Preparation of a TiO$_2$-based dye-sensitized solar cell comprising anthocyanin from mangosteen pericarp (Garcinia mangostana, L.) as the sensitizer: co-pigmentation effect on sensitizer and solar cell efficiency

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Abstract. A dye-sensitized solar cell (DSSC) is a device that converts solar energy into electric energy. In this study, TiO$_2$ nanotubes (TiO-NTs) sensitized with anthocyanin extracted from mangosteen pericarp (Garcinia mangostana L.) were used as part of a working electrode, whereas fluoride-doped tin oxide–platinum (FTO-Pt) was used as counter electrode. TiO-NTs were grown on a titanium plate via a two-step anodization method. Pt from an HPltCl solution was deposited on an FTO surface prepared by spray pyrolysis. The anthocyanin extract was copigmented with benzoic acid to increase the stability of the DSSC and its visible light absorbance. The TiO$_2$ prepared by anodization was characterized by scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, and diffuse reflectance UV–Vis spectroscopy. Photocurrent evaluation using linear sweep voltammetry and multi pulse amperometry indicated that TiO$_2$-NTs were activated by UV light. Sensitization with anthocyanin–benzoic acid increased TiO$_2$-NT’s response to visible light. The anthocyanin extract absorbed light in the visible region (400–600 nm), and as a result of its co-pigmentation with benzoic acid, absorbance increased. The efficiency of various DSSCs was evaluated, and data indicated that with sensitizers like anthocyanin alone or anthocyanin co-pigmented with benzoic acid at different ratios (1:0.5; 1:0.8; and 1:1 (v/w)) efficiency values were 0.2273 %, 0.2297 %, 0.2884 %, and 0.3709 %, respectively. The results indicate that the addition of benzoic acid to anthocyanin can improve DSSC performance.

1. Introduction

Sunrays are a promising source of alternative energy owing to their availability and their free and renewable nature. From 1.7 × 10$^9$ TW (1.7 × 10$^9$ J/s) of solar energy that reach the earth’s surface, a practical terrestrial global solar potential value is estimated to be ~600 TW (6 × 10$^9$ joule/second). Therefore, by only utilizing 10% of the solar energy available, or ~60 TW (6 × 10$^9$ joule/second), the world’s future energy demands would be fulfilled [1]. One approach to harness solar energy is to convert sunrays into electricity using a photovoltaic cell.

A dye-sensitized solar cell (DSSC) is a type of photovoltaic cell that enables the conversion of sunrays into electricity through the sensitization of a wide-bandgap semiconductor (usually TiO$_2$). DSSCs were first introduced by O’Regan and Grätzel in 1991 [2], who created systems displaying an efficiency of up to 7.1 %. Notably, a DSSC is a low cost photovoltaic cell compared to conventional silicon-based solar cells [3].

The conversion efficiency of DSSCs using TiO$_2$ nanotubes as semiconductors is low compared to their counterparts using TiO$_2$ nanoparticles as semiconductors. The main reason for this observation is that TiO$_2$ nanotubes have a lower surface area than TiO$_2$ nanoparticles. Therefore, the amount of loading dye present on a TiO$_2$ semiconductor is small, and it will consequently generate a photocurrent...
of lower density. The efficiency of a TiO$_2$-nanotube-based DSSC can be enhanced by decreasing the diameter of the nanotubes, an objective that may be achieved by preparing TiO$_2$ through a two-step anodization method [4].

The sensitizer (the dye molecule) is the main component of DSSCs determining the cell’s performance. So far, DSSCs with the highest efficiency make use of ruthenium(II) complexes as sensitizers. However, since these complexes are costly to prepare and require the implementation of complicated synthetic procedures, an alternative sensitizer is needed. Owing to their availability, low cost, non-toxicity, and biodegradability, natural dyes are appealing alternative sensitizers to ruthenium(II) complexes. Anthocyanin from mangosteen pericarp (Garcinia mangostana L.) is a natural dye that can be used as a sensitizer in DSSCs. Anthocyanin displays absorbance in a wide range of the visible spectrum, and it has anchoring groups (carbonyl and hydroxyl groups) that enable it to get attached to the surface of TiO$_2$, thus allowing electrons to be transferred from the sensitizer to the semiconductor [5].

Anthocyanin isolated from mangosteen pericarp has unstable color owing to the fact that this molecule degrades easily [6]. Co-pigmentation, an interaction between anthocyanin and other species, such as metal ions or organic molecules, is a way to enhance anthocyanin’s stability. DSSCs based on co-pigmented anthocyanin have been studied before [7], and according to evidence, DSSCs using co-pigmented anthocyanin as a sensitizer are more efficient than their counterparts comprising non-co-pigmented anthocyanin.

In the present study, an anthocyanin extract was co-pigmented with benzoic acid to increase the sensitizer’s stability and absorbance of visible light. The co-pigmented anthocyanin was subsequently used as a sensitizer on a TiO$_2$-nanotube-based DSSC, and the system’s performance was evaluated.

2. Experimental

2.1. Sample preparation and anthocyanin extraction from mangosteen pericarp

Mangosteen pericarp was dried with temperature ± 40 °C; the sample was subsequently ground to a powder and extracted using methanol:HCl (99:1, v/v). The mixture was stirred at 400 rpm for 24 h. The solid residue and the supernatant solution obtained were separated by vacuum filtration. Then, the filtrate’s solvent was removed via evaporation. The anthocyanin extracts obtained from evaporation process were characterized by UV–Vis spectrophotometry and by thin layer chromatography using BAA as eluent (4:1:5 volume ratios).

2.2. Anthocyanin co-pigmentation with benzoic acid

The anthocyanin extract was eluted using ethanol. Benzoic acid was then added to solid anthocyanin according to the following ratios 1:0.5; 1:0.8 and 1:1 (v/w). The pH of the resulting mixture was set to 3.7 using ammonium acetate 25 % and HCl 10 M. The co-pigmented anthocyanin extract was finally characterized by UV–Vis spectrophotometry.

2.3. Preparation of TiO$_2$ nanotubes by a two-step anodization method

Titanium foils were degreased ultrasonically in acetone, ethanol, and water, sequentially, for 20 min with each solvent, and subsequently dried in an air stream. Anodization was achieved through a two-electrode configuration, whereby titanium foil was the working electrode (anode), and aluminum foil was the counter electrode (cathode). The electrolyte comprised an ethylene glycol solution containing 0.3 % NH$_4$F and 2 % H$_2$O. The distance between working and counter electrode was set to 1.5 cm. Anodization was performed in two steps: the first imposing a potential of 30 V, and the second imposing potential of 15 V with three variation time in each step (1h, 2h, and 3h). By this approach, the TiO$_2$ layer that forms is expected to be characterized by TiO$_2$ nanotubes that are long and have a small diameter. Therefore, the specific surface area of the nanotubes and the amount of dye loaded onto TiO$_2$ will increase. The anodized titanium was then heated to a temperature of 500 °C for 2 h. The anodized Ti obtained was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and diffuse reflectance UV–Vis spectrophotometry.

2.4. TiO$_2$ nanotube photocurrent evaluation

The photocurrent within TiO$_2$ nanotubes (TiO$_2$-NTs) was evaluated using a three-electrode cell configuration, with the working electrode composed of anodized TiO$_2$-NT/Ti, the counter
electrode of Pt, and the reference electrode was Ag/AgCl. The three-electrode cell was connected to a potentiostat, and the photocurrent was measured by the linear sweep voltammetry (LSV) method using a NaNO₃ solution as the electrolyte.

2.5. Preparation of TiO₂-NT/anthocyanin
Anthocyanin-sensitized TiO₂-NTs (TiO₂-NT/anthocyanin) were prepared by soaking the anodized TiO₂ in an anthocyanin extract solution for 24 h. Subsequently, the TiO₂-NT/anthocyanin was dried in an air stream. Then, the TiO₂-NT/anthocyanin plate was characterized by diffuse reflectance UV–Vis spectrophotometry and Fourier transform infrared (FT-IR) spectrometry.

2.6. Preparation of a fluorized-doped tin oxide (FTO) glass plate by the spray pyrolysis method
A glass plate (2.5 cm × 7.6 cm) was cleansed ultrasonically in acetone, ethanol, and water, sequentially, then dried in an air stream (see section 2.3). The glass plate was then heated to a temperature of 520 °C for 10 min. The glass plate was sprayed with the SnO₂:F precursor. The glass plate was sprayed for 2 min using a modified nebulizer compressor characterized by a flow rate of 0.4 mL/min and a spray range of 10 cm. The glass plate was heated again to a temperature of 520 °C for 10 min. The spraying is performed for 8–10 times.

2.7. Preparation of the Pt counter electrode
The FTO glass was cleansed ultrasonically in ethanol for 2 h. The FTO glass was then placed in a 5 mM H₂PtCl₆, 2-propanol solution. The FTO glass was dried and subsequently heated to a temperature of 450 °C for 30 min.

2.8. Fabrication of DSSC
A single DSSC was assembled in a sandwich structure with the following arrangement: TiO₂-NT/anthocyanin, spacer, I⁻/I₃⁺ electrolyte current, and FTO/Pt. The efficiency of the DSSC was evaluated using a potentiostat under visible light illumination (provided by a wolfram lamp) in a reactor box.

3. Results and discussion

3.1. Preparation of TiO₂-NTs
The formation of a TiO₂ layer on titanium foil can be monitored by looking at the change in current density while the anodization procedure is being performed. In figure 1 shows the current density change when the titanium foil was anodized for 1 h during the first step and for 3 h during the second step.

In the first step of the anodization process (section I of the graph in figure 1), the current density decreased due to formation of an oxide layer on the titanium foil surface (equation (1)). In fact, the oxide layer is less conductive than the titanium substrate. During the second step of the anodization process (section II of the graph), the current density increased slightly, due to a chemical dissolution reaction (equation (2)). Afterwards (section III of the graph) the current density decreased slowly and steadily owing to the equilibrium between the oxide formation and oxide dissolution reactions, which is an indication of the formation of nanotubes.
Figure 2. Diffuse reflectance spectrum of anodized TiO$_2$.

Figure 3. SEM image of anodized TiO$_2$.

Figure 4. FT-IR Spectrum of anodized TiO$_2$.

$\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H} + 4\text{e}^{-}$ \hspace{1cm} (1)

$\text{TiO}_2 + 6\text{F}^- + 4\text{H} \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O}$ \hspace{1cm} (2)

3.2. Characterization of TiO$_2$-NT

Figure 2 shows the diffuse reflectance UV–Vis spectrum of anodized TiO$_2$. This spectroscopic approach is utilized to determine the absorbance characteristic of TiO$_2$ in the UV and visible regions of the electromagnetic spectrum. The reflectance value obtained can also be used to calculate the bandgap energy of TiO$_2$ using the Kubelka–Munk (F(R)) and Tauc equations. Calculations indicate that the value for the bandgap of TiO$_2$ is 3.15 eV. This value is in accordance with that of TiO$_2$ in the anatase phase (~3.2 eV) [8]. Furthermore, based on XRD data, two peaks characteristic of TiO$_2$ anatase (based on JCPDS 21-1272 database) are present, at 20° ~ 25.38°, 37.32°, 47.86°, 69.6° and 75.26°. This indicates that TiO$_2$ is in the anatase phase.

In figure 3 is reported the SEM image of as-prepared anodized TiO$_2$. Evidence indicates that the as-prepared TiO$_2$ is nano-sized (50.53 ± 6.442 nm) and has nanotubular morphology.

Figure 4 shows the FT-IR spectrum of anodized TiO$_2$. The absorbance at 700–850 cm$^{-1}$ is characteristic of the vibration of the Ti–O–Ti group, whereas the absorbance at 3000–3650 cm$^{-1}$ is characteristic of the –OH bond stretching of H$_2$O molecules absorbed on the TiO$_2$-NT surface.

3.3. TiO$_2$ nanotube (TiO$_2$-NT) photocurrent activity evaluation

Figure 5 shows the linear sweep voltammogram (LSV) and the multi pulse amperogram (MPA) of TiO$_2$-NT. LSV data indicate that TiO$_2$ is only active when it is illuminated by UV light. TiO$_2$ did not display a significant current response in the dark or when it was illuminated by visible light. This behavior results from the fact that the value for the TiO$_2$ anatase bandgap energy is 3.2 eV, which
corresponds to the energy of UV light at a wavelength of 388 nm; therefore, when TiO$_2$ anatase is illuminated with light at a wavelength ($\lambda$) < 388 nm, an electron from the compound’s valence band is excited to the conduction band, thus causing a flow of electrons to occur. The MPA data also indicate that TiO$_2$ does not display any significant response to being illuminated by visible light; however, when it is illuminated with UV light, the current density increases significantly.

### 3.4. Co-pigmentation of an anthocyanin extract

The absorbance spectrum of anthocyanin is reported in figure 6. Evidence indicates that the absorbance of anthocyanin in the visible region (≈500 nm) increases as benzoic acid is added to the anthocyanin; in other words, a hyperchromic shift occurs. This behavior suggests that co-pigmentation with benzoic acid increases the ability of anthocyanin to absorb sunlight.

### 3.5. Fabrication and performance evaluation of DSSC

Table 1 contains DSSC parameters obtained from the current versus voltage (I–V) curve. The data reported in the table indicate that a DSSC using anthocyanin–benzoic acid (1:1 (v/w)) as the sensitizer has the biggest efficiency (0.3709 %). Therefore, the use of anthocyanin–benzoic acid as sensitizer can increase the performance and efficiency of a DSSC.
Table 1. Parameters for different anthocyanin and anthocyanin-based DSSCs

| Sensitizer | J<sub>max</sub> (mA/cm<sup>2</sup>) | V<sub>max</sub> (mV) | J<sub>sc</sub> (mA/cm<sup>2</sup>) | V<sub>oc</sub> (mV) | FF | P<sub>max</sub> (mW/cm<sup>2</sup>) | P<sub>in</sub> (mW/cm<sup>2</sup>) | η (%) |
|------------|-------------------------------|-----------------|-----------------------------|-----------------|----|-----------------------------|-----------------------------|------|
| 1 : 0      | 0.0042                        | 168             | 0.0069                      | 260             | 0.389 | 0.00070                     | 0.309                      | 0.2273 |
| 1 : 0.5    | 0.0075                        | 94              | 0.0125                      | 158             | 0.359 | 0.00071                     | 0.309                      | 0.2297 |
| 1 : 0.8    | 0.0038                        | 234             | 0.0043                      | 314             | 0.662 | 0.00089                     | 0.309                      | 0.2884 |
| 1 : 1      | 0.0046                        | 250             | 0.0065                      | 364             | 0.484 | 0.00115                     | 0.309                      | 0.3709 |

4. Summary

In summary, a two-step anodization method was implemented that can be utilized to produce TiO<sub>2</sub> in anatase phase and with nanotube morphology (TiO<sub>2</sub>-NT). Anthocyanin can be extracted from peels of mangosteen pericarp, and it can be used as a TiO<sub>2</sub>-NT sensitizer as part of a DSSC. Furthermore, use of anthocyanin–benzoic acid as a sensitizer on a TiO<sub>2</sub>-NT-based DSSC can enhance the efficiency of the solar cell.

Acknowledgements

The authors would like to thank Enago (www.enago.com) for the English language review.

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