results of 5.91 mA/cm² and 4.36 mA/cm², respectively. DSSC sensitized with 3.16 μm thick ZnO achieved $V_{OC} = 0.33$ V, $FF = 0.52$ and $\eta = 1.09\%$ which is higher compared to ZnO 1.83 μm and 7.60 μm in thickness. These results indicate that the efficiency of DSSC also depends on the thickness of ZnO photoanode together with the types of sensitizers used. 3.16 μm of ZnO thickness shows better properties perhaps due to thicker photoanode which can absorb more photons for more electron-hole pairs formation and provide more sites for natural dye to attach onto. However, thicker ZnO film also can causes high resistance and leading to the recombination of electron. For 7.60 μm film, it seems that the electrons will take longer time to diffuse to the conductive substrate. This can increase recombination and efficiency of DSSC. The thickness of ZnO affects the photovoltaic performance of DSSC because ZnO is necessary in DSSC as it acts as an electron carrier after the electron was excited by the dye-sensitizer when photon was absorbed. The increase in carrier amount as the thickness increases or when it reaches optimum thickness will increase the efficiency of the excitation-recombination process of the electrons which in turn results in increased output [11].

| Thickness of ZnO | $J_{SC}$ (mA/cm²) | $V_{OC}$/V | $FF$ | $\eta$ (%) |
|------------------|-------------------|-----------|-----|----------|
| 1.83 μm          | 4.36              | 0.24      | 0.44| 0.46     |
| 3.16 μm          | 6.35              | 0.33      | 0.52| 1.09     |
| 7.60 μm          | 5.91              | 0.29      | 0.48| 0.82     |

4. Conclusion

The extracts obtained from P. betle was used as sensitizer in ZnO photoanode. The broad absorption of P. betle resulted in absorption of photon energy at broader wavelengths, bringing the generation of more photoelectrons, affecting the photovoltaic performance. P. betle indicated the highest photovoltaic performance from 3.16 μm thick ZnO layer. P. betle produced 1.09% of $\eta$ with $V_{OC}$, $J_{SC}$, and $FF$ values of 0.33 V, 6.35 mA/cm², and 0.52, respectively.

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