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Article

The Effect of Graphite Concentration in TiO_2 Semiconductors on Efficiency of Dye Sensitized Solar Cells (DSSC) Using Dye *Melastoma malabathricum L* Fruit Extract

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Abstract. The effect of graphite mass in TiO_2 semiconductors on the efficiency of Dye-Sensitized Solar Cell (DSSC) based on dye extract of Melastoma malabathricum has been investigated. This study aims to determine the effect of mass variations of graphite-TiO_2 on the efficiency of DSSC and bandgap produced in the manufacture of DSSC. The mass variation of graphite added in TiO_2 semiconductors is 10%, 12%, 14%, and 16% of the mass of TiO_2. The result shows the maximum wavelength (λmax) for anthocyanin at 544 nm with an absorbance of 5.7 Á. The calculation results obtained by the optimal bandgap value in the variation of graphite mass 14% is 3.15 eV. The results of characterization using XRD obtained tetragonal TiO_2 crystal structure with a particle size of 49.8 nm. The DSSC test results obtained optimal results found in mass variations of 14% graphite with a current strength of 140,001 µA, a voltage of 1446.9 mV, and DSSC efficiency of 0.2026%.

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1. Introduction

The use of petroleum and coal as energy sources is very limited. alternative energy sources must be developed to be utilized. One of them is the sun as a solar cell. Solar cells based on photovoltaic effects, photons from absorbed solar radiation are then converted into electrical energy [1]. The solar cells that are widely used today are solar cells based on silicon technology. However, the high production costs of silicon-based solar cells have limited the use of this technology. Solar cells based on photovoltaic effects, photons from absorbed solar radiation are then converted into electrical energy. Silicon-based SC has been mass-produced and applied in many applications with high efficiency of 15-25%. however, the cost of producing silicon-based solar cells has limited the use of this technology [2, 3].

Dye-sensitized Solar Cells (DSSC) is the first breakthrough in solar cell technology since silicon solar cells [4]. The use of natural dyes is very good as a coloring agent because it is cheap and easy to obtain. The performance of dyes is also determined by the availability of functional groups such as carbonyl and hydroxyl to form chelates with Ti on the TiO_2 surface [1,5]. Anthocyanins contain a carbonyl functional group of hydroxy functional groups are found in *Melastoma malabathricum* fruit. *Melastoma malabathricum* is a plant that is easy to grow and has not been used optimally

TiO_2-based solar cells have weaknesses. TiO_2 bandgap as a semiconductor is quite wide at 3.2 to 3.8 eV. Addition of graphite powder reduces TiO_2 bandgap. Graphite has the advantages of mechanical and electronic properties, energy band 0.04 eV, Resistivity 50 μΩcm, and heat conductivity 3000 Wm-1K-1, making it suitable for solar cell applications [6]. Therefore, this study aims to determine the effects of adding graphite at various concentrations on the efficiency of DSSC.

2. Experimental Section

2.1. Preparation of natural dye sensitizer

Melastoma malabathricum fruit (MMF) 100 g is crushed and soaked in ethanol. The extract was dissolved with 50 ml ethanol and soaked for 24 hours. And then, the solution is filtered. The filtrate was concentrated with a Rotary Evaporator to obtain thick extracts and was characterized using a UV-Vis spectrophotometer to determine the wavelength. The *Transparent Conductive Oxide* (TCO) substrate was cut in size 5 x 2.5 cm and soaked in ethanol for 10 minutes to remove impurities. Subsequently, the substrate is dried using a hairdryer. Powder of TiO_2 3.5 gram with a variation of graphite mass 10%, 12%, 14%, and 16% mixed with 15 ml ethanol and homogenized using a magnetic stirrer. graphite-TiO_2 calcined at 450ºC for 60 minutes. Graphite-TiO_2 obtained was characterized using UV-Vis and XRD spectrophotometers.

Paste-shaped graphite-TiO_2 (added by ethanol) was doped on the TCO substrate using the doctor blade method and heated with a hot plate at 450ºC for 30 minutes. Chitosan 2.5 gram was dissolved with 5 mL polyethylene glycol (PEG) and stirred using a magnetic stirrer until homogeneous. In another glass, 0.8 gram KI and 0.127 gram I_2 are dissolved with 5 ml PEG then stirred until homogeneous. Then the chitosan gel solution was poured slowly into the KI / I_2 solution while stirring and left homogeneous and stored in a dark bottle. It is an electrolyte solution.

TCO substrate coated with TiO_2 graphite was immersed in a dye solution for 24 hours. After that, the TCO layer is rinsed with distilled water and dried with a tissue. Graphite paste was coated on another glass TCO substrate as a comparison electrode and heated at 200ºC for 20 minutes. The TCO glass substrate with a graphite-TiO_2 layer and a reference electrode joined together on both side each other to form a sandwich structure. the electrolyte solution is dropped at both ends of the electrode and the electrolyte solution is left absorbed into the oxide layer. Then clamped on both sides so that the electrode attaches perfectly. Tests are carried out using sunlight sources to determine the voltage and current produced using a digital multimeter [4, 7]

2.2. Data Analysis Technique

Data analysis in this study was carried out qualitatively and quantitatively. Characterization results were analyzed using XRD and UV-Vis spectrometer. The characterization of DSSC current and voltage strength was carried out by using a series of DSSC electrical measurements using a digital multimeter. The final result of the DSSC characterization measurement is the efficiency value, obtained from the current and voltage strength shown on the digital multimeter.

3. Results and Discussion

3.1. *Melastoma malabatricum Fruit(MMF)* Extract

Fruit extract produces a purple filtrate which shows anthocyanin (Fig.1). Several studies have reported reported that the purple fruit of melastoma contains anthocyanins [8,9,10]. Dye preparation using MMF was carried out with ethanol solvent macerated for 24 hours. anthocyanin dyes can be dissolved in ethanol solvents. The ethanol solvent serves to pull out the anthocyanin dyes contained in the MMF. Graphite-TiO_2 semiconductor for 24 hours is immersed in MMFextract solution so that the anthocyanin color pigment can be absorbed into the pores of the semiconductor. The color of MMF extract after filtering is purplish-red as shown in Figure 1.

Figure 1. *Melastoma malabatricum Fruit* (MMF) Extract Solution

The MMF extract was characterized using UV-Vis spectroscopy. Characterization was carried out to determine light absorption by secondary metabolites in MMF. Figure 2 shows the absorption at a wavelength of 400-800 nm in ethanol solution. This indicates that the presence of a conjugated double bond and the presence of a lone pair in the secondary metabolites which causes the solution to have a color [11]

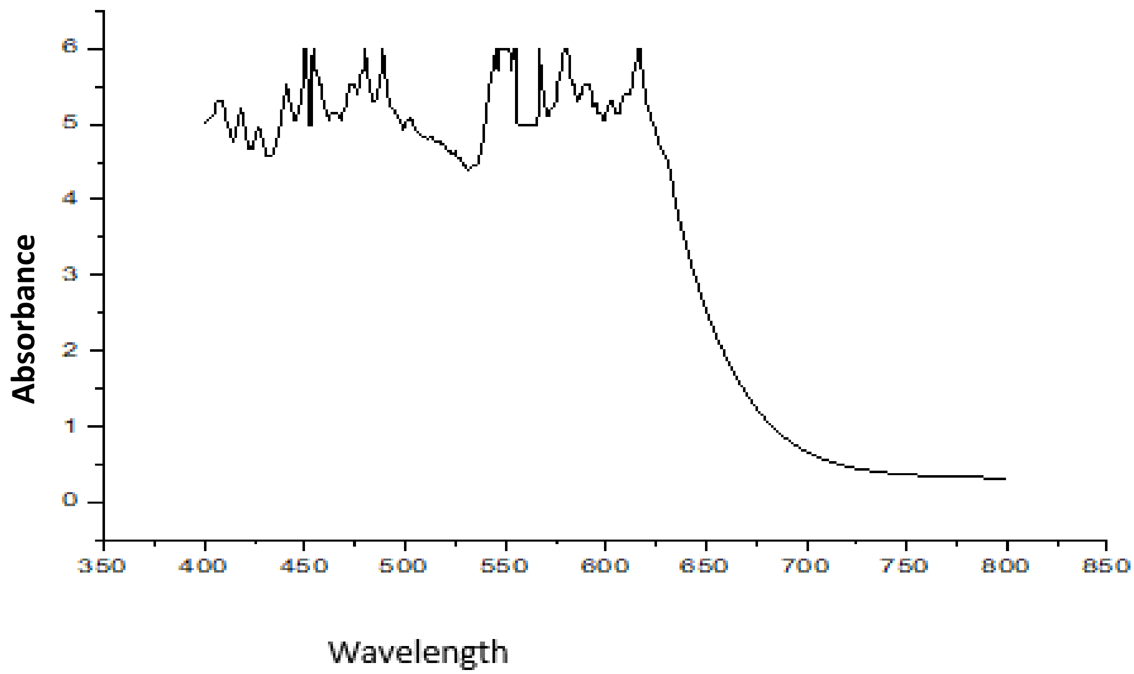

Figure 2. The wavelength spectrum of absorption from MMF extract using UV-Vis spectrometer

3.1. X-Ray Diffraction (XRD)

XRD spectra (fig. 2) shows that calcite Graphite-TiO_2 crystals which have been calcined at 450ºC are diffractogram in the same shape as tetragonal crystal systems which correspond to JCPDS standards numbers 96-500-0224. In addition, the peaks on the TiO_2 XRD data are anatase-based. It appears that all pure peaks have an anatase phase with a tetragonal crystal structure. The anatase phase has a higher photoactive ability compared to the rutile phase because of anatase surface area is larger than rutile so that the active side of per-unit anatase is greater [12]. Agustini *et al* (2013) reported, anatase phase has the ability to adsorb more dyes and electron diffusion coefficients [13]. Anatase is a form of polymorph TiO_2 which tends to be more stable at low temperatures, the shape of anatase crystals occurs in the heating of powder TiO_2 from temperatures of 150-500ºC 3.2 eV [14]

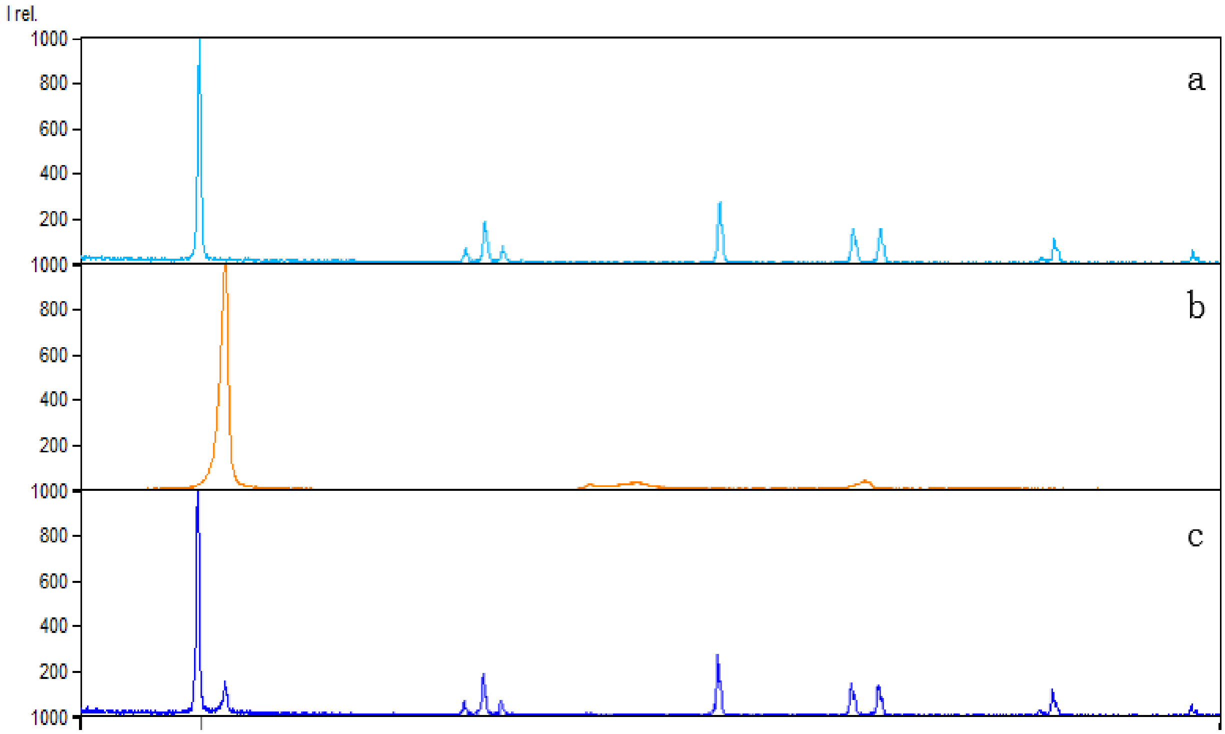

Figure 3. XRD Spectra a) TiO_2 b) Graphite c) Graphite-TiO_2

The XRD spectrum of graphite identifies 2θ at the position of 26.57° and has a hexagonal crystal structure at a distance of 3.3544 and intensity of 13.30%. The XRD spectra show the particle size of the graphite-TiO_2 semiconductor in table 1. Table 1 shows TiO_2 without doping graphite resulting in a larger crystal size than the sample with doping. doped graphite reduces the size of TiO_2 aggregate so that the size of the crystal becomes smaller. Small particle size causes the particle's surface area to become larger and the pores between particles increase so that more dye molecules are absorbed. Crystal size determination uses the Debye Scheerer equation[13,14, 15,16]:

$$P = k\,\lambda / (\beta \cos\theta) \qquad (1)$$

Where k is the shape factor, λ is the X-ray wavelength 0.154 nm, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle.

Table 1**. Graphite-TiO_2 Semiconductor Particle Size**

Sample	Cos *θ*	FWHM (rad)	Particle Size (nm)
Graphite	0.765724443	0.3998	25.9869
TiO_2	0.988222198	0.1599	50.3462
Graphite-TiO_2	0.998562289	0.1599	49.82486

3.2. Band gap energy

Table 2 shows that the doping value given by gap energy from doping TiO_2 graphite decreases. In 14% graphite doping, the smallest bandgap value was 3.15 eV. Daniyati, et al., (2015) showed the bandgap value for TiO_2 is 3.20. Its means, the TiO_2 coupling with graphite managed to reduce the bandgap from TiO_2 to 3.15. The bandgap value obtained does not continuously decrease, because of several factors such as the uneven surface of the TiO_2 layer and cause light reflection at different angles so that it seems as if absorption occurs at the wavelength of visible light. In addition, with the decrease in the bandgap of TiO_2 resulting from the coupling. The light energy (photons) needed for the excitation of electrons from the valence band to the conduction band will be smaller. The bandgap energy calculation method using the touch plot method is carried out by exploration of the relationship graph (hv) and $(\alpha hv)^2$ as the ordinate to cut the energy axis so that the bandgap energy value is obtained. The touc plot equation is calculated by equation 2.[16,17,18]

$$(\alpha hv)^2 = A\,(hv - Eg) \qquad (2)$$

where α is the absorption coefficient, hv is the photon energy, Eg is the optical band-gap, A is a constant which does not depend on photon energy

Table 2. *Band gap* Energy Value

	Grafit-TiO_2 10%	Grafit-TiO_2 12%	Grafit-TiO_2 14%	Grafit-TiO_2 16%
Energi *Band gap* (eV)	3.25	3.20	3.15	3.18

3.3. Photoelectrochemical Properties

Testing of electrochemical properties is carried out using a digital multimeter. The test was carried out for one day to determine the stability of the performance of the DSSC which began at 11.00 am to 3.00 pm at that time, the sun emits optimum heat. The performance of DSSC in the form of a sandwich structure can be known by measuring the voltage-current (I-V) under the conditions of the light source shine by adjusting the resistance used. The obstacles used are regulated by increasing the optimum resistance value. Comparison of Characteristics of I-V DSSC MMF dyed is presented in Table 3.

Table 3 illustrates that the value of current (I) and voltage (V) solar cell DSSC with dye MMF has increased with increasing intensity of radiation given and increased doping of graphite. Increasing the value of current and voltage is also due to the smaller band gap value. The small band gap, the energy (photons) needed for the excitation of electrons from the valence band to the conduction band is also small so that electron transport is good and results in increased current and voltage. The increase in current and voltage is also due to the smaller size of the crystal. The smaller the size of the crystal, the larger the surface area of particles per volume. The more pores between particles and the more dye molecules that can be absorbed. Table 3 shows that the stress value and current strength generated are the highest 14% graphite exposure of 1446.9 mV and 140,001 μA. However, the mass variation of graphite 16% produces a voltage value and decreases the current strength. It is because of the amount of graphite is added so that it exceeds the maximum limit and causes the surface of the area to be covered by graphite which causes the semiconductor to not work optimally[19,20].

Table 3. The efficiency of Solar Cells with Graphite Mass Variations

Graphite Mass/ (Graphite + TiO_2) Mass Total	Voltage (mV)	Current (μA)	η (%)
10%	1369.2	132.304	0.1811
12%	1409.6	135.904	0.1915
14%	1446.9	140.001	0.2026
16%	1418.2	137.330	0.1948

4. Conclusion

Graphite mass variation affects decreasing the bandgap of graphite-TiO_2 semiconductor with the smallest bandgap value in the variation of graphite mass 14% at 3.15 eV. DSSC using MMF dye variation of 14% graphite mass in TiO semiconductor produces efficiency of 0.2026%, the current strength of 140,001 μA and voltage of 1446.9 mV. Graphite mass variation affects decreasing the bandgap of graphite-TiO_2 semiconductor with the smallest bandgap value in the variation of graphite mass 14% at 3.15 eV. DSSC using MMF dye variation of 14% graphite mass in TiO semiconductor produces efficiency of 0.2026%, the current strength of 140,001 μA and voltage of 1446.9 mV.

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