The Structural and Optical Band Gap Energy Evaluation of TiO₂-Fe₂O₃ Composite

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Abstract. Solar cells, one of which is Dye Sensitizer Solar Cell (DSSC), are promising alternative energy in the 2000s. Compared to many other energy sources, solar cell does not emit waste (clean energy). An important component that generates electricity in DSSC is photoanode. TiO₂, the most widely used materials as photoanodes in the current era, is widely used photoanode although the energy gap of the TiO₂ band is quite large (3.43 eV). This study aims to reduce the energy gap of TiO₂ band by forming composites with Fe₂O₃. Various compositions of TiO₂ and Fe₂O₃ fine powders mixtures were dispersed in methanol and stirred until homogeneous in order to synthesize the photoanode. The methanol was then evaporated to obtain a dried mixture of solids, followed by calcination to form composites. The resulted composites were characterized by XRD and Diffuse Reflectance UV-Vis Spectrophotometer. XRD analysis results showed that the composites are composed of TiO₂ and Fe₂O₃ mixtures. Diffuse Reflectance UV-Vis analysis results showed that there was a change in bandgap energy due to the mixing of TiO₂ with Fe₂O₃. The lowest band gap energy is 2.67 eV at 1:4 ratios. The smallest and largest refractive index values calculated by the Ravindra relation are 2.0725 and 2.4286, respectively. The refractive index value is the reversely proportional of the band gap energy value, the greater the band gap energy, the smaller the refractive index value.

1. Introduction

Energy requirement is increasing every year so that in the future petroleum is no longer able to fulfil energy necessary. In particular, the demand for electricity produced by the Diesel Power Plant will be threatened if its oil will be depleted in the future. Thus, the development of alternative energy sources became the main choice by researchers in the 21st century.

Alternative energy sources can be create using potential natural resourced in Indonesia, one of which is the promising solar cells (dye sensitizer solar cell). If term of sustainability, a technology that utilizes photons from the sun does not have restrictions such as petroleum that can run out in the near future [1]. DSSC technology is very promising to be developed in areas that have high continuous sunlight intensity. Palangka Raya is one of the cities in Kalimantan and has a position close to the equator. Although it does not exactly on the equator line, the intensity of sunlight in Palangka Raya is high...
enough so that it has great potential in the development of DSSC as an alternative energy to produce electricity.

One of the devices in DSSC is a semiconductor-based material which called as photoanode. The material interact with photons to produce electron transfer from the valence band to the conduction band [2], as well as the formation of current electric due to holes and electron movements in the semiconductor structure. The most well-known and widely used semiconductor material in DSSC is the expensive difficult to synthesize SiGe. Some other materials have been reported to replace SiGe such as ZrO$_2$ [3], Cu-doped TiO$_2$ [4], and TiO$_2$ [5] with the band gap energy above 3 eV which is very active in UV light. However, the materials require more energy to produce the electron movement from the valence band to the conduction band. One way to reduce band gap energy is through the doping process. However, the process requires more energy which uses heating at a certain temperature to form a new material. On the other hand, combinations with materials that have lower band gap energy through the physical mixing process to form a composite have not been widely reported.

According to Apte et al. [6], Fe$_2$O$_3$ has a band gap energy of 2.2 eV. Hence, it has the potential to be combined with TiO$_2$ to reduce the gap energy of the pit through the process of physical mixing with alcohol dispersants and followed by the calcination process to form a composite. The making of the composite offers a new alternative to the use of visible light-based photoanodes, this is because visible light has a wider wavelength range than the UV rays (Vis: 400 - 800 nm). This is strongly supported by the location of the city of Palangka Raya which has continuous very good sunlight intensity throughout the year because it is closer to the equator. Based on the above explanation, this research will examine the structure of TiO$_2$-Fe$_2$O$_3$ and the effect of the TiO$_2$/Fe$_2$O$_3$ ratio on the gap energy of the pit.

2. Methodology

2.1. Materials

The materials that were used in this works were TiO$_2$ (Merck, 99%), Fe$_2$O$_3$ (Merck, 99%), and methanol (Aldrich, 99.6%).

2.2. Synthesis and Characterization of TiO$_2$-Fe$_2$O$_3$ Composite

TiO$_2$ and Fe$_2$O$_3$ were mixed in a beaker with mass ratio of 1: 1, 1: 2, 1: 3, and 1: 4. Each solid mixture with different of mass ratio was then dispersed into 50 mL methanol and stirred for 2-3 hours until homogeneous mixture was obtained. The homogeneous mixture was allowed to settle at room temperature and then decanted to separate the dispersant from the solid TiO$_2$-Fe$_2$O$_3$ precipitate. The precipitate was dried in an oven at 90 °C for 1 hour to vaporize the methanol which was still trapped on the surface of TiO$_2$-Fe$_2$O$_3$ composite particles before being calcined at 500 °C for 1 hour.

TiO$_2$-Fe$_2$O$_3$ composites were characterized by Panalytical X-Ray Diffraction (XRD) using a Cu-Kα light source ($\lambda = 1.5406$ Å) which is operated at 30 mA and 40 kV. The step size of measurement was set at 0.02°. The TiO$_2$-Fe$_2$O$_3$ composites were also characterized by SEM-EDX to observe the morphology and elemental mapping. UV-Vis Diffuse Reflectance spectrophotometer Shimadzu-2450 was used to determine the maximum wavelength and band gap energy of the TiO$_2$-Fe$_2$O$_3$ composite. The band gap energy was evaluated using Equation 1, where A is a constant, h is the photon energy, and $E_g$ is the optical band gap energy. $E_g$ can be observed from the extrapolation of Tauc plot when the curve (ahv)$^2$ as y axis = 0 [4].

\[(ahv) = A (hν - E_g)^{1/2}\]  \(\text{(1)}\)

After $E_g$ was successfully determined by the Tauc plot, the $E_g$ value was used to determine refractive index ($n$) using Ravindra relation as shown in Equation 2 [7].

\[n = 4.084 - 6.02E_g\]  \(\text{(2)}\)
3. Result and Discussion

3.1. Structural Study

X-Ray Diffraction pattern of TiO$_2$-Fe$_2$O$_3$ is shown in Figure 1. According to JCPDS Card No 21-1272 for TiO$_2$ and JCPDS Card No 39-1346 for Fe$_2$O$_3$, the identity peaks of TiO$_2$ appeared at 2θ angles of around 25°, 32°, 47°, 53°, and 63° while the peaks for Fe$_2$O$_3$ are observed at 2θ angles of around 33°, 35°, 40°, 49°, and 62°. The diffraction pattern of the composite has identical profile with the diffraction pattern from both JCPDS standards which indicates that the TiO$_2$ and Fe$_2$O$_3$ are both present and merged to form a new composite material.

The XRD analysis of composite in several mass ratios of TiO$_2$:Fe$_2$O$_3$, resulting in different intensity in their diffraction pattern. As shown in Figure 1, the intensity of TiO$_2$ peak decreases as the amount of Fe$_2$O$_3$ in composite increases.

![Figure 1. XRD pattern of TiO$_2$-Fe$_2$O$_3$ composite.](image-url)

Figure 1 also shows that heating the mixture at 500°C did not change both crystal structures. The diffractogram exhibits that each oxide has their signature peaks which represented by the diffraction pattern and it can be estimated that the composite is likely having new properties compared to the starting materials [8].

Microstructural characterization was also carried out with SEM-EDX, the results are shown in Figure 2. The figure shows that TiO$_2$ and Fe$_2$O$_3$ materials in a ratio of 1:2 are uniformly mixed as indicated by the spreading of the same shape of all particles. In addition, elemental mapping shows the distribution of elements. Oxygen is distributed to all parts with brighter color intensity, and Fe also spread with greater intensity compared to Ti. This is due to the different composition of the material forming the
TiO$_2$-Fe$_2$O$_3$ composite. The intensity of Fe is higher than Ti which correspond to Fe$_2$O$_3$ present in the composite than TiO$_2$.

3.2. **Optical properties evaluation**

Optical properties is important for photoanode material which will be used in Dye Sensitizer Solar Cell (DSSc) system. The band gap energy can be determined by Tauc plot from absorption spectra, in which the band gap energy plays an important role on electron movement from the valence band to the conduction band [9]. For the material with low band gap energy, it needs electromagnetic radiation with longer wavelength [10]. In contrast, material with high band gap energy will require electromagnetic radiation with a shorter wavelength to impu the movement of electrons. It is expressed with Equation 3, in which $E$ is energy, $\hbar$ is planck constant, $c$ is the velocity of light, and $\lambda$ is wavelength.

$$E = \hbar c \lambda^{-1}$$  (3)
Based on Equation 3, energy has a value that is inversely related to the wavelength. Thus, the band gap energy is one of the parameters which interesting to study. Tauc plot of TiO$_2$-Fe$_2$O$_3$ with different ratio in Figure 3 shows that the composition directly influence the band gap value. Higher Fe$_2$O$_3$ content reduce the band gap of composite and also shows that the formation of TiO$_2$-Fe$_2$O$_3$ composites produce new band gap value. According to Riyani et al. [11], when TiO$_2$ with gap energy = 3.43 eV was combined with Fe$_2$O$_3$ (band gap energy = 2.2 eV), the band gap of the composite will decreased. At TiO$_2$ and Fe$_2$O$_3$ ratio of 1:1, the band gap energy is 3.24 which was lower than the pure TiO$_2$. The gap energy is also becoming closer to Fe$_2$O$_3$ band gap at the highest composition of Fe$_2$O$_3$ i.e. 2.67 eV.

The band gap energy influenced optical absorption properties in solid materials. The optical absorption spectra of the composite are shown in Figure 3. The peak around 200-300 nm only appears for composite with TiO$_2$ and Fe$_2$O$_3$ ratio of 1:1. This is due to TiO$_2$ to still dominate the optical properties for its composition. The UV light has a high energy and electron in the valence band of TiO$_2$ which make the electrons easy to move [12]. The band gap energy of composite with all ratio is shown in Table 1.

| Material          | Band Gap Energy (eV) | Reference  |
|-------------------|----------------------|------------|
| TiO$_2$-Fe$_2$O$_3$ (1:1) | 3.24                 | This work  |
| TiO$_2$-Fe$_2$O$_3$ (1:2) | 3.08                 | This work  |
| TiO$_2$-Fe$_2$O$_3$ (1:3) | 3.12                 | This work  |
| TiO$_2$-Fe$_2$O$_3$ (1:4) | 2.67                 | This work  |
| TiO$_2$            | 3.43                 | [11]       |
| Fe$_2$O$_3$        | 2.2                  | [6]        |

Figure 3. Optical absorption spectra and Tauc plot of TiO$_2$-Fe$_2$O$_3$ with different ratio.
The optical absorption of composite also appears on visible area. TiO$_2$: Fe$_2$O$_3$ with ratio of 1:4 has a high absorbance due to the high content of Fe$_2$O$_3$. It will give more advantages to the composite if it is used as a photoanode which active under visible light. 

The composition of composite also plays an important role to determine optical and structural properties. The different composition of composite obtained many results from some parameters such as the refractive index. Refractive index describes how fast the light travels through the material [13]. It can be determined by Ravindra relation which uses band gap energy value as one of the parameters. Figure 4 shows the relation of composition with refractive index and band gap energy.

Based on calculation by using Ravindra equation, as shown in Figure 4, the highest refractive index is 2.4286 and the lowest one is 2.0752. The refractive index decreases as the Fe$_2$O$_3$ content in composite increased. Inversely, the band gap energy increases as the Fe$_2$O$_3$ content in the composite is getting higher.

![Figure 4](image-url)

**Figure 4.** The effect of composite content on band gap energy and refractive index

Another property which important to study is dielectric constant which has a direct relation to the band gap energy. The dielectric constant was classified as the high frequency of dielectric constant which denoted as $\varepsilon_a$ and static dielectric constant was denoted as $\varepsilon_o$. The high-frequency dielectric constant and static dielectric constant were calculated by Equations 4 and 5, respectively.

$$\varepsilon_a = n^2$$

$$\varepsilon_o = 33.26876 + 78.61805E_g - 45.70795E_g^2 + 8.32449E_g^3$$

Figure 5 shows the result of a high frequency dielectric constant (HFDC) calculation and static dielectric constant (SDC) which plotted into a graph. As shown in Figure 5, the highest value of HFDC is 5.8981 while the lowest one is 4.306. On the other hands, the highest value of SDC is 24.764 and the lowest one is 9.243. The HFDC was reversely proportional to band gap energy, which means that when
the band gap energy increases, the HFDC decreases. Inversely, the SDC is suitable with the increasing of band gap energy of TiO$_2$–Fe$_2$O$_3$.

Figure 5. The relation of band gap energy and dielectric constant.

4. Conclusion
The composite of TiO$_2$–Fe$_2$O$_3$ was successfully synthesized in this work. The result of XRD characterization shows that the identity peak is fit with the peaks of TiO$_2$ (JCPDS Card No 21-1272) and Fe$_2$O$_3$ (JCPDS Card No 39-1346). The micrograph and elemental mapping results show that the composite has regularity on the particle’s shape and uniformity of element in all areas of SEM micrograph. Analysis results using Diffuse Reflectance UV-Vis analysis shows that there was a change in band gap energy. The lowest band gap energy is 2.67 eV for TiO$_2$–Fe$_2$O$_3$ of 1:4. The refractive index, calculated by Ravindra equation, shows that the lowest value is 2.0752 and the highest value is 2.4286. The refractive index was reversely proportional to the band gap energy, which means that when the band gap energy increases, the refractive index decreases.

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