Fabrication and analysis of photoelectrochemical properties of dye sensitized solar cell using Local Borneon Natural Dye Extracts

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Abstract
Natural dyes were extracted from the plant species Etlingera elatior, Duranta erecta and Amaranthus spp. that were collected from Keningau and Tambunan, Sabah, Malaysia. The possibility of photon-electron conversion was then assessed based on their absorption ability in the region of wavelength between 400-900nm. In addition, FT-IR analysis was carried out to determine if functional groups exists in their extracts. Finally, the DSSCs were assembled and their efficiency measured. It shows the successful conversion from visible sunlight to electricity by using the extracts from Etlingera elatior, Duranta erecta and Amaranthus spp. as raw natural dye sensitizers in Dye Sensitized Solar Cells (DSSCs) with efficiency of 0.1%, 0.06% and 0.04%, respectively. This result shows that local natural dyes can be used as sensitizer in DSSCs. However, further investigations are required to improve the efficiency.

Introduction
In 1991, O'Regan and Gratzel discovered the dye sensitized solar cells (DSSCs) [1]. Subsequently, dye sensitized solar cells were proposed as an alternative to commercial silicon based solar cell due to DSSCs have low production cost, ease of assembly, and environmental friendly due to the production of less contaminants [2]. The DSSCs are comprised of a nanocrystalline porous semiconductor, dye sensitizer, an electrolyte containing redox couple and a counter electrode. In DSSCs, the dye sensitizer mimics the natural photosynthesis process in chlorophyll which harvest the sunlight and transforming the solar energy to electric energy [3]. Therefore, conventional ruthenium based dye sensitized solar cell has several disadvantages such as limited resources, costly production due to the multistep processing steps and complicated purification steps [4]. Consequently, researchers search for new substitute and natural dyes appear to be suitable candidate because of the wide availability sources, environmentally friendly and minimal production cost. Sabah which located at north part of the Borneo island has a wide diversity of the flora. The purpose of this work is to investigate on the performance of the natural local Borneo flora dye sensitizers which extracted from Etlingera elatior, Duranta erecta and Amaranthus spp. in DSSCs.

Methodology
Collection of Flora Samples and Extraction of Dye Sensitizers
Flower of Etlingera elatior was taken in Tambunan while fruit of Duranta erecta and leaf of Amaranthus spp. were taken in Keningau, Sabah. The samples were first mixed with water and blended in a mortar. Then, the natural dyes solution were obtained by removing the solid residues and the solutions were prepared for the characterization.
Characteristics of Natural Dye Solution
Absorption spectra of each natural dye solutions was measured to identify the absorption properties of the dye sensitizers using JASCO UV-Vis spectrophotometer 650. In addition, Fourier transform infrared spectroscopy (FT-IR) analysis was also carried out for each sample to determine if functional groups exists in the dye extracts.

Cell Assembly
Potassium iodide (KI) was weighed at 3.25g and iodine (I\textsubscript{2}) at 0.5g and then dissolved with 30ml propylene carbonate (PC) in a 250ml conical flask. Then, the mixture was stirred for about 30min at room temperature and another 20.0 ml of polyethylene glycol 400 (PEG 400) was added into the flask. The mixture was heated at 100°C for 24hr to form homogeneous mixture. Then, the mixture was cooled to 60°C to form a polymer gel electrolyte.

At the same time, a photoanode was prepared using TiO\textsubscript{2} nanoparticles of 1.0g that was blended in a mortar with 2.0ml nitric acid (HNO\textsubscript{3}) solution (0.1M), 0.50g of polyethylene glycol 10,000 (PEG 10,000) and 1 ml of nonionic surfactant, Triton X-100. The paste was then continously blended for 15min until it becomes thick without any aggregates. Finally, the paste was allowed to equilibrate for 15min.

The paste was then deposited on FTO glass slide by using doctor blade method. The layer was allowed to dry before removing the scotch tape. After that, the slide was heated and sintered on hot plate at 450°C for 30min and then cooled in room temperature and immersed in natural dye extract for 24 hours. The scientific name and the TiO\textsubscript{2} semiconductor film after immersed in the natural dye extract for 24 hours are shown in Table 1.

The cathode counterpart was prepared by holding the slide above a candle flame to produce a layer of carbon. The slide was then heated on a hot plate at 150°C for 15min and allowed to cool in room temperature. Then, the two electrodes were clipped together to produce the dye sensitized solar cells. Alligator clips were clipped onto the two edges of the FTO slide and connected to the multi-meter. The light source which was the bright sun light was measured by using a lux meter to obtain the light intensity. Point by point current and voltage data can be gathered at each incremental resistance value.

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Scientific Name</th>
<th>Sample</th>
<th>After 24 Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torch Ginger</td>
<td>Etlingera elatior</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pigeon Berry</td>
<td>Duranta erecta</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leaf Amaranth</td>
<td>Amaranthus spp.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Result and Discussion

Absorption Spectrum of Natural Dyes

Fig. 1: Absorption Spectrum of natural dye extracts of (a) Etlingera elatior (b) Duranta erecta (c) Amaranthus spp.

Fig. 1 showed absorption spectrum of the natural dye extracts of Etlingera elatior, Duranta erecta, and Amaranthus spp.. Due to the difference in chemical composition and structures, different natural dye extracts show different absorption ability in the visible to near infrared region which confirmed by the studies elsewhere [5,6,7]. The main absorption range of flowers of Etlingera elatior was in 350-550 nm with an absorption peak at 508nm. This peak may indicate the presence of anthocyanin component in the extract. In 2009, Mai et al reported that the flower of Etlingera elatior contains 1.05mg of cyanidin-3-glucoside per 100g of fresh plant. On the other hand, the absorption range for the fruits of Duranta erecta was between 550-650nm. The orange colour solution that extracted from the fruits of Duranta erecta showed absorption peak at 608nm which may corresponds to the component of saponin. This is because various researchers reported that the fruit of Duranta erecta contains saponin [13,14]. Finally, Amaranthus spp. has two absorption range 450-580nm and 650-600nm with two absorption peaks at 534nm and 677nm. The absorption peak at 534nm may attributes to the betanin content in the leaf of the Amaranthus spp. as reported by Stintzing et al.[2004]. Besides, the chlorophyll compounds that contained in the leaf of the Amaranthus spp. showed the absorption peak at 677nm.
Fig. 2: FT-IR Spectrum of natural dye extracts of 
(a) Etlingera elatior  (b)Duranta erecta  (c) Amaranthus spp.
As shown in the fig. 2, *Etlingera elatior* (Figure 2a) and *Duranta erecta* (Figure 2b) had the similar shape of the FT-IR spectral spectrum in the range from 600 cm\(^{-1}\) to 4000 cm\(^{-1}\). Crossed reference with [9], it implied that the broad absorption range and the absorption spectra peak near wavenumber 3300 cm\(^{-1}\) may corresponds to O-H stretching in alcohols and phenols. Besides, the peak at wavenumber 1637 cm\(^{-1}\) may be due to the presence of the C=O bonding and C=C bonding while the wavenumber 1045 cm\(^{-1}\) may attributes to the C-O-C stretching vibration of esters acetates [9]. Therefore, this results show that there is possibility that all the natural dye extracts may contain hydroxyl and carbonyl groups. However, further research needed to be done to confirm chemical structures and composition for the natural dye extracts.

I-V Performance of DSSCS

**Table 2: The photoelectrochemical properties of the natural dye extracts for *Etlingera elatior*, *Duranta erecta* and *Amaranthus spp***

<table>
<thead>
<tr>
<th>Species</th>
<th>Voc (mV)</th>
<th>Jsc (mA)</th>
<th>FF</th>
<th>(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Etlingera Elatior</em></td>
<td>380</td>
<td>0.24</td>
<td>0.30</td>
<td>0.10</td>
</tr>
<tr>
<td><em>Duranta Erecta</em></td>
<td>564</td>
<td>0.08</td>
<td>0.56</td>
<td>0.06</td>
</tr>
<tr>
<td><em>Amaranthus Spp.</em></td>
<td>395</td>
<td>0.08</td>
<td>0.46</td>
<td>0.04</td>
</tr>
</tbody>
</table>

**Fig. 3: I-V Curve of natural dye extracts of *Etlingera elatior*, *Duranta erecta* and *Amaranthus spp***.

Table 2 and Fig 3 showed the photoelectrochemical properties and IV profile of the natural dye extracts for *Etlingera elatior*, *Duranta erecta* and *Amaranthus spp.* respectively. It can be seen that *Duranta erecta* and *Amaranthus spp* had lower current density which may be due to the less available bonds that can be occurred between the dye molecules and TiO\(_2\) semiconductor surface as reported by Garcia et al., [2003] and thus less electrons transfer from the dye molecules to the TiO\(_2\). Besides, aggregates that exist in the dye sensitizers may resulted in stronger steric hindrance which prevent the anchoring groups of the dye sensitizers to be attached to the TiO\(_2\) semiconductor surface [10]. Consequently, *Etlingera elatior* showed better photoelectrochemical conversion that maybe attributable to more available bonds between dye molecules and TiO\(_2\) surface, thus increase electron transfer which result in higher efficiency in Dye Sensitized Solar Cell.
Conclusion

In this study, it showed the successful conversion from visible sunlight to electricity when extracts from *Etlingera elatior*, *Duranta erecta* and *Amaranthus spp.* were used as raw natural dye extracts in Dye Sensitized Solar Cells (DSSCs). The cell sensitized by *Etlingera elatior*, *Duranta erecta* and *Amaranthus spp.* has the efficiency of 0.1% , 0.06% and 0.04% respectively. By using UV-Vis Spectrophotometer and FT-IR Spectroscopy, the absorption ability and the possible functional groups can be determined. This result showed that local natural dyes can be used as natural dye sensitizers in DSSCs. Nevertheless, further investigations are required to improve the efficiency and further research can be done on the locally sourced dye to evaluate their performance in Dye Sensitized Solar Cells.

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Reference