A Novel of Buton Asphalt and Methylene Blue as Dye-Sensitized Solar Cell using TiO$_2$/Ti Nanotubes Electrode

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Abstract. A study of TiO$_2$/Ti nanotubes arrays (NTAs) based on Dye-Sensitized Solar Cell (DSSC) used Asphalt Buton (Asbuton) extract and methylene blue (MB) as a photosensitizer dye has been conducted. The aim of this research is that the Asbuton extract and Methylene Blue (MB) performance as a dye on DSSC solar cells is able to obtain the voltage-currents produced by visible light irradiation. Electrode TiO$_2$/Ti NTAs have been successfully synthesized by anodizing methods, then characterized by using XRD showed that the anatase crystals formed. Subsequently, the morphology showed that the nanotubes formed which has coated by Asbuton extract. The DSSC system was formed by a sandwich structure and tested by using Multimeter Digital with Potentiostat instrument. The characteristics of current (I) and potential (V) versus time indicated that the Asbuton was obtained in a high-performance in 30s of 14,000µV; 0.844µA, meanwhile MB dyes were 8,000µV;0.573µA. Based on this research, the Asbuton extract from Buton Island-Southeast Sulawesi-Indonesia was potential for natural dyes in DSSC system.

1. Introduction
The rapid development of technology and science in the few decades raised many problems as well as the energy problem [1,2]. Today, dependence on fossil energy causing the natural source supply to become thinner, are needed an alternative source of electrical energy as a substitute for fossil energy [3,4]. The renewable energy sources like solar energy is a more potential energy to serve as an alternative energy source [5,6]. The existence of solar energy from sunlight is very abundant on earth and it is the most potential as a power plant applied to solar cells with photovoltaic technology [7,8]. The principle of solar energy by converting sunlight into electrical energy, one of them is Dye-Sensitized Solar Cell (DSSC) [9]. DSSC is a solar cell based on the semiconductor sensitivity using dye as a sensitizer [10].

In practice, DSSC requires a semiconductor to be able to transfer electrons to generate potentials [11]. The semiconductors commonly used in DSSC are the metal oxide materials such as ZnO, TiO$_2$, Fe$_2$O$_3$, etc. [12,13]. Titanium dioxide (TiO$_2$) is commonly used as a DSSC material because of good optical properties, inert, harmless, and high-ability of dye absorption [14,15]. In addition, it also used for high-performance for electron transfer as a light-absorbing molecule [16,17].

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The usual dyes used as a sensitizer in DSSC are organometallic synthetic dyes such as ruthenium metal complexes [18]. Although it has achieved an efficiency more than 10%, these dyestuffs in natural are very limited because they are expensive and not easily synthesized [19]. Meanwhile, the natural dyes derived from plant extract such as leaves, flowers, and fruits, but the resulting conversion efficiency is lower than the ruthenium complex [20]. Various dyes have been widely used so it is needed the other alternatives of natural source like button asphalt (Asbuton) extract as a natural dye that has never been reported before compared to methylene blue (MB). This research, the Asbuton was used as a dye and a renewable alternative because it has a yellowish black color that predicted to absorb the visible light [21,22], while MB as the standard dye that previously used many researchers because of strong adsorption power. The photon absorption of visible light allows it to be carried out by the dyestuff as electric current and electron transfer to the TiO₂ material [23,24].

The surface area in a semiconductor is very influential on cell efficiency so the TiO₂ was made in nanotubes arrays (NTAs) in order to produce a wider particle surface. The high ordered TiO₂ NTAs was grow on a titanium (Ti) plate can be done on spatial condition, low-energy, and environmental friendly with an electrochemical system called an anodizing method [25,26]. This research, TiO₂/Ti NTAs was synthesized by anodizing method followed by a coating of Asbuton extract and MB dye for photon absorb into DSSC system. The Asbuton extract is expected to be sensitized on visible light irradiation in order to be able to convert the sunlight to electrical energy.

2. Experimental Method

2.1. Extraction of Asbuton
Asbuton bitumen preparation was performed by using mortal to minimize size, then it sieved at 100 mesh. The extraction of Asbuton was carried out by using two separation step using a soxhlet and an evaporator. The first step in the preparation of Asbuton extract was weighed 50 grams, then it inserted into filter paper and input into thimble tube. The 300 mL n-hexane as a solvent agent which was extracted for 3 hours with 30 cycles at a temperature of 70°C. The second step used an evaporator to separate the solvent with Asbuton extract. The separation process is stopped after the solvent has completely separated.

2.2. Preparation of Ti plate
Ti plate preparation was done by cutting Ti plate with 99% purity and 0.5 mm thickness which cut into size of 1 cm × 0.75 cm then it sanded using fine sandpaper size 1200CC until the surface is clean and shiny then washed by using a detergent, water, and distilled water (D.I. H₂O). Subsequently, the Ti plate was etched using a mixture of HF, HNO₃ and D.I. H₂O (1: 3: 6) solutions for 2 minutes. The final step was rinsed Ti plate and then dried [27].

2.3. Fabrication of TiO₂/Ti Nanotubes Arrays (NTAs)
The Titanium plate was inserted in the probe which had been filled with an electrolyte solution of NH₄F 0.27 M and D.I. H₂O in 98% glycerol. The anodizing process was carried out by placing the Ti plate as an anode and Cu plate as a cathode, as well as providing a bias potential of 25 Volts connected to the power supply. The anodizing process was done in 4 hours, then it annealed for 1.5 hours to a temperature of 500°C [28,29].

2.4. Design of DSSC
ITO glass was cut with size of 2.0 cm × 1.5 cm then it was cleaned with ethanol solution. A conductor substrate of ITO was dropped with TiO₂/Ti NTAs and Asbuton dyes. Meanwhile, the counter electrode was coated with a formed carbon layer. The solar cells were prepared with sandwich structures were the working electrode and counter electrode affixed face to face then it was added with electrolyte solution. The determination of current-potential used multimeter digital and potentiostat DY2100B to obtain data when irradiation used 500 Watts Halogen visible light.
3. Results and Discussion

3.1. Extraction of Asbuton

Asbuton extract has been prepared from large black rocks at Buton Island, Southeast Sulawesi. The microscale structure of Asbuton has been obtained with 200 mesh sieve to high extraction and uniform shape of asphalt rock to high contact with the solution agent [30]. The extraction process was done by using Soxhlet based on the high-temperature extraction in 30 cycles [31]. Then evaporated with n-hexane solution. The n-hexane solvent has good extraction ability to obtain the non-polar component [32,33]. The main purpose of Asbuton extraction process is to separate bitumen with other substances, either quartz sand or limestone. Asbuton bitumen extraction resulted through extraction method with soxhlet and evaporator obtained in this study from 50 grams of Asbuton bitumen by 14.22%. It shows that the inside of Asbuton consist about 80% impurities.

3.2. Fabrication of TiO$_2$/Ti Nanotubes Arrays (NTAs)

The fabrication of TiO$_2$ NTAs was carried out on Ti plate using anodizing method by giving a bias potential of 25.0 Volts for 4 hours in NH$_4$F and glycerol as electrolyte solution. The anodizing process based on an electrolysis process, in which Ti metal was placed at anode and Cu metal placed at cathode which was connected to the Power Supply [21,24]. The anodizing process, bias potential will cause Ti$^{4+}$ ions to migrate from Ti metal to electrolyte and join the F$^-\bar{}$ ion forming the titanium hexafluoride complex [TiF$_6$]$^{2-}$. F$^-\bar{}$ ion in the electrolyte solution will move to the anode and will destroy the oxide layer formed to produce a tubular shaft based on the following reaction:

$$\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow [\text{TiF}_6]^{2-} + 2\text{H}_2\text{O}$$

(1)

The anodized Ti plate was calcined at 500$^\circ$C for 3 hours to evaporate an organic solvent trapped in the Ti plate and to oxidize the chained and attached ligand. In addition, the calcination process was performed to obtain an anatase type of TiO$_2$ crystal structure.

![Figure 1. The result of TiO$_2$/Ti NTAs by Anodizing method.](image)

According to Nurdin et al. anatase structure is the highest structure to be applied in solar cells because it has a larger surface area compared to other crystal structures [34]. The larger surface area will be absorbing dyes so the photons will be converted into electric current. TiO$_2$/Ti formed on the surface of the Ti electrode (Figure 1) shows the difference of Ti surface between TiO$_2$ resulting from the anodizing method with TiO$_2$ which hasn’t overgrown yet. The grayish color indicate that the anodizing results obtained a smooth surface with a fairly good layer thickness. TiO$_2$ NTAs has a tube-shaped structure and a more orderly shape compared to other mesoporous structures. It has nano size scale, wider surface, then it was resulted in the amount of dyestuff adsorbed on the TiO$_2$/Ti surface will become more numerous [17]. It is proportional to the absorption of photons will also increase to produce a more efficient light absorption process [25].

3.3. Coated Asbuton-TiO$_2$/Ti NTAs

TiO$_2$/Ti electrode has been formed by the anodizing method, then coated with Asbuton extract using a dip-coating technique. The dip-coating method has been widely used to form thin layers on the TiO$_2$/Ti surface because the good transparency and adhesion [21]. Asbuton-TiO$_2$/Ti NTAs was heated
in an oven at 80°C temperature for 5 minutes to obtain the high binding between Asbuton extract and TiO₂/Ti NTAs.

![Ti plate and Asbuton-TiO₂/Ti NTAs](image)

**Figure 2.** The result of coated Asbuton-TiO₂/Ti NTAs.

3.4. **Characterization Materials**

3.4.1. **X-ray diffraction (XRD).**

The XRD characterization was performed to obtain the crystal structure information of a synthesized TiO₂/Ti semiconductor. The crystal structure obtained is anatase crystals as an evidence by comparing the sample peaks against the standard peaks of JCPDS No.21-1272. Figure 3 shows the results of XRD analysis with specific peaks which is the form identity of TiO₂ crystals.

![XRD pattern of TiO₂/Ti NTAs](image)

**Figure 3.** XRD pattern of TiO₂/Ti NTAs.

3.4.2. **Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX).**

Characterization using SEM-EDX was performed to provide information about the form of Asbuton-TiO₂/Ti surface morphology, and the doped substance of Asbuton on TiO₂.

![Morphology of Asbuton-TiO₂/Ti NTAs](image)

**Figure 4.** Morphology of Asbuton-TiO₂/Ti NTAs (a) Magnification 1 µm, (b) Magnification 10 µm.
Figure 4 shows nanotubes formed on Asbuton-TiO$_2$/Ti NTAs, the presence of Asbuton dopant didn’t damage or mask NTAs all pores in TiO$_2$/Ti surface. The coating process results of Asbuton extract on TiO$_2$/Ti NTAs showed the uniform formation. It is a good condition for sensitizer using Asbuton as a dye in DSSC. In addition, to provide the success of dip-coating process coated on a substrate. Supported by EDX data, showed that the present Carbon (C) element of Asbuton coated on TiO$_2$/Ti NTAs. According to Odebunmi et al. Asbuton extract contain C element such as saturated hydrocarbons, hydrogenated polycyclic aromatic compounds, and high molecular weight phenols and carboxylic acids [35].

![EDX Spectrum of Asbuton-TiO$_2$/Ti NTAs.](image)

EDX characterization (Figure 5) shows the results of Asbuton-TiO$_2$/Ti NTAs that were the presence of element content on the electrode surface. The intensity of S and C peaks as an indication of sulfur (S) and carbon (C) elements on the TiO$_2$/Ti electrode (Ti$_2$O$_3$C$_1$S$_{0.025}$). According to Chilingar and Yen have reported that Asbuton contains an organic component of hydrocarbons, asphaltenes, and other organic compounds with sulfur, oxygen and nitrogen content [36]. The composition data of Asbuton-TiO$_2$/Ti electrode elements can be seen in Table 1.

| Element | KeV | Composition (Wt%) |
|---------|-----|-------------------|
| C       | 0.277 | 15.54          |
| O       | 0.525 | 36.95          |
| S       | 2.307 | 0.83           |
| Ti      | 4.508 | 46.67          |

3.5. **Performance Test of DSSC**

The performance quality of solar cell can be determined by efficiency because it is a measure in determining the characteristics of voltage-current (I-V) using poteniosat, and digital multimeter. The solar cell testing was performed using the illumination of 500 Watts halogen visible light lamp as a light. The light source of the halogen lamp was directed perpendicularly on the solar cell surface.

The DSSC solar cells have been fabricated by sandwich structure then current and potential were characterized by digital multimeter. Determination of potentiometer based on resistance (R), a potential (V), and current (I). In this research, DSSC has been tested by visible light irradiation showed the high-performance of Asbuton-TiO$_2$/Ti NTAs compared to MB-TiO$_2$/Ti NTAs in 30s was obtained that the potential and current were 14,000 µV; 0.844 µA and 8,000 µV; 0.573 µA, respectively. The high time irradiation has decreased the data because of exposure of visible light which made damage of dyes and the electrolyte will be evaporated. The high resistance which
Reduced the current flowing in the DSSC was not detected on the multimeter. We can determine the current with the Ohm Law equation,

\[ I = \frac{V}{R} \] (2)

Where, \( I \) is the current through the conductor in units of amperes, \( V \) is the voltage/potential measured across the conductor in units of volts, and \( R \) is the resistance of the conductor in units of ohms. Based on the data obtained in measurement results are presented in Table 2.

**Table 2.** Results of DSSC performance test using MB and Asbuton extract.

| Time (seconds) | DSSC MB | DSSC Asbuton extract |
|---------------|---------|----------------------|
|               | V (µV)  | I (µA)               |
| 30            | 8000    | 0.573               |
| 60            | 6000    | 0.508               |
| 90            | 6000    | 0.504               |
| 120           | 4000    | 0.430               |
| 150           | 2000    | 0.393               |
| 180           | 800     | 0.383               |
|               | 14000   | 0.844               |
|               | 12000   | 0.802               |
|               | 11000   | 0.771               |
|               | 9000    | 0.758               |
|               | 9000    | 0.643               |
|               | 6000    | 0.614               |

The performance quality of each solar cell is presented by voltage and current graph changes in both DSSC cells against time presented in Figure 6.

**Figure 6.** Current and potential changes; (A) The potential-time (V-t), and (B) The current-time (A-t).

This condition has saturated on TiO₂/Ti NTAs surface and the coating process of organic dyes were not equal. In other hands, the electrolyte effect has been decreased caused by visible light irradiation with high intensity that produced thermal condition. Based on the electrolyte function as the electron transfer medium, if the electrolyte is discharged or even absent, the electron transfer activity will be reduced or virtually absent, this affects the output current and voltage generated in the DSSC system.

DSSC cell performance which continued its measurement using Potentiostat is an electrochemical instrument consisting of electrical circuits that are useful for maintaining potential and regulating a fixed potential at a certain value. This instrument is intended to provide a voltage scan of the working electrode while measuring the magnitude of the voltage and current passed through the working electrode. The capabilities of each solar cell are presented with graphs of the voltage-to-current relation can be seen in Figure 7.
The performance test based on I-t (Figure 7) shows that the two tested DSSC have produced different current outputs and the the longer of irradiation time that produced the low-current. The results show that Asbuton extract was in high-performance than MB dye due to the black characteristic which is able to absorb energy in visible light.

The overall results obtained in this study ranging from current and voltage measurements using digital multimeters and portable potentiostats showed that Asbuton extract emitted greater current and voltage than MB dye, so Asbuton extract can be increased as a dye in the DSSC system, and can be used as a renewable alternative, since the utilization of Asbuton extract on DSSC manufacture has not been previously reported. The ability of each solar cell is presented with a graph of the time-relation voltage in Figure 8.

**Figure 7.** The performance test of DSSC current (A) against time (s), (A) MB-TiO$_2$/NTAs (B) Asbuton-TiO$_2$/NTAs.

4. **Conclusion**

In this paper, we have employed an Asbuton extract and MB as dyes in DSSC system using TiO$_2$/Ti NTAs and have evaluated its current-potential as a sensitizer. The characteristics of current (I) and potential (V) against time indicated that the Asbuton was obtained in high-performance in 30 s of 14,000µV; 0.844µA, meanwhile MB dyes were 8000µV;0.573µA, respectively.

5. **References**

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