

# Modification of Methyl Orange dye as a light harvester on solar cell

*by Harsasi Setyawati*

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## Modification of Methyl Orange dye as a light harvester on solar cell

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**Abstract.** The purpose of this research is to modify methyl orange be a complex compound Fe (II) -methyl orange and apply it as a light harvester on DSSC (Dye-Sensitized Solar Cell) technology. Titanium dioxide was used as a semiconductor and synthesized from tetrabutylorthotitanate (TBOT). The wavelength spectra of Fe (II)-methyl orange was characterized by UV-Vis spectrophotometer and showed d-d transition at 420.50 nm and charge transfer at 262 nm. The interaction of metal-ligand bonding (Fe-N) was characterized by FTIR spectrophotometer and shown at wavenumber 316.33 cm<sup>-1</sup>. Fe(II)-methyl orange was a paramagnetic compound with magnetic moment 3.9 BM and ionic compound because of its conductivity higher than its solvent. The photovoltaic analysis confirmed that Fe(II)-methyl orange produced a current of 40 mA, a voltage of 0.38 V and an efficiency of 0.24%.

### 1. Introduction

Nowadays, an energy issue is one of a challenging problem faced by many countries in the world. Scientists are racing to find an effective energy source to tackle that problem. In Indonesia, the most promising renewable energy source is sunlight. Potency sunlight in Indonesia is almost 112000 GWp/day and illuminated most of the year. The best technology, which can be applied to utilize sunlight energy, is a Dye-Sensitized Solar Cell (DSSC). DSSC is one of the solar cell technologies which harness a dye as a light harvester which capturing the energy of sunlight and convert them into electricity. DSSC has many advantages such as easy to modified, easy to fabricate, low cost and environmental friendly [1-4]. On the other hand, as a developing country, environmental pollution in Indonesia is a significant problem too. Dye waste in the water is one of a big issue. One of the dyes that highly contribute to the waste is methyl orange. Methyl orange is one of the chemical compounds which really hard to degrade and has high stability [5]. In terms of the structure, methyl orange is photo-reactive, has the ability to capture photon from the sun and highly suitable utilized as a light harvester on a solar cell [6]. Therefore, in this research, dye waste methyl orange will be applied to solar cell technology.

The incorporation of metal and dye structure was proven increasing the ability of dye as a light harvester. The presence of metal can improve the chemical and thermal stability of dye. Besides, the interaction of metal to the dye structure will produce a charge transfer phenomenon that will facilitate the electron transfer process [7-9]. Hence, in this research iron (II) will be used to modify a methyl orange structure. Based on the energy and environmental issues, this research will be investigating the



5 modification of methyl orange as a light harvester on a solar cell. This research can be an excellent solution to produce green energy from dye waste. The modification process will be conducted by inserting an iron to the methyl orange structure through the formation of metal complexes process. The modified methyl orange will be characterized by spectrophotometer UV-VIS and Fourier Transform Infra-Red (FTIR). The semiconductor that will be used is titanium dioxide from organic precursor tetrabutylorthotitanate (TBOT). The counter electrode will utilize graphite and potassium three iodide (KI<sub>3</sub>) as an electrolyte. The photovoltaic performance of modified methyl orange will be assay by multimeter and lux meter.

## 2. Methods

### 2.1. Determination of metal-ligand mole ratio

Determination of metal-ligand ratio was conducted by UV-VIS spectrophotometer. A metal solution in a fixed mole (Fe (II)) was reacted by methyl orange solution in a various mole. The mixture was determined their absorbance from the maximum wavelength of methyl orange. Then, the absorbance from each solution was plotted into a regression line to determine the metal-ligand ratio.

### 2.2. Modification of methyl orange through metal insertion

In this research, the modification process has been done by inserting a metal to the methyl orange structure through the formation of metal complexes. A metal complex has been synthesized with ratio metal to a ligand which suitable with the previous step. Weighed 1 mole of (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and 3 mole of methyl orange powder then each of them was dissolved in ethanol. The two solutions were mixture, stirred and refluxed at 78 °C until the volume is one third from the initial volume. After that, the mixture was left overnight until the sediment was formed. The synthesized sediment then purified by hot ethanol and dried.

### 2.3. Characterization of the modified methyl orange

The compound from the modified process that over mentioned above was characterized by some instruments to determine its structure and its characteristics. The compound was characterized by spectrophotometer UV-VIS to determine the wavelength characteristics and spectrophotometer FTIR to determine the interaction of metal and methyl orange.

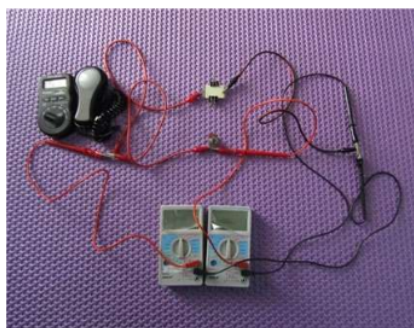
### 2.4. Photovoltaic assay of the modified methyl orange

2.4.1. Preparation of sol-gel titanium dioxide as a semiconductor on solar cell. Titanium dioxide was prepared by reacting 10 mL of tetrabutylorthotitanate (TBOT) with 30 mL of ethanol and stirred using a magnetic stirrer for 30 minutes. Then, the mixture was added by 1 mL of hydrochloric acid (HCl) and stirred again for 30 minutes. Furthermore, the mixture was left overnight until a sol-gel formed [3].

2.4.2. Preparation of a working electrode on solar cell. 4 In this research, the body of the solar cell was constructed by a conductive glass (Fluorine Thin Oxide, FTO glass). For a working electrode, first, a glass plate with a size of 2.5 cm x 2.5 cm with 1 mm of thickness was sanded to obtain a rough-surfaced. Then, the glass plate was soaked with ethanol for 24 hours. Furthermore, the glass plate was coated by sol-gel titanium dioxide using a Doctor Blade technique to obtain the thin layer titanium dioxide. A sol-gel solution of TiO<sub>2</sub> was dropped on the glass plate surface and flattened using a stirring rod until obtained a homogenous coating. Then, a coated glass plate was calcined at a temperature of 450°C for 30 minutes. The obtained titanium dioxide was characterized by X-Ray Diffraction. Second, the coated glass was soaked by solution of 10<sup>-5</sup> M of dye (methyl orange; Fe-methyl orange, respectively) for 24 hours until the optimal absorption was obtained. Then, the glass was stored in a dark container and protected from scratches that can damage the coating.

*2.4.3. Preparation of a counter electrode on solar cell.* A counter electrode was prepared by shading the glass surface using graphite pencil homogenously. After that, the surface was re-coated by carbon until obtained a dark intensively coating.

*2.4.4. Assembling of solar cell device.* The solar cell device was assembled by attaching a working electrode and a counter electrode where the working electrode was placed on the top position. Between the two electrodes were dropped an electrolyte solution  $KI_3$ . Then, the two electrodes were clamped with clips and connected to the multimeter and potentiometer  $100\text{ k}\Omega$ . The circuit was described in Figure 1. The solar cell circuit was connected to a multimeter cable where the positive pole was connected to the counter electrode and the negative pole was connected to the working electrode. Then, the solar cell device was irradiated for 2 weeks by direct sunlight and every day the maximum current and voltage were measured. The intensity of the sunlight was also measured using a lux meter.



**Figure 1.** The circuit of solar cell device.

### 3. Results and discussion

#### *3.1. The result of mole ratio determination and modification of methyl orange*

This research has successfully investigated the modification of methyl orange as a light harvester on solar cell application. The modification of methyl orange was conducted by inserting metal to the methyl orange structure. Before the insertion process, firstly we determined the mole ratio of metal to methyl orange. In this research, a methyl orange is deemed as a ligand on complex compounds. The mole ratio of metal to ligand was determined by Job methods [10] and the result is described in Figure 2. Figure 2 shows that mole ratio of metal (iron) to ligand (methyl orange) is 0.3. It means that one mole iron could bind 3 mole of methyl orange. Based on this result, the structure of modified methyl orange is predicted as octahedral and described in Figure 4. After knowing the suitable proportion of metal and ligand, the modified methyl orange was synthesized through the formation of metal complexes process. The result of this modification was a blackish brown solids.

#### *3.2. Characterization of the modified methyl orange*

In order to ensure the modification of methyl orange structure was successfully done, the solid of modified methyl orange characterized by spectrophotometer UV-VIS (shown in Table 1) and spectrophotometer FTIR (shown in Figure 3 and Table 2). Based on Table 1, we can see that after inserted by a metal, the modified methyl orange shows a hypsochromic shift of the maximum wavelength from methyl orange, namely from 464 nm to 420.50 nm. This phenomenon proved that the structure of methyl orange has been inserted by an iron metal and it means that the modification process has been successfully conducted. If we notice the UV absorption, we can see that the methyl orange shows a charge transfer phenomenon at 278 nm and the modified methyl orange at 262 nm. This charge

transfer phenomenon is a highly beneficial for solar cell application because this character will facilitate an electron transport on solar cell easily [11,12].

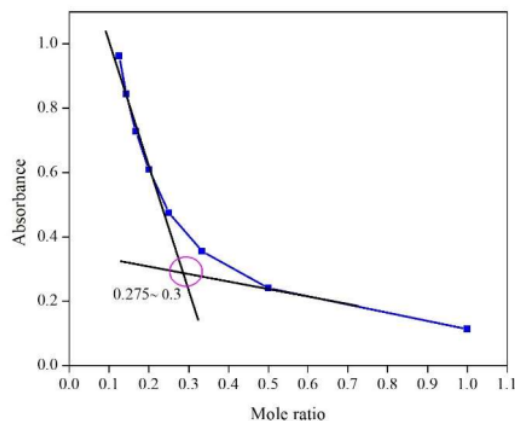


Figure 2. The ratio mole of metal to methyl orange.

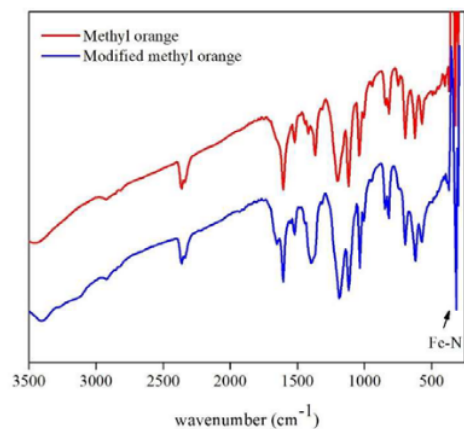
Table 1. The wavelength characteristic of dye.

Compound	Wavelength (nm)	
Modified methyl orange	420.50	262
Methyl orange	464	278

An interaction of metal in this case iron with the ligand (methyl orange) structure have been investigated by spectrophotometer FTIR and described in Figure 3 and Table 2. Using this characterization, we can determine what a functional group of ligand which bind with a metal [12-15]. Figure 3 shows that the modified methyl orange obtain coordination bonding between iron and methyl orange through Fe-N bonding at 316.33 nm. The chemical bonding is beneficial for a light harvester application because the strong bonding between metal and ligand will increase the chemical and thermal stability of compound. This condition is really support the light harvester function in catching a photon of sunlight [11, 12, 14, 16]. Based on the result of metal to ligand bonding characterization, the structure prediction of iron and methyl orange is described in Figure 4.

### 3.3. Photovoltaic assay of the modified methyl orange

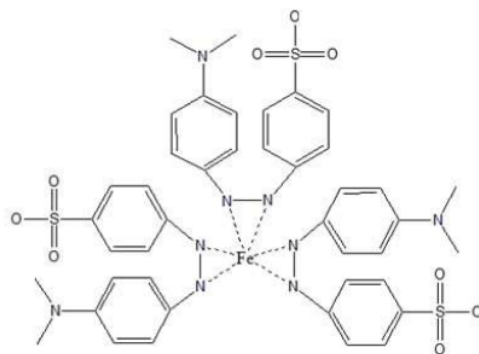
**3.3.1. The result of sol-gel titanium dioxide preparation.** The making of sol-gel titanium dioxide was carried out by reacting tetrabutylorthotitanate (TBOT/ $C_{16}H_{36}O_4Ti$ ) as a precursor of  $TiO_2$  with ethanol as a solvent. Ethanol was chosen as a solvent because ethanol is a versatile solvent that can not only disperse TBOT but can also hydrolyse TBOT. The adding of HCl was function as an alkoxide hydrolysis catalyst [3]. After coated to a plate glass surface and dried by oven, the thin layer of TBOT was calcined with furnace to eliminate organic compounds in TBOT so that the remain was  $TiO_2$ . Furthermore, the thin layer of titanium dioxide was characterized by XRD and described in Figure 5. The diffractogram on Figure 5 shows that the obtained titanium dioxide from TBOT precursor has amorphous structure. This amorphous crystal of semiconductor gives advantages namely give more surface for active particle (dye) wide spread in the top of semiconductor surface [19, 20].



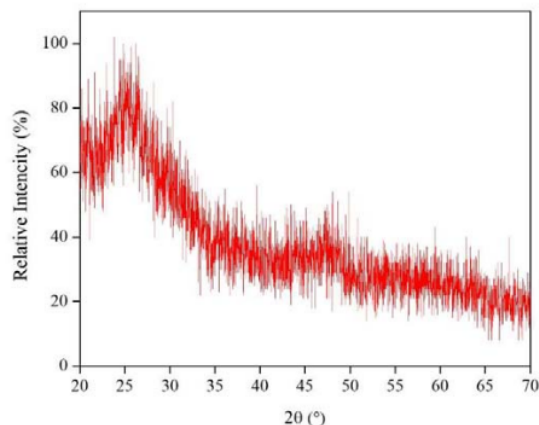
**Figure 3.** The interaction of metal-ligand bonding on the modified methyl orange.

**Table 2.** Functional group and wavenumber of dye on solar cell.

Functional Group	Wavenumber (cm <sup>-1</sup> )			Theoretical value
	Methyl orange	Modified methyl orange		
Fe-N	-	316.33	300 – 400	[17]
SO <sub>3</sub> Na	1118.71	1118.71	1070 – 1235	[18]
C=C aromatic	1604.77	1604.77	1510 – 1607	[18]
N=N	1365.60	1396.48	1400 – 1500	[18]



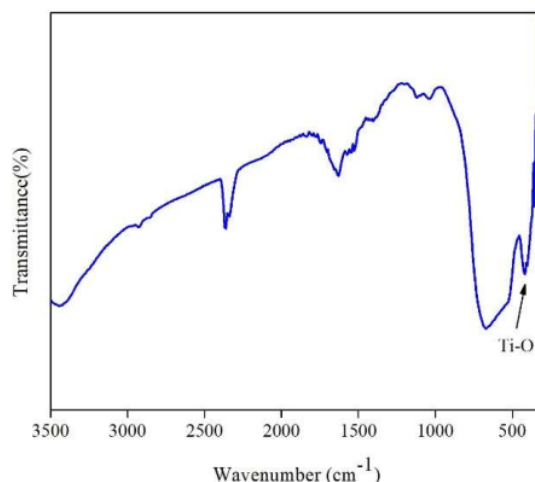
**Figure 4.** The prediction structure of modified methyl orange.



**Figure 5.** The diffractogram of the obtained thin layer titanium dioxide.

*3.3.2. The interaction of semiconductor and modified methyl orange as a dye.* The interaction of semiconductor ( $\text{TiO}_2$ ) and dye (methyl orange) on the work electrode has been characterized by FTIR spectrophotometer and described in Figure 6. This characterization was done to investigate the bonds that occur between Ti from semiconductors and functional group from modified methyl orange. The bond between Ti and O on  $\text{SO}_3$  group in the modified methyl orange at wavenumbers  $416.62 \text{ cm}^{-1}$ . This result is appropriate with theory that Ti-O bonding will appear in  $400\text{-}600 \text{ cm}^{-1}$  [17].

*3.3.3. The result of photovoltaic performance assay.* The measurement of photovoltaic performance of a light harvester on solar cell was conducted by giving an external load to the solar cell device and then measuring the current and voltage produced by the light [21]. The result of this assay is shown in Table 3. Table 3 shows that the modified methyl orange obtain the highest efficiency compare with methyl orange and semiconductor. It means that the modification of methyl orange structure with inserting a metal is proved can increase their ability in capturing a light from sunlight. The presence of metal on the modified methyl orange can increase their thermal and chemical stability so that can increase their performance on catching photon of sunlight. The more energy of sunlight could catch by a light harvester, the more electron regenerate in solar cell device, the more efficiency obtained [6].



**Figure 6.** The interaction of titanium dioxide with modified methyl orange.

**Table 3.** The photovoltaic parameter of modified methyl orange, methyl orange and semiconductor.

Compound	$V_{oc}$ (Volt)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF	$\eta$ (%)
Semiconductor (TiO <sub>2</sub> )	0.06	1.25	0.250	0.030
Methyl orange	0.15	3.00	0.830	0.756
Modified methyl orange	0.15	3.75	1.000	1.137

#### 4. Conclusions

The modification of methyl orange through metal insertion mechanism was proven increasing the photovoltaic performance of methyl orange from 0.756 % to 1.137%. The modified methyl orange showed the maximum wavelength at 420.50 nm and the charge transfer phenomenon at 262 nm. The interaction of metal to methyl orange was shown by a metal-ligand bonding at 316.33 cm<sup>-1</sup>. The thin layer of titanium dioxide as a semiconductor bind to the modified methyl orange structure through the Ti-O bonding at 416.62 cm<sup>-1</sup>.

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