The electrical conductivity and energy band gap of ‘bunga belimbing buluh’/tio₂ nanocrystals as hybrid solar cell

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Abstract. This research intends to explore the effect of thickness of inorganic titania nanocrystals (TiO₂ NC) materials and Averrhoe bilimbi’s flower towards the electrical conductivity. Averrhoe bilimbi’s flower or also known as ‘bunga belimbing buluh’ was used for the first time as a natural dye in hybrid solar cells. The performance of electrical conductivity can be improved in bilayer heterojunction hybrid solar cell (HCS). The TiO₂ NC was deposited on the ITO substrate using Electrochemistry method at room temperature. The dye extracted from Averrhoe bilimbi’s flower was deposited on the top of TiO₂ NC layered using the same method. The electrical conductivity can be recorded using Four Point Probe (FPP) under dark and light radiation (range of 0 Wm⁻² to 200 Wm⁻²). From the results, electrical conductivity was increased by the increment light intensity and suitable for further solar cell fabrications.

1. Introduction

Renewable energy is any source that generated from natural resources such as wind, solar geothermal and hydropower. The search for clean and renewable energy sources has become one of the greatest challenges in our society, due to the rapid depletion of fossil fuels and increasing demand on energy supply. One of the most promising alternative energy sources is solar energy which is in exhaust, purity, cheap and flexible use [1]. Solar cell is one of the potential candidates for solving the present world’s energy crisis. The solar cells used in harvesting the solar power are commonly categorized into different types with respect to the composition of their material such as organic dye solar cells, hybrid solar cell, non-crystal, multiple crystal, and single crystal silicon solar cells. In a few years, hybrid solar cell (HSC) has drawn attention as an alternative to traditional silicon or other inorganic technologies. HSC is the combination of both organic and inorganic semiconductors [2].

The advantage of organic material are good process ability with low cost deposition techniques, environmental, cost-effective, mechanical properties of the constituent materials, including the use of plastic-based substrates and encapsulates, open the possibility of manufacturing flexibility and low weight solar modules [3]. Foremost, the natural dyes abundantly available in plant parts, like flowers, seeds, barks, leaves, and stem can be extracted by simple procedure. Due to their cost efficiency, easily extractable using cheap organic solvents, non-toxicity, and environmental friendly, natural dyes are still a popular research [4].
Solar energy with natural dyes is not fully utilized in Malaysia. This research will be conducted to reduce energy consumption and the data and knowledge acquired will assist in the development of hybrid solar cell specifically for Malaysian climatic conditions. In this study, *Averrhoa bilimbi*’s flower was used for the first time as a natural dye in hybrid solar cells. Therefore, this research attempt to express the significant impact of *Averrhoa bilimbi*’s flower with Titanium dioxide photo-anode in bilayer heterojunction. Varied thicknesses of TiO$_2$ coating occurred with different techniques in Electrochemistry Impedence Spectroscopy (EIS). TiO$_2$ semiconductor coating thickness has favourable impact to the photovoltaic response to adsorbs more dye molecules [5, 6]. Furthermore, this combination absorbed a wide range in solar spectrum.

In Malaysia, the fruit of Belimbing buluh or known as *Averrhoa bilimbi* is very popular and commonly used in Malay cuisine. Every part of this plant has its own benefits. Therefore, the dye used in this research was extracted from the flower of this plant. This *Averrhoa bilimbi* prefers direct sunlight and seasonally humid climate [7]. The flower begins to bloom in yellowish green or purplish marked with dark-purple colour around February and continuously blooms and fruitful until December [7]. The flower was chosen because it is widely used in traditional medicine to treat many symptoms and it is said to be effective against coughs and thrush [7-9]. Figure 1 and 2 shows the *Averrhoa bilimbi*’s flower and the structure of *Averrhoa bilimbi*.

![Image of Averrhoa bilimbi’s flower](image1.png)

**Figure 1.** Averrhoa bilimbi’s flower

![Image of chemical structure of cyanidin](image2.png)

**Figure 2.** Chemical structure of cyanidin [10]

Anthocyanin generally found in most species of plant such as in fruits, flower and vegetables. Anthocyanins are one of the derived structures taken from flavanol. Examples of anthocyanidins are delphinidin (blue to red), pelargonidin (orange) and cyanidin (orange to red) [9]. The colours and stability are affected by substitution patterns and the glycosyl group of anthocyanin. The natural pigment compounds in many fruits and flowers can be determined by the colours. Red, blue and purple are the colours usually appear in anthocyanins [11]. Anthocyanins are most distinguished by their colour range, which is determined by the wavelength. The wavelength for *Averrhoa bilimbi*’s flower in visible range fall between 400 nm and 650 nm and also absorb under acidic condition.
Intensity and type of colour was affected by hydroxyl and methoxyl group [10]. Methoxyl group was determined by red colour and hydroxyl group go to blue colour.

2. Experimental
The organic dye was extracted from nature plant and this research was conducted in few stages.

2.1 Sample Collection and Extraction of Belimbing buluh’s flower
*Averrhoa bilimbi*’s flower was collected from a small village in Dungun, Terengganu. The fruits are red in colour. After that, the flower was transported to the laboratory on the same day. It was cleaned using tap water and then rinsed with distilled water. Then, it was crushed into fine powder before pouring into 100 ml ethanol. The mixture was kept for one week at room temperature. Subsequently, the solution was filtered using filter paper and dark red extract was collected. Then, the solution was placed in ultrasonic bath for 10 minutes at temperature 30°C. The extraction was concentrated and used as a dye to TiO$_2$ nanoparticles for the fabrication of solar cell [12, 13]. Ultrasonic bath was used to maximize the efficiency of natural colorant extraction [14]. The obtained samples were fabricated to be used as solar cell and tested in term of electrical efficiency.

2.2 Preparation of Indium Tin Oxide (ITO) Substrate
Indium tin oxide (ITO) coated glass was used as a substrate. The ITO glass was cleaned using ultrasonic bath (JEIOTECH, United Kingdom) to avoid dirt and dust. This step is very important to reduce any impurities present in the ITO and also to avoid contamination [2]. The ITO coated glass substrates which used as working electrode was cleaned with detergent solution for 10 minutes in ultrasonic bath at 30°C. Then, the ITO coated glass was put in distilled water for 10 minutes. Lastly, ITO was cleaned with acetone [2] for 10 minutes before final cleansing with the distilled water for another 10 minutes. After that, ITO coated glass substrate was dried using the hair dryer before it was kept in a Petri dish.

2.3 Fabrication of Hybrid Solar Cell

![Structure of bilayer heterojunction hybrid solar cell](image)

*Figure 3. Structure of bilayer heterojunction hybrid solar cell*

Based on Figure 3, the thin films were prepared using the electrochemistry method. The first and second layer was prepared using the same method. Electrochemistry method was used for depositing of TiO$_2$ thin film. Due to the deposition process, the TiO$_2$ thin films were subjected to a sonication treatment. The suitable temperature was recorded at 450°C for 120 minutes. The treatment will improve the electronic contact between TiO$_2$ nanoparticles. Then, it was rinsed with distilled water and ethanol. The second layer consisted of organic dye that was deposited on the thin film layer. Lastly, a thin layer of gold (Au) was deposited on the natural dye and it was used as counter electrode.

2.4 Electrical properties characterization
For this research, four point probes (FPP Jandel RM3 Test Unit) were used to determine the electrical conductivity of hybrid solar cell according to equation (1). The two outer probes supply a voltage
difference that drives a current through the film. The two inner probes picked up a voltage difference and the sheet resistivity is calculated from Equation (2) via a physical model of the current distribution. $R_s$ is the sheet resistance, 4.532 is the correction factor, $V$ is the voltage measured and $I$ is the current applied from the test unit. The unit of sheet resistance is ohms per square ($\Omega$/m$^2$):

$$\sigma = \frac{I}{R_s}$$  

(1)

where the $R_s = 4.532 \times \frac{V}{I}$

Ultraviolet-Visible (UV-Vis) Spectrometer Model Perkin Elmer Lambda 25 was used to measure the absorption of the spectrum light. Then it passed through a sample and the measurement was recorded after reflection from a sample surface. The selected wavelength range was analyzed between 200-1000 nm in the ultraviolet (UV) and visible (Vis) regions of the electromagnetic spectrum. The data was recorded from Absorption (A) versus wavelength ($\lambda$). The dye sensitised solar cells were illuminated using a 75 W Halogen lamp with an incident power of about 100 mW/cm$^2$ in an illumination area of 0.5 cm$^2$; UV and IR filter glasses were used in front of the sample [15]. Fourier transform Infra-red (FTIR) spectroscopy model IRTracer-100 was used to determine certain functional groups of pure compound and to confirm the presence of specific impurities. Fourier Transform Infrared spectra of the extracts dyes were recorded in the range of 650-4000 cm$^{-1}$ [16].

2.5 Thickness measurement
The thickness measurement was measured for different natural dyes using Dektak 150 Stylus Surface Profiler at Research center, Universiti Kebangsaan Malaysia (UKM).

3. Results and Discussion

3.1 Absorption Spectra of Natural Dyes (UV-Vis Analysis)
Figure 4 below shows the absorption spectrum of TiO$_2$ and it was recorded in the range of 250 nm to 320 nm. Wu et al stated that wavelength of TiO$_2$ was recorded 380 nm smaller in the ultraviolet (Uv) light spectrum [17]. In this research, the absorption spectrum range for Averrhoa bilimbi’s flower was recorded in the range of 320nm to 600 nm. Averrhoa bilimbi’s flower has a broad and strong absorption in the uv region at 320 nm and blue region at 438 nm with the maximum peak recorded at 350nm. Figure 5 shows the UV-Vis absorption of natural dye solution extracted from Averrhoa bilimbi’s flower.

![Figure 4. UV-Vis absorption of TiO$_2$](image-url)
Figure 5. UV-Vis absorption of natural dye solution extracted from Averrhoa bilimbi

3.2 Dye Structure (FTIR Analysis)
Figure 6 shows the FTIR spectra of Averrhoa bilimbi’s flower. The peak was assigned at 1440 cm\(^{-1}\) and 1319 cm\(^{-1}\) corresponded to C-H bond ortho-aromatic ring. The absorption peaks at 1645 cm\(^{-1}\) was recorded to the functional groups of stretching carbonyl C=C. Meanwhile, the peak at 2945cm\(^{-1}\) and 3335cm\(^{-1}\) were correlated with the –OH stretching modes.

Figure 6. FTIR Spectra of Averrhoa bilimbi’s flower

3.3 Thickness of bilayer heterojunction
The absorption spectra of thin films were recorded at different number of scans as shown in Figure 7. The number of scan or cyclic was determined in the different thickness of layers. It can also be seen in the Table 1. The thickness of TiO\(_2\) films were measured by using Profilometer (Bruker, Detakk Profilometer). The number of scan for the thin films was fixed at one, three, five and seven scan. From Figure 7, ITO/TiO\(_2\)(5) has the highest UV-Vis absorption compared to others. As can be seen, it was recorded in the range of 250 nm to 320 nm. The thickness of TiO\(_2\) films were recorded in Table 1.
Figure 7. UV-Vis absorption of TiO$_2$ thin film sample

| Number of Scan | Thickness (± 0.1 nm) |
|---------------|----------------------|
| 1             | 59.90                |
| 3             | 61.60                |
| 5             | 84.09                |
| 7             | 106.34               |

3.4 Electrical Conductivity

The electrical conductivity can be determined using Four Point Probe (FPP) under dark and light radiation. From the results, electrical conductivity was increased by the increment light intensity. Figure 8 shows the conductivity of ITO/TiO$_2$/AB at different number of scans.

Analysis shows the electrical conductivity was recorded between 0.032 Wm$^{-2}$ to 0.045 Wm$^{-2}$. The highest conductivity was obtained at 0.045 Wm$^{-2}$ for sample ITO/TiO$_2$ (7)/AB. The lowest conductivity recorded at ITO/TiO$_2$(3)/AB. The electrical conductivity was rapidly increased from dark condition at 0 Wm$^{-2}$ to light condition which is 200 Wm$^{-2}$. This is because the samples absorbed light energy and convert it into electrical energy. For dark condition, ITO/TiO$_2$(3)/AB shows the lowest electrical conductivity while for the highest conductivity measured for ITO/TiO$_2$(7)/AB under 200 Wm$^{-2}$ of light illumination. The increment of intensity of light affected the electrical conductivity. The colorant was affected by adding the layers. The polaron to be localized by 93% at one W-atom [18,19].

When the TiO$_2$NCs was irradiated, the conductivity changed at different intensity. This was due to the thermal activated mechanism added to photon mechanism [20]. The performance of electrical conductivity can be improved in bilayer heterojunction. This can be explain by the TiO2 semiconductor coating thickness. Futhermore, this combination absorbed a wide range in solar spectrum. As the thickness of TiO$_2$ increased, the electrical conductivity of the thin film also was increased.
4. Conclusion
In summary, the electrical conductivity was increased by the increment light intensity. The increment of layer or thickness into surface will improve the absorbance of the sample. The ITO/ TiO$_2$/ dye as Bilayer Heterojunction Hybrid Solar Cell deposited on the different thickness was successfully prepared by electrochemistry method. The effect of thickness on electrical conductivity bilayer thin film was studied. The highest conductivity was obtained at 0.045 Wm$^{-2}$ for sample ITO/TiO$_2$(7)/AB. The lowest conductivity recorded at ITO/TiO$_2$(3)/AB. The ITO/TiO$_2$(7)/AB thin film shows higher electrical properties. The presence of carbonyl and hydroxyl groups in the anthocyanin molecules bound to the surface of ITO is in favor to facilitate the photoelectric conversion effect. From results obtained, we conclude that our samples deposited on ITO substrate are successfully investigated and improve the electrical properties of the commercial ITO substrate. Furthermore, the study of these dyes is promising and can promote additional studies oriented to educate people on renewable energy sources, and disseminate knowledge for the optimization of solar cell components compatible with such dyes.

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