TiO₂ Based Solar Cell with Jacaranda Mimosifolia, Beta Vulgaris, and Carissa Ovata Sensitizers

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Abstract
Cheap dye-sensitized solar cells (DSSCs) were fabricated using TiO₂ nanoparticles and Natural dyes from Jacaranda Mimosifolia, Beta vulgaris, and Carissa ovata. Natural dyes are environmentally and economically better than ruthenium-based dyes because they are nontoxic and cheap. In this paper Jacaranda Mimosifolia and Carissa ovate sanitizers were reported for the first time, and the photoelectrochemical properties of these sensitizers were analyzed. Based on TiO₂ nanoparticles, and quasi solid state electrolyte, Carissa ovate and Jacaranda Mimosifolia sensitizers extracted using H₂O shows better rectification with Fillfactor (FF)=66%, and 69% and with efficiency of 0.22% and 0.20% respectively were obtained, under Air Mass (AM) 1.5 irradiation. The incident photon to current conversion efficiencies (IPCE) were measured and found that all sensitizer’s shows good conversion of photons to current in the visible region.

Keywords: Dye-sensitized solar cell, Nanoparticles, , photovoltaic, sensitizer

1. Background
Due to the demand for renewable cost-effective energy sources, dye-sensitized solar cells (DSSCs), which can be fabricated from low-cost materials (TiO₂, dye, etc.) have attracted academic and industrial attention. Dye-sensitized solar cells (DSSCs) are the third generation of photovoltaic devices for the conversion of visible light in electric energy. These new types of solar cells are based on the photosensitization produced by the dyes on wide band-gap mesoporous metal oxide semiconductors; this sensitization is produced by the dye absorption of part of the visible light spectrum. One aspect of these DSSCs photocells that is particularly attractive is the low cost of the solar energy conversion into electricity; this is possible mainly due to the use of inexpensive materials and the relative ease of the fabrication processes.

DSSCs consist of a dye-sensitized semiconductor material, where dye molecules attached onto the semiconductor act as light absorbers. Recent studies have shown that metal oxides such as ZnO, SnO₂, Nb2O5, but mainly TiO₂, have been successfully used as photo-anode when a dye is absorbed in the interior of the porous layer (Nazeeruddin et al. 2001). The performance of DSSCs can be understood as a competition between two principal redox processes: electrons injection with rate constants of the order of picoseconds (10⁻¹² s) and the regeneration of the oxidized dye with rate constants of the order of nanoseconds (10⁻⁹ s) (Caramori et al. 210). The injected electrons are transported through the TiO₂ film to a transparent electrode, while a redox-active electrolyte of I⁻/I₃⁻ is used to reduce the dye cation charge and transport the resulting positive charge to a counter-electrode; however, before this, the photo-induced electron injection from the sensitizer dye to the TiO₂ film conduction band, initiates the charge separation (Hagfeldt and Grätzel 2000). In this sense, the sensitized dye acts as the photo-driven electron pump of the device.

Several inorganic, organic and hybrid compounds have been investigated as sensitizer for DSSCs, including porphyrins (Odobel et al. 2003), phthalocyanines (Hagfeldt, and Lindquist 2001), platinum complexes (Islam et al. 2001), fluorescent dyes (Rehm et al. 1996). Among others Ru-based complexes sensitizers have been widely used because they have better efficiency and high durability. However these advantages are offset by their high expense and the tendency to undergo degradation in presence of water (Zhang et al. 2008).

The use of natural pigments as sensitizing dye for the conversion of solar energy in electricity is very interesting because, in one hand they enhance the economical aspect and on the other, produce significant benefits from the environmental point of view (Calogero et al.2010). Natural pigments extracted from fruits and vegetables, such as chlorophyll and anthocyanin, have been extensively investigated as DSSCs sensitizer (Garcia et al. 2003). In this study, we fabricated a DSSC’s using a natural dyes extracted from fruits of Carissa ovata, Beta vulgaris, and flowers of Jacaranda Mimosifolia using three extraction solvents water, HCl and Ethanol and TiO₂ nanoparticles as semiconductor.

2. Methods
The materials and the fabrication method employed for the fabrication of dye-sensitized Photo electrochemical cells based on TiO₂ nanoparticles are described below.

2.1 Natural dye extraction
Fresh flowers and fruits of plants including Jacaranda Mimosifolia, Beta vulgaris, and Carissa ovata were
collected. The collected samples were dried at room temperature in a shade to prevent pigment degradation. After drying for about 2 months the samples are completely dried in an oven at 70°C to avoid some moisture from it (Di Marco and Calogero, 2008). Then after, the samples were crushed with Micro Plant Grinding machine to produce the powder of the respective plant materials. The dye extraction from the powder was done as follows:

2 g of each powder sample was taken and soaked in 50 ml of extracting solvent in separate bottle. The solution is stored at room temperature for about 6 hours to dissolve the powder completely. Then the solution was filtered with glass filter to separate the solid from pure liquid. After filtration the extracted pigments are ready for soaking the electrode inside it, and also used for measuring the UV-vis absorption spectra.

2.2  Preparing the substrate for deposition
The substrate cleaning is believed to be a key process that influences the final performance of the devices. A significant effect on the photovoltage behavior can be observed experimentally depending on the extent of cleaning (Sheu et al. 2005). For this reason, TCO glass substrates have been thoroughly cleaned before film deposition. The glass cleaning protocol was, first cleaned with Acetone then with isopropanol finally with Ethanol. In all case the cleaning process was done in ultrasonic bath for about 20 minute in each solvent.

2.3  TiO$_2$ paste preparation
The TiO$_2$ Nano powder anatase nanoparticles from Degussa (25 nm) was obtained commercially. 30 mg of polyethylene glycol (dispersing agent) and 10 ml of distilled water was mixed. 1.8 g of TiO$_2$ powder continuously grinded down by using procelain mortar to break down the aggregated particle. Then 2.5 ml of the PEG solution was slowly added to the powder and completely mixed with each other by using the mortar. Finally the paste was ready for deposition.

2.4  Deposition of TiO$_2$ films
The simplest and most widely used method for depositing TiO$_2$ paste on a substrate is the so called doctor blade method. The technique is also known as slot coating in its mechanized version. It uses a hard squeegee, or doctor blade, to spread a portion of TiO$_2$ paste onto the glass (see Figure 1).

Figure 1. TiO$_2$ paste Deposition
With the conductive side facing up, we apply four parallel strips of tape on the edges of the glass plate, covering about small portion of glass. After making the paste ready for deposition we apply the portion of paste near the top edge of the TCO glass between the two pieces of tape with the help of a glass rod, then, the paste spread across the plate with the support of the tape on all sides. The preparation of electrode was completed by firing the deposited layer. The organic solvent burns away, leaving the TiO$_2$ nanoparticles sintered together. This process ensures electrical contact between particles and good adhesion to the TCO glass substrate. Sintering can occur in furnace at 400°C.

2.5  Electrode sensitization
Natural dyes were used for electrode sensitization in the course of this thesis. Before immersion in the dye solution, films were warmed up to higher temperature (80°C) to minimize the water vapor content inside the
porous of the semiconductor electrode. The sensitization was always performed at room temperature. The best method of adsorbing a natural sensitizer to the oxide layer is by dipping the electrode in a solution of the dye already prepared. After sensitization, the films were rinsed in the same solvent (ethanol, water) as employed in the dye solution.

2.6 Preparation of quasi-solid state electrolyte
The polymer gel electrolyte was prepared according to the method developed by (Seok-Jun et al. 2001) as described below. 0.9 M of 1-ethylene-3-methyl imidazolium iodide (EMIM-I) was added into acetonitrile (Aldrich) under stirring to form a homogeneous liquid electrolyte. In order to obtain a better conductivity, 0.5 M of sodium iodide (BDH) was dissolved in the above homogeneous liquid electrolyte, and then 0.12M iodine and 35 % (w/w) of PVP (Aldrich) were added. Then, the resulting mixture was heated at 70 -80°C under vigorous stirring to dissolve the PVP polymer, followed by cooling down to room temperature to form a gel electrolyte.

2.7 Coating counter electrodes
A CHI630 Electrochemical Analyzer and a three-electrode electrochemical cell were used for polymerization of EDOT. The poly (3, 4-ethylendioxythiophene) (PEDOT) film for the counter electrode was formed by electrochemical polymerization of 3, 4-ethylendioxy-thiophene (EDOT) (Aldrich), in a three electrode one-compartment electrochemical cell. The electro- chemical cell consisted of a pre cleaned ITO-coated glass working electrode, platinum foil counter electrode and quasi Ag/AgCl reference electrode dipped in LiClO₄ (Aldrich) acetonitrile (sigma-Aldrich) solution. The solution used for the polymerization contained 0.1 M EDOT and 0.1 M LiClO₄ in acetonitrile (Sigma-Aldrich). The monomer was used as received. The polymerization was carried out potentiostatically at +1.8 V. At this potential, the electrode surface becomes covered with blue-doped PEDOT film. The film was then rinsed with acetonitrile and dried in air.

2.8 Assembly of DSSCs for characterization
Device assembly is the final step for characteristics measurement. Here the sensitized electrode was washed by the solvent of the dye then by ethanol and dried using hair dryer to dry the electrode, and then the non-covered part of the film by the paste was covered by a tape spacer in all side by leaving some place for electrical contact. By facing the active sides of the photoanode and the cathode, the two electrodes are pressed together after putting the quasi electrolyte on the photoanode. Then the devices are ready for characterization.

3. Result and discussion
3.1 UV-Vis absorption spectra of sensitizers
The absorption measurement was carried using the Gensys-2 PC spectrometer for each extract. Figure 2 depicted UV-Vis absorption spectra of each natural sensitizer.

Figure 2. UV-Vis absorption spectra of a) Jacaranda Mimosifolia, b) Beta vulgaris c) Carissa Ovata in HCl
Absorption spectra of the Beta vulgaris in HCl (Figure 2. b), in Ethanol (Figure 3. b) with the spectrophotometer at wavelengths between 260 and 800 nm shows maximum absorbance between 450 and 650 nm. The natural Beta vulgaris extracts are likely a mixture of several pigments. The betalain pigments are characterized by a maximum absorbance at about 535 nm (λmax) for the red-purple betacyanins (betanin with λmax = 535 nm and betanidin with λmax = 542 nm) and near 480 nm for the yellow betaxanthins (indicaxanthin,
the common betaxanthin found in *Beta vulgaris* with $\lambda_{\text{max}} = 482$ nm); for the betalamic acid $\lambda_{\text{max}} = 424$ nm (Di Marco and Calogero, 2008). In Figure 3.b of ETOH extract two peaks were found: one around 480 nm associated with the presence of betaxanthins, while the second one at 535 nm is attributed to the betanin.

![Figure 3. UV-Vis absorption spectra of a) Jacaranda Mimosifolia, b) Beta vulgaris, c) Carissa ovata in ETOH](image)

The pigment extracted from *Carissa Ovata* using HCl shows an absorption peak at 553 nm (Figure 2.c), the spectra show an absorption peak in the region of 520-550 nm which is the peak of anthocyanin containing dyes. This is because of the diverse pigmentation from orange to red, purple, and blue pigment which are found in anthocyanin containing pigment and shows an absorption in the visible region (approximately 490-550 nm) (Sayama, et al. 1998).

*Beta vulgaris* showed an intense absorption peaks in the region 400-600 nm. Ethanol extract (Figure 3.b) shows strong absorption peak of betalains, at 470 nm and 533 nm due to the mixed contributions of the yellow-orange betaxanthins (480 nm) and of the red-purple betacyanines (540 nm) (Di Marco and Calogero, 2008).

Both HCl and water extract of *Carissa ovate* and *Jacaranda Mimosifolia* (Figure 2.a and 2.c, Figure 4.a and 4.b) shows absorption in the region b/n 535-550 nm which attributes to the presence of anthocyanin’s pigment. These peaks are because of the diverse pigmentation from orange to red, purple, and blue pigment which are found in anthocyanin containing pigment and shows an absorption in the visible region (approximately 535-550 nm) (Gómez-Ortíz et al. 2010).

![Figure 4. UV-Vis absorption spectra of a) Carissa ovate, b) Jacaranda Mimosifolia in H2O](image)

Some of the wavelength of these absorbance peaks shows a red and blue shift by a few nanometers among various pigments, depending on structure of each natural dyes and the solvent used for extraction of pigment. But in general the dyes used in these studies are effective photoreceptors because they contain networks of alternating single and double bond. When light is absorbed by the molecule of dye, the energy from the light excites an electron from its ground energy level to an excited energy level.
3.2 Current density versus voltage characteristics of TiO$_2$ based DSSCs

The J-V characteristic of all sensitizers were measured and plotted for analysis and comparison as shown below. Figure 5.a, Figure 6.a, Figure 7.b, are J-V characteristics of *Carissa ovata* extracted using HCl, ETOH, and H$_2$O respectively. Both HCl and H$_2$O extracts of *Carissa ovata* shows relatively better photo current and better open circuit voltage than ETOH extract.

![Figure 5](image1.png)

**Figure 5.** Current density versus Voltage characteristic of a) *Carissa ovata*, b) *Jacaranda Mimosifolia*, c) *Beta vulgaris* extracted using HCl.

The open circuit voltage for HCl (Voc= 0.65 V) and for H$_2$O extracts (Voc= 0.55 V) of *Carissa ovata* has shown a small difference but the photocurrent are almost the same, which indicates that there is a difference in the recombination rate, but almost similar injection rate of electron to the semiconductor conduction band. This recombination rate is relatively small for water extract of *Carissa ovata*. ETOH extract of *Carissa ovata* (Figure 6.a) shows relatively very small photoelectrochemical characteristics as compared to others, which may be because of high recombination rate and small injection efficiency. Figure 5.b, Figure 6.c, Figure 7.a, are J-V characteristics of *Jacaranda Mimosifolia* in HCl, ETOH, and H$_2$O respectively. In the J-V curve of *Jacaranda Mimosifolia* extracted with HCl the photo current (Jsc= 0.45 mA/cm$^2$) as well as the photo voltage (0.65V) is better as compared to the H$_2$O and ETOH extracts. The short circuit voltage for the case H$_2$O and ETOH extracts are very small (0.18 and 0.035) mA/cm$^2$ respectively.

![Figure 6](image2.png)

**Figure 6.** Current density versus Voltage characteristic of a) *Carissa Ovate*, b) *Beta vulgaris*, c) *Jacaranda Mimosifolia* in ETOH.

Figure 5.c, and Figure 6.b, is J-V characteristics of *Beta vulgaris* extracted with HCl and ETOH respectively. The HCl extract of *Beta vulgaris* has good conversion parameters with Jsc of 0.55 mA/cm$^2$ and Voc of 0.45 V as compared to the EOH extract. As indicated in the UV experiment (Figure1) Betalains in acidic environments have strong absorption in the 400 to 600 nm range due to the color combination of yellow orange betaxanthins and red pink betacyanins. In addition to the significant increase of absorption intensity, this change has caused variation in the electrical current of the cells. The absorptions range is approximately equal for both
HCl and ETOH extracts. An explanation for these results may come from the difference between compositions of the extracts. This means the concentration of dyes extracted using HCl is expected to be higher than H$_2$O and ETOH extracts, probably because of a higher solubility.

**Figure 7.** Current density versus Voltage characteristic of a) Jacaranda Mimosifolia, b) Carissa Ovata in H$_2$O

Most of the natural dyes which has a good and a broader absorption in the visible spectrum is expected to show a good rectification on the J-V curve, and is also responsible for relatively good current density and power conversion efficiency. The efficiency ($\eta$) of a DSC is calculated from the short current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF), and intensity of the incident light ($P_{in}$)

$$\eta = \frac{J_{sc} V_{oc} FF}{P_{in}},$$

and summarize as follows.

### Table 1. Photovoltaic performance of TiO$_2$ based DSSCs with different sensitizers

<table>
<thead>
<tr>
<th>Sensitizers</th>
<th>Extraction Solvent</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Carissa Ovate</em></td>
<td>HCl</td>
<td>0.54</td>
<td>0.62</td>
<td>66</td>
<td>0.220</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>0.075</td>
<td>0.40</td>
<td>52</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>0.184</td>
<td>0.51</td>
<td>61</td>
<td>0.058</td>
</tr>
<tr>
<td><em>Jacaranda Mimosifolia</em></td>
<td>HCl</td>
<td>0.45</td>
<td>0.64</td>
<td>69</td>
<td>0.198</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>0.036</td>
<td>0.34</td>
<td>38</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>0.490</td>
<td>0.53</td>
<td>66</td>
<td>0.170</td>
</tr>
<tr>
<td><em>Beta vulgaris</em></td>
<td>Ethanol</td>
<td>0.053</td>
<td>0.34</td>
<td>40</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>HCl</td>
<td>0.540</td>
<td>0.45</td>
<td>53</td>
<td>0.130</td>
</tr>
</tbody>
</table>

We achieved a better sensitization using the dye from *Carissa Ovate* and *Jacaranda Mimosifolia* both extracted using HCl. It was found that the best results were *Carissa Ovata*. This is because these extracts both have anthocyanin pigment with absorption between 500-550 nm wavelengths, helping the cell to capture more photons. The best FF was obtained by the *Jacaranda Mimosifolia* extract with water showing $V_{oc}$ and $J_{sc}$ values of 0.64 V and 0.45 mA/cm$^2$ respectively, with an active area = 0.86 cm$^2$. Dye extracted from *Carissa Ovate* displays a promising photoelectrochemical performance showing a $J_{sc}$ = 0.62 mA/cm$^2$, a $V_{oc}$ = 0.54 V, a fill factor $= 66\%$, $\eta = 0.222$, with an active area = 0.82 cm$^2$.

The photoelectrochemical characteristic values of *Beta vulgaris* are in agreement with those obtained in (A. Dumbravía et al. 2012). *Carissa Ovata* and *Jacaranda Mimosifolia* were tested for the first time, and they showed better photoelectrochemical properties with relatively better efficiencies.

### 3.3 IPCE characteristics of TiO$_2$ based DSSCs

Photo action spectra provide further insights on the photoelectrochemical behavior of natural dyes. All the following figures shows the incident photon to current conversion efficiency (IPCE) spectra of TiO$_2$ electrodes sensitized with extracted natural dyes as a function of wavelength. The IPCE values were determined between 300 and 800 nm. The IPCE was then calculated according to the following equation:
\[ IPCE(\%) = \frac{1240 \cdot J_{sc}}{\lambda (\text{nm}) \cdot \phi (\text{mW/cm}^2)} \], \quad \text{where} \ \lambda \ \text{is the wavelength and} \ \phi \ \text{is the power of the incident radiation per unit area.}

The IPCE can be also expressed by
\[ IPCE(\%) = LHE(\lambda) \times \phi_{\text{inj}} \times \eta_{\text{coll}}, \]
where LHE is the light harvesting efficiency, \( \phi_{\text{inj}} \) is the quantum yield of electron injection, and \( \eta_{\text{coll}} \) is the electron collection efficiency, which depends on the structure and morphology of the TiO\(_2\) layer (Hagfeldt et al. 2000).

**Figure 8.** An incident photon-to-current conversion efficiency (IPCE) spectrum of a TiO\(_2\) sensitized solar cell using a) Carissa ovata, and b) Jacaranda Mimosifolia extracted using HCl, c) Jacaranda Mimosifolia, and d) Beta vulgaris extracted using HCl, and e) Carissa ovata extracted using H\(_2\)O.

In both IPCE plot of (Figure 8 and 9) maximum photon is converted in to current in the Uv region of the spectrum which indicates that the conversion of photon to current is dominated by the semiconductor at that wavelength, but there is also conversion of photon up to 600nm region which is due to the presence of natural dyes or the sensitization effect. Figure 8.a, 8.d, and 8.c indicates these results with the IPCE curve extends up to 600nm even 700nm for the case of Carissa ovata extracted with HCl (Figure 8.c) and Jacaranda Mimosifolia extracted with ETOH (Figure 9.a).

**Figure 9.** An incident photon-to-current conversion efficiency (IPCE) spectrum of a TiO\(_2\) sensitized solar cell using a) Jacaranda Mimosifolia, b) Carissa ovata, and c) Beta vulgaris extracted using ETOH.

As compared to the IPCE of Ruthenium dye, Natural dyes are characterized by low IPCE which is mainly due to inefficient light harvesting efficiency (LHE) by the dye, inefficient charge injection into TiO\(_2\), or inefficient collection of injected electrons. A low LHE can be due to a low dye absorption coefficient over the solar spectrum, a low dye concentration, a thin TiO\(_2\) film to support large concentration of adsorbed dye which absorbs a significant fraction of the incident light, insufficient light scattering within the film, absorption of light by TiO\(_2\) or the redox electrolyte, and dye degradation. In Figure (8.d and 8.e) Beta vulgaris extracted using HCl, Carissa ovata extracted using H\(_2\)O, and (Figure 9.c) Beta vulgaris extracted using ETOH, show relatively low IPCE which may be:
- Due to a small amount of dye is adsorbed by the semiconductor, which results low LHE
- Due to dye desorption, dye aggregation or the excited state levels of the dye lying below the conduction

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band edge of TiO$_2$, the presence of the surrounding electrolyte, the wavelength of the exciting photon, which results low $\eta_{\text{inj}}$.

- Due to fast recombination of photo-injected electrons with the redox electrolyte or oxidized dye, which result low $\eta_{\text{cc}}$.

4. Conclusion

This paper describes an investigation of flowers of *Jacaranda Mimosifolia*, fruits of *Carissa ovata* (for the first time), and roots of *Beta vulgaris* whose HOMO and LUMO levels match the conduction-band level of the semiconductor and the iodine redox potential for using them as photosensitizers for dye sensitized solar cell. Extracts of *Jacaranda Mimosifolia*, *Carissa ovata*, and *Beta vulgaris* with HCl show relatively better photoelectrochemical characteristics with efficiency of 0.220%, 0.198% and 0.130% respectively.

Natural dyes based solar cells appear to be limited by low Voc and Jsc. The chemical structure of these natural dyes hence to be study further especially the extraction methods for achieving larger conversion efficiencies. Although natural dyes are still present below the current requirements, the results are encouraging and may boost additional studies oriented to the search of new natural dye sensitizers.

5. References


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