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# PERFORMANCE OF DOPED MONTMORILLONITE ON PHOTOSENSITIZER BASED NATURAL DYES *Gardenia Jasminoides*

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## ABSTRACT

Dye Sensitized Solar Cell (DSSC) is an electrochemical cell capable of converting solar energy into electrical energy. In this study, we evaluated the addition of montmorillonite to dyes extracted from Gardenia jasminoides to obtain better DSSC performance. The electrolyte polymer used in DSSC is Nafion. The extraction of dyes was carried out by the maceration method. The composition of MMT-nafion used is 0:100; 25:75; 50:50; 75:25; 100:0. Characterization of DSSC performance is done by measuring the relationship between strong current (mA) and voltage (Volt). Determination of the maximum absorption that can be absorbed by the dye was determined using a UV-Vis spectrophotometer. The results of the characterization of G. jasminoides fruit coloring using UV-Vis showed the presence of quercetin and crosin compounds. The performance of DSSC technology is evaluated by measuring efficiency (η). The measurement results show that the highest efficiency produced is 0.9160% with the optimum composition of MMT-nafion 50:50. Surface topography analyzed using Atomic Force Morphology (AFM) showed that the surface of the TiO2 layer after added dye was more evenly distributed than without dye. The surface topography ensures that the dye has filled the surface area of the working electrode and is able to promote electrons to the conduction band in TiO2. Thus, the dye from G. Jasmoide has the potential as a dye sensitizer for DSSC. The addition of MMT and nafion was able to improve the performance of the photosensitizer in DSSC.

Keywords: dye sensitized solar cell; montmorillonite; nafion, dye; *gardenia jasminoides*.

## INTRODUCTION

Recently, energy has become one of the problems in the world due to producing energy from petroleum and coal, which is getting low. This causes the development of energy technology that is renewable energy, environmental friendly and can be used continuously is solar technology. Dye Sensitized Solar Cell (DSSC) is solar technology that the most developed today [1]. It is a third-generation solar cell developed by Michael Gratzel in 1991. The principle of DSSC is that converts solar energy into electrical energy based on semiconductors which following an electrochemical phenomenon [2]. DSSC is one of the low-cost and easily fabricated technologies compared to conventional solar cells that require high costs. As technology advances, DSSC has also been developed to increase the Power Conversion Efficiency (PCE) and obtain a more attractive appearance [3].

The PCE can be increased by changing some of the compositions contained in the DSSC component. The main components in DSSC technology are semiconductors, dyes, electrolytes, working electrodes and comparative electrodes. Several other studies have modified semiconductor components and dyes [3,4]. The semiconductors that have been successfully modified in the following research were Cu-doped titanium dioxide ($TiO_2$) using ammoniumhexafluorotitanate dan hexamethylenetetramine dyes produced PCE 0.2% to 0.4% and Na-doped $TiO_2$ nanorods with dyes extracted from the *Kigelia Africana* petals resulted PCE 1.09% to 1.56% [5,6]. Some studies have also carried out the development of dyes such as dyes extracted from Mangosteen fruits using $TiO_2$ semiconductor produced PCE 0.0022% and dyes extracted from eggplant fruit using $TiO_2$ semiconductor produced PCE 0.47% [7,8]. Actually, inorganic dyes are often used such as complex metals with the highest PCE value currently being 14.30% [9]. But inorganic dyes have disadvantages namely not friendly and very dangerous for the environment. So, natural dyes become option used in DSSC components because they are quite affable and able to convert solar energy into electrical energy.

Therefore, this research has successfully fabricated DSSC by modifying semiconductor components. The semiconductor used in this study is $TiO_2$ which has been modified by the addition of a composite layer of Montmorillonite (MMT) and nafion. MMT has an ion exchange capacity so that $TiO_2$ easily transfers electrons to the electrode. It also has space between the layers so that the dyes of organic compounds are easily absorbed [10]. In addition, MMT is a clay that is easily applied and obtained. Nafion is used to maintain ionic conductivity and it is also capable of binding MMT to a more stable semiconductor layer [11]. In this study also uses dyes from *Gardenia jasminoides* fruit extract because it has good heat stability of 60-90$^{o}$C and is stable in light rays of 5000-20000 lux [12].

## METHODS

### Materials

The materials used in this study are indium tin oxide (ITO) 15-25 Ω it was purchased from solaronix, titanium dioxide (TiO2) was purchased from Merck, nafion 212 from China, natural Montmorillonite (MMT) from Western Java Bogor Indonesia, Gardenia jasminoides fruits was sourced from China, triton X-100, ethanol 96%, methanol potassium iodide and iodine were purchased from Sigma Aldrich, distilled water and deionized water.

### Methods

Dye was extracted from *Gardenia jasminoides* using 10 mL solvent of ethanol:acetic acid:distilled water (50:8:42) %v/v[7]. The dye was used for sensitizer of DSSC and it was analysed using UV-vis spectrophotometer Shimadzu 1700 in range of wavelength 260-550 nm. Potassium iodide/Iodine was used for electrolyte solution. ITO glass is prepared with a size of $2 \times 3$ cm$^2$. It is cleaned and soaked using ethanol. Then it is sonicated for 30 minutes. The last, ITO glass is dried and tested for resistance using a multimeter with a resistance value of 15-25 Ω. Preparation of working electrode was started by 0.5 g $TiO_2$ powder was added to 2 mL of deionized water and 5 drops of X-triton and stirred for 30 minutes until it becomes a $TiO_2$ paste. Then, the $TiO_2$ paste was coated on the ITO glass and it was heated in a furnace to a temperature of ± 350$^{o}$C for 30 minutes [13]. On to the top layer of $TiO_2$ in the working electrode was added MMT-nafion composite. MMT was activated a long 4 h at 500 C [14]. Composition of MMT-nafion varied by (0:100, 25:75, 50:50, 75: 25, 100: 0) % w/w. Then, the working electrode was immersed in the dye for 1 hour. Activated carbon was used as comparative electrodes, and its spreaded onto surface of ITO. Potentiostat E-DAQ and e-corder 410 was employed to observe the relation between current density and voltage of DSSC. Topography surface analysis was investigated byatomic force microscope (AFM) Nanosurf Easy Scan 2.

## RESULTS AND DISCUSSION

Dye of *Gardenia jasminoides* fruits after isolation by maceration method is shown in Figure-1. Dyes that are often used in DSSC are organic compounds and it is belonged to flavonoids group [15]. Flavonoids have different types of compounds so that a comparison of solvents such as distilled water, acetic acid and ethanol is used to produce in the high total yield[16].

**a** **b**

**Figure 1**. a. *Gardenia jasminoides* fruits and b. Dye extracted from *Gardenia jasminoides* fruits

Figure 2 showed three absorbances maximum at 460.6 nm; 436.2 nm and 329.2 nm and this indicated that dyes contained quercetin (a) and crocin (b)[7,18,19].

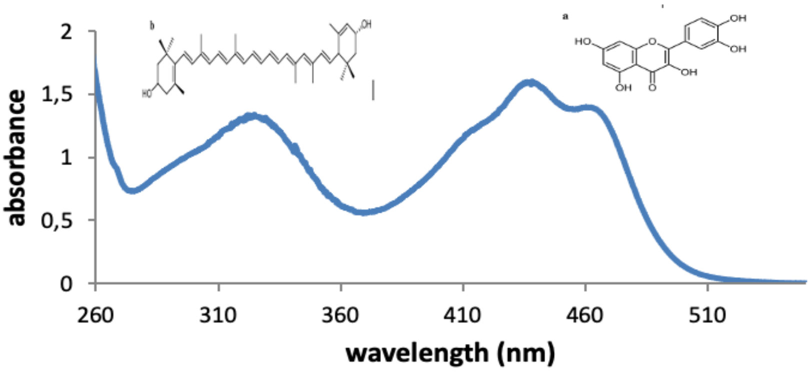



**Figure 2.** UV-vis absorption spectrum of quercetin (a) and crocin (b)

DSSC formed of 4 main components are working electrode, dye, electrolyte and comparative electrode. The first component is a working electrode consists of conductive glass and semiconductor (Figure 3). In this study using conductive glass is ITO because it has ideal transparency with transmittance over 80% so that light can pass through the ITO glass to the active dye. It is also able to collect the current product [3,4] The semiconductor used is TiO2 because it has good chemical stability under sunlight irradiation [20].

This study used Montmorillonite (MMT) and nafion to modify the working electrode because they were able to improve DSSC performance. MMT is a clay mineral that contents layer 2:1 which are 2 tetrahedral sheets that flank 1 octahedral sheet. MMT's chemical property is capable of ion exchange which makes TiO2 easy to transfer electrons to the electrode. Its physical properties can absorb the dyes because it has space between the layers. MMT is also a type of clay that is available to found. Whereas nafion is used to bind the MMT so that it is stable and nafion also maintains ongoing ionic conductivity.[10,11,21,22] The second component is the dye from the extraction of Gardenia jasminoides. The third component is electrolytes made from potassium iodide and iodine. The fourth component is a comparative electrode consist of ITO conductive glass coated with carbon. The method used for the DSSC series is the sandwich method is shown in Figure 4.

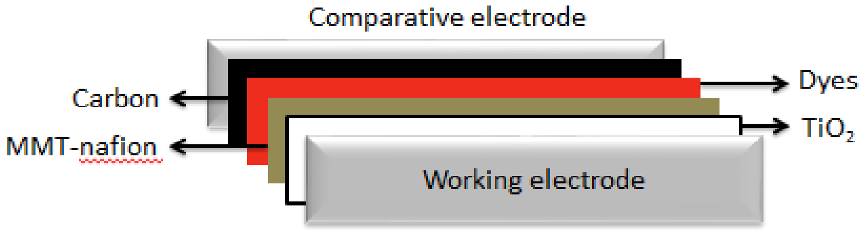



**Figure 3.** DSSC components sequence with sandwich method

The working principle of DSSC is photoelectrochemistry where the dyes (S) absorb photons (hv) which will cause electrons in the highest occupied molecular orbital (HOMO) state to be excited in the lowest unoccupied molecular orbital (LUMO) state. The dyes (S*) in the excited state will undergo an oxidation reaction which results in the electrons being released and leading to the $TiO_2$ conduction band. Then regenerate the dyes ($S^+$) with electrolyte solutions where the electrolyte will experience a reduction from triiodide is shown in Figure-4. The mechanism of oxidation reactions can be seen as below[15,23]

$$S + hv \longrightarrow S^*$$
$$S^* \longrightarrow S^+ + e^-$$
$$S^+ + \frac{3}{2} I^- \longrightarrow S + \frac{1}{2} I_3^-$$
$$\frac{1}{2} I_3^- + e^- \longrightarrow \frac{3}{2} I^-$$

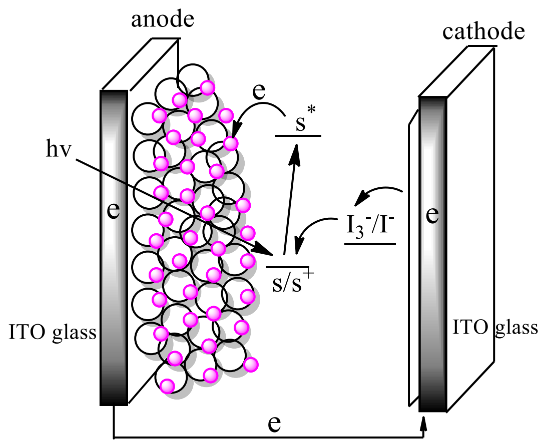
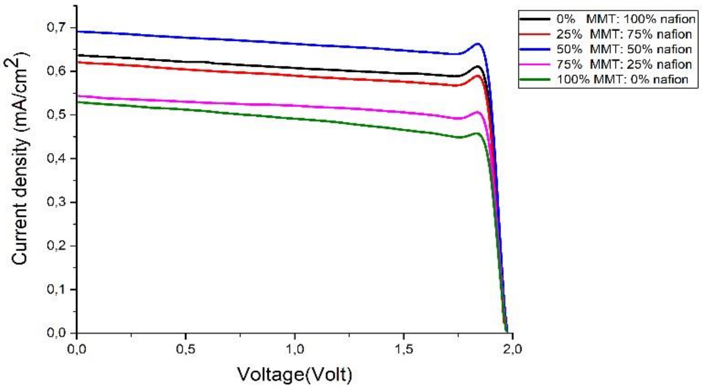
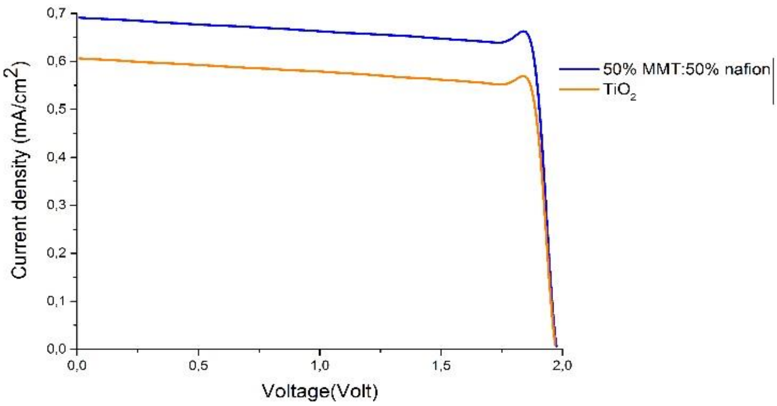



**Figure 4.** Principles of DSSC technology[24]

DSSC efficiency value is determined by the current and voltage curve method. Figure-5a shows the I-V curve for the variations in composition of the working electrode component using MMT:nafion composite, respectively. It was found that the current density of DSSC increased with adding MMT-nafion (1:1) Figure-5b shows the I-V curve about working electrode component modification by MMT:nafion and without modification. This result shows MMT and nafion succeed increase if compared DSSC just made of $TiO_2$. MMT shows behavior that it was increasing the electron transfer and stabilize of dye. Nafion can be explained that defend the ion conductivity and stabilize MMT.




(a)




(b)

**Figure 5.** (a) I-V curve based on the composition of MMT and nafion; (b) Comparison of the I-V curve between MMT-nafion and $TiO_2$

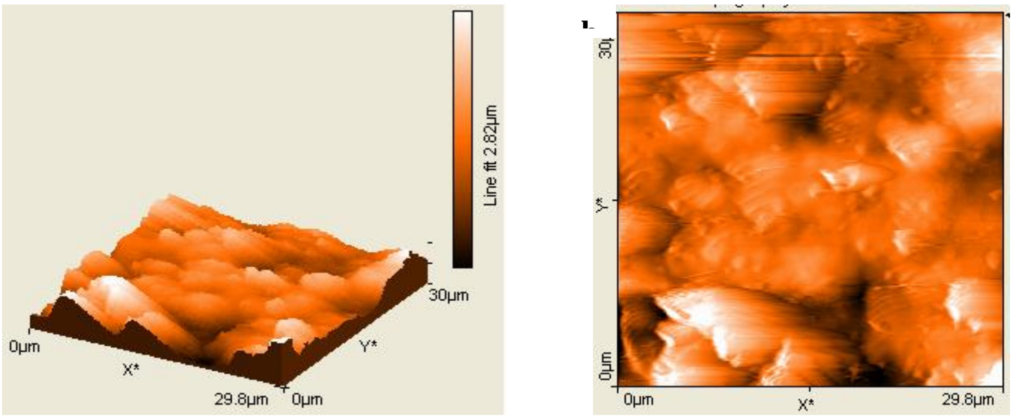
**Table 1.** Performance data of DSSC

| Sample | Isc ($mA/cm^2$) | Voc (V) | FF (%) | η (%) |
|---|---|---|---|---|
| MMT:nafion (0:1) | 0.6366 | 1.9750 | 89.4131 | 0.7665 |
| MMT: nafion (0,25:0,75) | 0.6205 | 1.9600 | 89.1555 | 0.7393 |
| MMT: nafion (1:1) | 0.6909 | 1.9750 | 89.3797 | 0.8316 |
| MMT:nafion (0,75:0,25) | 0.5430 | 1.9700 | 86.9886 | 0.6344 |
| MMT: nafion (1:0) | 0.5294 | 1.9700 | 80.5405 | 0.5727 |
| $TiO_2$ | 0.6061 | 1.9700 | 87.7581 | 0.7144 |

Based on Table-1 it can be seen that highest power conversion efficiency (PCE) of DSSC was shown by MMT and nafion composition with 1:1. Montmorillonite (MMT) has a nanolayered structure and belongs to the phyllosilicate mineral. The layered structure (about 1 nm thick) consists of stacked layers, and each layer consists of two single O bonds O single bond tetrahedral sheet flanking one O single bond Al(Mg) single O bond octahedral sheet (approximately 100 nm × 100 nm, width and length). Due to the isomorphic substitution, a positively charged layer and then cations exist in the MMT interlayer space. The neighboring layers are held together mainly by van der Waals forces and electrostatic forces to form MMT primary particles. These particles then aggregate to form secondary micrometer- to millimeter-scale particles. This increase the excitation of electrons to the conduction band in the semiconductor.

### The characteristic of MMT-nafion surface

Topography surface of MMT-Nafion was the Figure-6. The AFM analysis results show that the surface that looks rough can be stated that many *Gardenia jasminoides* dyes are absorbed on the surface. It can be seen also that the uniform distribution of *Gardenia jasminoides* dyes on the surface.[25] The root mean square (RMS) roughness value obtained is 0.22 µm.




**(a)** **(b)**

**Figure 6.** (a) Topography analysis of DSSC in semiconductors 50% MMT: 50% of nafion using AFM and (b) Surface semiconductors 50% MMT: 50% of nafion using AFM.

## CONCLUSION

The characterization of dyes extracted from *Gardenia jasminoides* fruits using a UV-Vis spectrophotometer showed that peaks produced at wavelengths of 460.6 nm and 436.2 nm were crocin, while peaks at wavelengths of 329.2 nm were quarcetin. Furthermore, the highest power conversion efficiency (PCE) value was obtained at 0.8316% with modification of the semiconductor using 50% MMT: 50% nafion in the top layer of TiO2. Topography surface analysis on the optimum semiconductor shows the uniform distribution of dyes on surface of $TiO_2$ and increased solar energy absorption. MMT-nafion showed há a great potency as a dye sensitizer.

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