Synthesis of TiO$_2$ nanorods from titania and titanyl sulfate produced from ilmenite dissolution by hydrothermal method

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Abstract. TiO$_2$ powder has been synthesized through hydrolysis-condensation of titanyl sulfate solution to a starting material of TiO$_2$ nanorods formation. This processing was conducted by the solid separation of TiO$_2$ from ilmenite by roasting ilmenite, acidic leaching (hydrolysis), and co-precipitation (condensation). Roasting of ilmenite was carried out by the addition of Na$_2$S at a temperature of 800°C. While the acidic leaching process was conducted by sulfuric acid at various concentrations of 3, 3.5, 4.5, 6, and 9 M. The result shown that the solubility optimum occurs in H$_2$SO$_4$ 6 M condition. Separation of Fe impurities of TiO$_2$ gel from titanyl sulfate (TiOSO$_4$) solution was done through complexation using KCNS addition. The characteristic of TiO$_2$ obtained using X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) showed good crystallinity and purity. Further treatment of the TiO$_2$ is the formation of one-dimensional nano-size (1-D nanorods) through a hydrothermal method under basic condition NaOH 12M solution. TiO$_2$ nanorods were confirmed by Transmission Electron Microscope (TEM) which indicated that the diameter of TiO$_2$ nanorods was about 7.02 nm in size.

1. Introduction
The main problems in the world is the energy crisis, it is caused by the impact of the increasing number of population in the world. So, we need alternative energy which has a high potential as a source of renewable energy is the sun. The development of solar cell technology from silicon solar cells to Dye-sensitized Solar Cell (DSSC) was increased recently [1]. In the DSSCs system, absorption of light and charge separation was occurred in a separate process, unlike in the silicon solar cells that the whole process does not separate. Absorption of light is carried by the dye molecules and the charge separation was done by inorganic semiconductor nanocrystal having a wide band gap. Titanium dioxide (TiO$_2$) has become the preferred semiconductors in a variety of studies because it possesses good photo-sensibility [2] and has a large band gap energy (> 3.00 eV) so as to absorb the energy of photons on most of the spectrum of sunlight [3]. TiO$_2$ is also a material that is inert, harmless and inexpensive, and has good optical characteristics.

The synthesis an characterization of one-dimentional (1-D) nanostructured materials (nanotubes, nanorods, and nanowires) have received considerable attention due to their unique properties an novel applications [4-7]. Much effort has concentraced on the important metal oxide such as TiO$_2$ and ZnO [4]. Among them, TiO$_2$ and TiO$_2$-derived materials are of importance for utilizing solar energy an
environmental purification. TiO$_2$ has been widely use for applications such as a semiconductor in dye sensitized solar cell, water treatment materials, catalyst [8]. In our previous works, nanorods TiO$_2$ were synthesized by hyrothermal method under basic condition using TiO$_2$ and titanyl sulfate (TiOSO$_4$) source.

2. Experimental Method

Ilmenite was roasted at a temperature of 800°C for 2 hours. Then the roasted ilmenite calcination results was characterized using XRD. About 100 grams of roasted ilmenite was washed with hot water at a temperature of about 90°C for 2 hours. The resulting precipitated was then dried and characterized using XRD. While the filtrate was characterized by ICP-OES. Dissolution of ilmenite performed using H$_2$SO$_4$ with concentration variations of 3; 3.5; 4.5; 6; 9 M in a three-neck flask, then was heated at refluxing process under 90°C for 2 hours. The result obtained was precipitated a few minutes in order to separate the resudu of the solution. The resulting filtrate was TiOSO$_4$ then characterized using ICP-OES.

About 200 mL of aquades heated to 60°C then added 0.25 mL 1M KCNS. After it was added a solution of 10 mL TiOSO$_4$ then was stirred for one hour. After the hydrolysis process was done a deposition for one hour to obtain a white precipitate at the bottom. After the deposition process, the precipitate be washed with 0.1 M HCl and aquades. The precipitate obtained and then dried at a temperature of 100°C. Titania solids added to a concentration of 12 M NaOH, then stirred for 1 hour at room temperature, then refluxed for 24 hours at a temperature of 120°C. The result refluxed then washed using 0.1 M HCl solution and then dried at a temperature of 60°C for 24 hours. Titania then calcined for 2 hours at of 400°C and characterized using XRD.

3. Results and Discussion

Characterization of ilmenite was characterized by XRF to determine the composition of chemical constituents in the form of metal oxides.

| Content    | Level (%) | Content    | Level (%) |
|------------|-----------|------------|-----------|
| TiO$_2$    | 45.35     | Al$_2$O$_3$ | 2.35      |
| Fe$_2$O$_3$| 31.48     | SO$_3$     | 2.24      |
| Na$_2$O    | 3.86      | Cr$_2$O$_3$| 1.87      |
| ZrO$_2$    | 3.57      | MnO        | 1.58      |
| SiO$_2$    | 3.29      |            |           |

Table 1 shows the composition of the which is dominant in TiO$_2$ ilmenite is as much as 45.35% and 31.48% Fe$_2$O$_3$. While the remaining 23.17% is of other metal oxides such as Na$_2$O, ZrO$_2$, SiO$_2$, Al$_2$O$_3$, SO$_3$, Cr$_2$O$_3$, MnO.

Roasting of Ilmenite

Roasting of ilmenite was added by Na$_2$S to simplify the extraction process TiO$_2$ which will be done in the process of dissolution. The roasting process will produce a surface that is modified for their diffusion processes that occur at high temperatures. Iron moves faster than titanium and they tend to migrate toward the high oxygen potential region [9]. This oxidation processes occur during roasting process shown in equation 1.
2FeOTiO$_2$(s) + $\frac{1}{2}$ O$_2$(g) ⇌ Fe$_2$O$_3$(s) + 2TiO$_2$(s)

(Diffraction data from Figure 1)

**Figure 1.** Diffractograms roasting ilmenite at 800°C. N= Na$_2$SO$_4$; S= NaFeS$_2$; O= NaFeO$_2$; H= Fe$_2$O$_3$; A= TiO$_2$ anatase; R= TiO$_2$ rutile

Diffractogram (Figure 1) showed the results of the roasting ilmenite decomposed into hematite, TiO$_2$ anatase, TiO$_2$ rutile and double salts. Peaks at 23.85° (d$_{012}$); 32.85° (d$_{104}$) characteristic peaks of hematite in accordance with the standard JCPDS No. 88-2359. The peak of the value 25.53° (d$_{101}$) and 37.79° (d$_{004}$) in accordance with the characteristic peaks of anatase TiO$_2$ standard JCPDS No. 21-1272. Peaks at 36.15° (d$_{101}$); 54.43° (d$_{211}$) showed characteristic peaks of rutile TiO$_2$ in accordance with the standard JCPDS No. 87-0710.

**Leaching**

Leaching of roasted ilmenite product was carried out by H$_2$SO$_4$ at various concentration. In this process, roasted ilmenite dissolved by sulfuric acid, thus obtained titanyl sulfate (TiOSO$_4$) and ferrous sulfate (FeSO$_4$). In this study, the variation in the concentration of sulfuric acid used were 3 M, 3.5 M, 4.5 M, 6 M, and 9 M.

Reactions that may occur in the process of leaching with sulfuric acid is the following equations.

FeTiO$_3$(s) + 2H$_2$SO$_4$ → FeSO$_4$(aq) + TiOSO$_4$(aq) + 2H$_2$O(l) (2)

TiO$_2$(s) + Fe$_2$O$_3$(s) + 4H$_2$SO$_4$(aq) → TiOSO$_4$(aq) + Fe$_2$(SO$_4$)$_3$(aq) + 3H$_2$O(aq) (3)

NaFeO$_2$(s) + NaFeS$_2$(s) + 4H$_2$SO$_4$(aq) → Na$_2$SO$_4$(aq) + Fe$_2$(SO$_4$)$_3$(aq) + 2H$_2$O(aq) + 2H$_2$S(aq) (4)

**Figure 2.** Percentage of ilmenite dissolved in H$_2$SO$_4$ solutions
The concentration of sulfuric acid with variations can affect the dissolution process ilmenite. Ilmenite solubility increases with increasing concentration of \( \text{H}_2\text{SO}_4 \) at a concentration of 4.5 M to 6 M in the sample ILM1 with a percentage of 88.4% and 88.7%. Highest solubility occurred at the dissolution of ilmenite at \( \text{H}_2\text{SO}_4 \) 6 M. Filtrate dissolution were then characterized using ICP-OES (Table 2) to determine levels of Fe and Ti in the sample. Table 2 shows the content of Ti in the sample about 6 grams / liter and the Fe content in the sample about 4 grams / liter.

| No  | Concentration of \( \text{H}_2\text{SO}_4 \)(M) | Analysis result of ICP (g / l) | Ti : Fe |
|-----|---------------------------------|---------------------------------|---------|
| 1   | 9                               | 6.4425                         | 4.5624  | 1.41 : 1 |
| 2   | 6                               | 6.2595                         | 4.3373  | 1.44 : 1 |
| 3   | 4.5                             | 6.6153                         | 4.8408  | 1.36 : 1 |
| 4   | 3.5                             | 5.8653                         | 4.9271  | 1.19 : 1 |
| 5   | 3                               | 4.3614                         | 3.8826  | 1.12 : 1 |

Table 2. Result of leachant roasted ilminate by ICP-OES (Sample ILM1)

Preparation \( \text{TiO}_2 \) from Titanyl Sulfate (\( \text{TiOSO}_4 \))

\( \text{TiO}_2 \) is synthesized from titanyl sulfate (\( \text{TiOSO}_4 \)) with the addition of KCNS. The addition of this KCNS can be separated the iron content with titania to obtain high-purity \( \text{TiO}_2 \). Reactions hydrolysis that happened shown in equations 5 and 6.

\[
\begin{align*}
\text{TiOSO}_4^{4(aq)} + 2\text{H}_2\text{O}(l) &\rightarrow \text{TiO(OH)}_2(s) + \text{H}_2\text{SO}_4(aq) \quad (5) \\
\text{TiO(OH)}_2(s) &\rightarrow \text{TiO}_2(s) \quad (6)
\end{align*}
\]

\( \text{TiO}_2 \) white solids were then washed using 0.1 M HCl and aquades to reduce impurities that exist in the solids \( \text{TiO}_2 \).

| Content  | Level (%) |
|----------|-----------|
| \( \text{TiO}_2 \) | 88.03     |
| \( \text{SO}_3 \) | 7.94      |
| \( \text{Fe}_2\text{O}_3 \) | 2.67      |
| \( \text{SnO}_3 \) | 0.49      |
| \( \text{P}_2\text{O}_5 \) | 0.35      |

Table 3. Chemical composition of \( \text{TiO}_2 \) hydrolysis and complexation
Synthesis of TiO$_2$ Nanorods

TiO$_2$ nanorods preparation was done by mixing TiO$_2$ nanoparticles (4.664 nm) and 12 M NaOH for ± 1 hour to obtain a white solution. Result of the hydrothermal process obtained white material such as mud at the bottom of the autoclave. White solids are then washed using 0.1 M HCl and aquades to reduced impurities.

Figure 3. Diffractograms of TiO$_2$ hydrolysis and complexation

H = Fe$_2$O$_3$; A = TiO$_2$ anatase; R = TiO$_2$ rutile

TiO$_2$ rutile showed at a peak of 27, 49º (d$_{110}$), while TiO$_2$ anatase showed at peak 25,28º (d$_{101}$). TiO$_2$ rutile characteristic peak has a higher intensity than TiO$_2$ anatase that indicated that TiO$_2$ rutile has high crystallinity. TiO$_2$ nanorods were characterized by TEM (Transmission Electron Microscope) to determine the morphology of the inside of TiO$_2$ nanorods (Figure 5) and shows that was formed rod-shaped samples with a diameter of 7.02 nm.

Figure 4. Diffractograms of TiO$_2$ nanorods H = Fe$_2$O$_3$; A = TiO$_2$ anatase; R = TiO$_2$ rutile
In conclusion, morphology of TiO$_2$ nanorods from condensation preparation has been formed by hydrolysis and complexation using KCNS, with a hydrothermal process under alkaline conditions. Powder of TiO$_2$ nanorods has obtained with a diameter of nanorods 7.02 nm.

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